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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

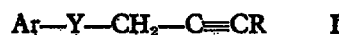
Propynyl Ethers and a process for the manufacture thereof

We, F. HOFFMANN-LA ROCHE & Co., AKTIENGESSELLSCHAFT, a Swiss Company of 124—184 Grenzacherstrasse, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

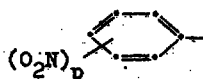
The present invention is concerned with novel propynyl ethers, a process for the manu-

facture thereof and novel compositions containing same.

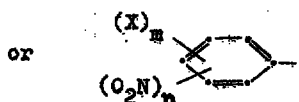
The novel propynyl ethers provided by the invention are compounds of the general formula



wherein Y stands for an oxygen or sulphur atom, R stands for a hydrogen or halogen atom and Ar stands for a grouping of the formula

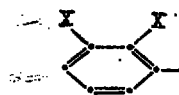


Ia



Ib

or, except where R stands for a hydrogen atom, a grouping of the formula



Ic

According to the process provided by the invention, the novel propynyl ethers aforesaid are manufactured either by reacting a compound of the general formula



, wherein Y and Ar have the significance given earlier, with a 3-halo-propyne and, where required, halogenating the reaction product of the formula



, wherein Y and Ar have the significance given earlier, or by condensing a compound of formula II hereinbefore with a 1,3-dihalo-propyne.

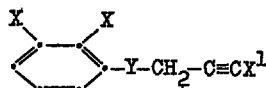
The compounds of formula II hereinbefore (that is to say, phenols or thiophenols) are

in which groups X stands for a halogen atom, p stands for an integer of from 1 to 5 (the nitro group in the grouping of formula Ia being in the *ortho*- or *meta*-position where p stands for 1, Y stands for an oxygen atom and R stands for a hydrogen or iodine atom) and m and n stand for integers of from 1 to 4 according to the availability of position or positions.

[Price 4s. 6d.]

known and can be obtained according to known methods.

- One interesting class of novel ethers provided by the invention are compounds of the general formula



IV

- wherein X and Y have the significance given earlier and X¹ stands for a halogen atom. The halogen substituents denoted by the symbol X on the phenyl ring can be either chlorine, bromine, iodine or fluorine, but are preferably chlorine or bromine. Moreover, they can be the same or different and can also be the same or different to the halogen atom denoted by X¹ on the acetylenic carbon atom. X¹ preferably stands for an iodine or bromine atom. Compounds falling within formula IV are, for example, 2,3-dichloro-phenyl 3-iodo-propyn(2)-yl ether, 2,3-dibromo-phenyl 3-iodo-propyn(2)-yl ether, 2,3-dichloro-phenyl 3-bromo-propyn(2)-yl ether, 2-chloro-3-bromo-phenyl 3-bromo-propyn(2)-yl ether and 2,3-dichloro-phenyl 3-iodo-propyn(2)-yl thioether. Compounds of formula IV in which Y stands for an oxygen atom are preferred.

- The compounds of formula IV are useful as antibacterial and fungicidal agents. For example, they are useful as disinfectants or sanitizers or they can be used in human or veterinary medicine as medicaments, especially in diseases caused by a wide variety of bacteria and fungi for which these compounds have shown a high inhibitory effect. More particularly, the compound 2,3-dichloro-phenyl 3-iodo-propyn(2)-yl ether has exhibited un-

usual broad spectrum antibacterial activity of extremely high potency against both Gram-positive and Gram-negative bacteria; for example, against *Streptococcus pyogenes* 4 *Diplococcus pneumoniae* 6301, *Staphylococcus aureus* 209, *Escherichia coli* 7 and *Salmonella typhosa*.

In addition to the extraordinary activity against Gram-positive and Gram-negative bacteria 2,3-dichloro-phenyl 3-iodo-propyn(2)-yl ether shows an inhibitory effect on a variety of fungi such as *Candida albicans*, *Trichophyton mentagrophytes*, *Microsporum audouinii* and *Aspergilli*. Of particular importance is the unexpectedly high activity against the fungi *Aspergillus niger*, *Aspergillus flavus* and *Aspergillus oryzae*. 2,3-Dichloro-phenyl 3-iodo-propyl(2)-yl ether, when tested against *Aspergillus niger*, *Aspergillus flavus* and *Aspergillus oryzae* in a modified Czapek media, produced 100 per cent inhibition of growth at less than 5 parts per million. This activity renders the compound particularly useful as an additive for the prevention of mildew in such things as fibrous materials, leather, textiles, wood and paper. In particular, this compound can be utilized, for example, as an additive in paints where it has been found to have a total inhibitory effect on the aforesaid fungi when used in amounts of 1 per cent by weight or less.

For example, various concentrations of 2,3-dichloro-phenyl 3-iodo-propyn(2)-yl ether were incorporated into a polyvinyl-acetate latex paint and an outside linseed oil plant. The paints were brush-coated on to both sides of sheets of filter paper and dried in air for 48 hours. One inch squares of the coated paper were placed on modified Czapek media in petri dishes, inoculated with a spore suspension of *Aspergillus oryzae* and incubated for 7 days at 28°—30° C. The results of these tests are indicated in the following Table:

TABLE I

Concentration (Per cent by weight of paint)	Paint	Growth on Paint	Zone of Inhibition
2.0	Latex	No growth	5 mm
1.0	"	" "	1 mm
0.5	"	Trace	0
0.25	"	Moderate	0
Control	"	Heavy	0
2.0	Oil	No growth	10 mm
1.0	"	" "	10 mm
0.5	"	" "	1 mm
Control	"	Moderate to heavy	0

Again, for example, one inch squares of vegetable tanned leather were immersed in alcohol solutions of 2,3-dichloro-phenyl 3-iodo-propyl-(2)-yl ether and dried in air. The treated samples were placed on modified Czapek media, inoculated with a spore suspension of *Aspergillus niger* and incubated for 7 days at 28°—30° C. The results are indicated in the following Table:

TABLE II

Concentration, per cent in alcohol (wt/vol)	Growth on leather	Zone of Inhibition
0.5	No growth	10 mm*
0.2	" "	10 mm*
0.1	" "	10 mm*
Control	Moderate growth	0

*Complete inhibition of growth on agar.

The compounds of formula IV can be used as antibacterial and antifungal agents in the form of pharmaceutical preparations containing said compounds in admixture with a compatible pharmaceutical organic or inorganic carrier suitable for local administration. They can be used, for example, as contact disinfectants or sanitizers or can be applied topically to affected areas. As carriers there can be used inert substances; for example, gelatin, lactose, starch, talc, vegetable oils, polyethylene-glycols and other compatible carriers use-

ful for the preparation of medicaments. The pharmaceutical preparations may be, for example, in the form of powders, sprays, salves, creams or suppositories or in liquid form as solutions (e.g. tinctures, suspensions or emulsions). If desired, they may be sterilized and/or may contain auxiliary substances such as preserving, stabilizing, wetting or emulsifying agents.

A conventional pharmaceutical formulation such as a cream or tincture containing a 2,3-dihalo-phenyl 3-iodo-propyl-(2)-yl ether of

formula IV in amounts of about 1 per cent or less by weight of the total formulation provides an effective antibacterial and anti-fungal composition for the treatment of inflammatory conditions amenable to topical therapy. A suitable ointment composition can be made up using 1.02% of 2,3-dichlorophenyl 3-iodo-propyn-(2)-yl ether, 13.50% of stearic acid, 1.35% of light mineral oil, 2.25% of sorbitan monostearate, 0.08% of methyl *p*-hydroxy-benzoate, 0.02% of propyl *p*-hydroxy-benzoate, 4.50% of sorbitol, 1.60% of polyoxyethylene-(20) sorbitan monostearate and distilled water *ad* 100%. The pH is

approximately 5.1. The ability of the foregoing ointment composition to inhibit various organisms in conventional microbiological tests is shown as follows:

The ointment composition was dissolved in dimethyl-sulphoxide, diluted with water and incorporated into Sabouraud-Agar. At the desired concentration, the agar was flooded with suspensions of *Candida albicans* and dermatophytes and incubated at 25° C for 48 hours in the case of *Candida* and for 7 days in the case of dermatophytes. The minimum inhibitory concentrations (M.I.C.) are given in the following Table:

TABLE III

Activity of ointments containing 2,3-dichlorophenyl 3-iodo-propyn-(2)-yl ether against bacteria and fungi *in vitro*

Organism	M.I.C. (µg./ml.)
<i>T. mentagrophytes</i>	0.1
<i>M. audouinii</i>	0.1
<i>C. albicans</i>	1.0

The ointment was tested by the agar-hole technique. Using a cork borer measuring 12.0 mm in diameter, holes were cut in the centre of an agar plate seeded with either bacteria or fungi and filled with the foregoing ointment composition. Incubation for bacteria was car-

ried out at 17° C. for 24 hours. *Candida albicans* was incubated at 25° C for 48 hours while the dermatophytes were incubated at 25° C for 7 days. The results of these experiments are expressed as zone inhibition and radius inhibition in the following Table:

TABLE IV

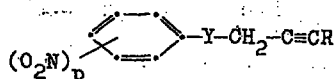
Activity of ointments containing 2,3-dichlorophenyl 3-iodo-propyn-(2)-yl ether against bacteria and fungi *in vitro*

Organism	Zone of Inhibition (mm)	Radius of Inhibition (mm)
<i>S. aureus</i> 209	43.0	1.40
<i>E. coli</i> 7	21.0	3.5
<i>C. albicans</i>	62.0	24.0
<i>S. pyogenes</i> 4		3.0
<i>D. pneumoniae</i> 6301		3.0

The novel compounds of formula IV can, for example, be manufactured by reacting the appropriate 2,3-dihalo-phenol or 2,3-dihalo-thiophenol with a 3-halo-propyne (preferably 3-bromo-propyne) in the presence of a base (e.g. an alkali-metal hydroxide or carbonate such as anhydrous potassium carbonate or bicarbonate), isolating the propynyl ether which forms and thereafter halogenating the acetylenic hydrogen in accordance with any of the usual methods for halogenating acetylenic compounds, for example by treating with the appropriate halogen in the presence of a strong base (e.g. sodium hydroxide). Alternatively, where X^1 in formula IV is to be an iodine atom, the terminal acetylenic carbon can be iodinated by first forming the copper salt by treating a solution of a copper-ammonia complex and thereafter iodinating the copper salt (for example, by treatment with a mixture of potassium iodide and iodine). The foregoing reaction can suitably be carried out in an inert organic solvent such as an alcohol or acetone. The reactions can be conveniently carried out at room temperature or at a temperature above or below room temperature. However, it is preferred to operate at a temperature within the approximate range of from 0°C to 30°C . The desired propynyl ether or thioether of formula IV can be readily recovered by any of the usual techniques such as filtration or evaporation.

Alternatively the compounds of formula IV can be manufactured by directly condensing a 1,3-dihalo-propyne with a 2,3-dihalo-phenol or a 2,3-dihalo-thiophenol. The condensation is suitably carried out in an inert organic solvent in the presence of a base. The temperature is not critical though it is preferred to operate at an elevated temperature, suitably at the reflux temperature of the mixture.

Another interesting class of novel ethers provided by the invention comprises compounds of the general formula



V

wherein Y and R have the significance given earlier and p is an integer of from 1 to 5 (the nitro group being in the *ortho*- or *meta*-position where p stands for 1, Y stands for an oxygen atom and R is a hydrogen or iodine atom).

Compounds of formula V in which p stands for 1 or 2, Y stands for an oxygen atom and R stands for a halogen atom (especially a bromine or iodine atom) are preferred. The 2,4-dinitro compound is specifically distin-

guishable by virtue of its antifungal activity, particularly against *T. mentagrophytes* and *M. audouini*.

The compounds of formula V are specifically distinguished by their toxicity to moulds, algae, yeast and especially to fungi. They are useful in the formulation of pharmaceutical formulations for local application in the treatment of fungal infections. Because of their fungicidal/fungistatic activity when used in minute quantities, they are particularly adapted to industrial uses. Those compounds having a terminal iodo group ($R=\text{iodo}$) have been found to be especially well suited for use as industrial fungicides. They are, for example, particularly well adapted for use as additives to plastics, paints and cosmetic emulsions, and in treating leather, wood, paper and fabrics to prevent deterioration resulting from fungal action in these materials or in surfaces protected by these materials. When used in this way, these compounds have been found to be highly effective at low concentrations, extremely resistant to diminution of their antimicrobial action and conferring substantially no undesirable properties to the systems treated therewith. The compounds can be made suitable for antimicrobial application by adding microbicidal amounts to the compositions or materials to be protected or by mixing a microbicidal amount with any conventional carrier (for example, by dissolving them in an alcohol or acetone).

The suitability and effectiveness of the compounds of formula V in treating fabrics is demonstrated by the test results shown in Table V hereinafter. The tests were conducted by immersing replicate one inch squares of cotton sheeting in alcohol solutions containing various concentrations of the test compounds. The treated fabrics were air-dried and subjected to petri dish inoculation tests against *Aspergillus niger* and *Chaetomium globosum*. For comparative purposes, samples of fabric were treated with a standard fabric fungicide, 2,2'-methylenebis(4-chloro-phenol). The inoculation materials were examined visually for the presence of growth after a 17-day incubation period and given a numerical rating. The numerical ratings used for this and all subsequent rates described herein have the following designations:

1. No growth on sample.
2. Trace growth on sample.
3. Slight growth on sample.
4. Moderate growth on sample.
5. Heavy growth on sample.
- (A) Up to 20 mm zone of inhibition around sample.
- (B) Greater than 20 mm zone of inhibition around sample.
- (C) Complete inhibition on entire plate.

TABLE V
Fabric Tests

Compound	Concentration in Alcohol	<i>A. niger</i>	<i>C. globosum</i>
3-Nitro-phenyl 3-iodo-propyn-(2)-yl ether	0.1%	1 (C)	1
" " "	0.05%	1 (C)	1
4-Nitro-phenyl 3-iodo-propyn-(2)-yl thioether	0.1%	1	1
" " "	0.05%	1 (A)	1
2-Nitro-phenyl 3-iodo-propyn-(2)-yl ether	0.1%	1 (B)	1
" " "	0.05%	1 (B)	1
2,4-Dinitro-phenyl 3-iodo-propyn-(2)-yl ether	0.1%	1 (C)	1
" " "	0.05%	1 (C)	1
2,2'-Methylenebis(4-chloro-phenol)	0.5%	1 (A)	1
" " "	0.2%	1-2	1
" " "	0.1%	3	1-2
" " "	0.05%	4	4
Control	—	5	5



5 The suitability of the novel compounds of formula V for treating leather in order to prevent microbial deterioration thereof is demonstrated by the results of the following test. Replicate one inch squares of vegetable tanned leather were immersed in alcohol solutions containing various concentrations of the compounds and were dried in air. Leather samples treated with a standard leather preservative (4-nitro-phenol) were tested at the same time for comparative purpose. The treated samples were subjected to petri dish inoculation tests with *Aspergillus niger* before and after various ex-

posure tests. The exposure tests were as follows:

- (i) Twenty-four hours in a circulating air oven at 60° C.
- (ii) Twenty-four hours immersion in 100 ml of cold tap water with four complete water changes during this period.
- (iii) Exposed outdoors on an unsheltered rack for 13 days.

The results of the microbiological tests after a 14-day inoculation period are recorded in Table VI

Purposes

TABLE VI
Leather Tests (*A. niger*)

Compound	Concentration in Alcohol	Unexposed	Oven Aged	Leached	Weathered
3-Nitro-phenyl 3-iodo-propyn-(2)-yl ether	0.2%	1 (B)	—	1 (B)	1 (B)
" "	0.1%	1 (B)	—	1 (A)	1
" "	0.05%	1 (A)	—	1 (A)	1—2
4-Nitro-phenyl 3-iodo-propyn-(2)-yl thioether	0.2%	1	—	1—2	1
" "	0.1%	1	—	1	2—3
" "	0.05%	1	—	1—2	3
2-Nitro-phenyl 3-iodo-propyn-(2)-yl ether	0.2%	1 (B)	—	1 (A)	1 (A)
" "	0.1%	1 (A)	—	1 (A)	1
" "	0.05%	1	—	1	1
2,4-Dinitro-phenyl 3-iodo-propyn-(2)-yl ether	0.2%	1 (B)	—	1 (B)	1 (B)
" "	0.1%	1 (A)	—	1—2	1
" "	0.05%	1 (A)	—	1—2	2
4-Nitro-phenol	0.2%	1	1	3	2
" "	0.1%	1—2	3	4	4
" "	0.05%	3—4	4	4—5	4—5
Control	—	5	5	5	5

5 The suitability of the compounds of formula V for incorporation into plastic compounds so as to inhibit microbial deterioration thereof is demonstrated by the following test. Plastic films were cast from solvent solutions containing a (vinyl chloride)-acetate resin, a susceptible plasticizer and several concentrations of a

compound of formula V. The finished films were cut into small squares and subjected to petri dish inoculation tests with *Aspergillus flavus* on mineral salts (M.S.) and dextrose/ (mineral salt) agar media. The results of these tests are given in Table VII.

TABLE VII

Plastic Tests

Compound	Concentration by weight of plastic	Dextrose/ (M.S.) Agar	M.S. Agar
3-Nitro-phenyl 3-iodo-propyn-(2)-yl ether	0.5%	1 (A)	1
4-Nitro-phenyl 3-iodo-propyn-(2)-yl thioether	0.5%	2	3
2-Nitro-phenyl 3-iodo-propyn-(2)-yl ether	0.5%	1 (A)	2
2,4-Dinitro-phenyl 3-iodo-propyn-(2)-yl ether	0.5%	1 (A)	3
Control	—	4	4



Paint

5 Still another of the many antimicrobial applications in which the novel compounds of formula V have found particular usefulness is in preventing microbial growth and micro-
10 bially induced degradation in films formed from both oil- and water-base paints. Com-
pounds of formula V when incorporated into an oil-base paint or a water-base paint in an
amount between 0.2 per cent and 2.0 per cent
by weight and the resulting paint employed to
paint a wood surface, give excellent control
against mildew formation when exposed to
rigorous conditions of temperature and humid-

ity. The added compound does not adversely 15
affect the shelf life of the paint nor does it
modify the colour characteristics and remains
effective for an extended period of time.

The suitability of the compounds of formula 20
V for use as a paint additive against micro-
biological deterioration (e.g. by *Pullularia*
pullulans, *Aspergillus oryzae*, *Aspergillus*
niger) is demonstrated by the results given
in Table VIII hereinafter. The compounds
were milled by hand into a white latex paint. 25
The treated paints were brushed on to both
sides of sheets of filter paper and dried in air.

TABLE VIII

Paint Tests

Compound	Concentration by weight of paint	Unexposed		
		<i>P. pullulans</i>	<i>A. oryzae</i>	<i>A. niger</i>
3-Nitro-phenyl 3-iodo-propyn-(2)-yl ether	1.0%	1	1 (A)	1 (B)
4-Nitro-phenyl 3-iodo-propyn-(2)-yl thioether	1.0%	3-4	3	3
2-Nitro-phenyl 3-iodopropyn-(2)-yl ether	1.0%	1 (A)	1 (A)	1 (A)
2,4-Dinitro-phenyl 3-iodo-propyn-(2)-yl ether	1.0%	1	1 (A)	1 (A)

The suitability of the compounds of formula V for use as additives to cosmetic emulsions is demonstrated by the following tests. Cosmetic creams formulated from boiling water emulsions with a non-ionic surfactant were prepared containing various concentrations of compounds of formula V and also with methyl 4-

hydroxy-benzoate. Jars containing these creams were inoculated with *Aspergillus niger* and incubated for a 21-day period. Samples were re-inoculated after 7 and 14 days of incubation period. Table IX shows a summary of the results of these tests.

TABLE IX
Cosmetic Emulsion Tests

Compound	Concentration by weight	Growth
3-Nitro-phenyl 3-iodopropyn-(2)-yl ether	0.05%	1
4-Nitro-phenyl 3-iodopropyn-(2)-yl thioether	0.05%	1
2-Nitro-phenyl 3-iodopropyn-(2)-yl ether	0.05%	1
2,4-Dinitro-phenyl 3-iodo-propyn-(2)-yl ether	0.05%	1
Methyl 4-hydroxy benzoate	0.10%	2
Methyl 4-hydroxy benzoate	0.20%	1
Control	—	4

The compounds of formula V are particularly noteworthy antifungal agents because of their ability to protect oil-water or two-phase systems since most of the conventional microbicides are inactive in these systems. It is a particularly significant property of the present compounds that they are effective in the presence of non-ionic surface-active agents whereas other antifungal agents are not. The present compounds are especially valuable for industrial purposes because of their high antifungal action when used in minute quantities and the almost total lack of adverse effects. The present compounds are inert to the oils and pigments in paints and, therefore, do not cause discoloration or shorten the shelf life thereof. The small quantities required have no effect on such other properties of paints as brushing and spreading characteristics. The present compounds are also inert to the ingredients of conventional cosmetic preparations and, therefore, find a wide application in this area.

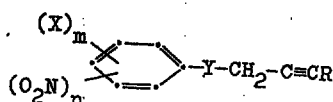
The compounds for formula V can be manufactured by reacting the appropriate nitro-phenol or nitro-thiophenol with a 3-halo-propyne (propargyl halide), preferably 3-bromo-propyne (propargyl bromide), in the presence of an acid-acceptor in a manner similar to the preparation of the 2,3-dihalo-phenyl propynyl ethers described earlier. Any

suitable base such as, for example, sodium hydroxide, sodium methoxide, alkali-metal carbonates (e.g. sodium carbonate or potassium carbonate) or bicarbonates (e.g. sodium bicarbonate) can be used as the acid-acceptor. The reaction is conveniently carried out in any inert solvent, preferably a polar solvent. Suitable solvents are, for example, water, ketones (e.g. acetone), alkanols (e.g. methanol and ethanol) and alkyl nitriles such as acetonitrile. In the case of the dinitro compounds, it is preferred to use a bicarbonate as the acid-acceptor and to work in a strongly polar solvent such as acetonitrile or methanol or ethanol. The reaction temperature is not critical, although it is preferred to work at an elevated temperature, suitably at the reflux temperature of the reaction mixture. However, the reaction can be carried out at lower temperatures; that is, at room temperature or below. The reaction starts upon mixing the reactants and is ordinarily completed in about 5—15 hours. Upon completion of the reaction, the reaction mixture is cooled to precipitate the inorganic salt formed in the reaction. The salt is filtered off and the filtrate distilled to recover the desired nitro-phenyl propyn-(2)-yl ether. Halogenation of the ether can be readily accomplished in accordance with normal methods for the halogenation of acetylenic compounds, for example, by re-

action with a hypophalite. The reaction is suitably carried out in an inert solvent such as, for example, water and ethers (e.g., dioxan and tetrahydro-furan). The hypophalite can be added to a solution of the propynyl ether or dissolved in an appropriate solvent to which the hypophalite can be added or the hypophalite can be prepared *in situ* by adding a halogen and a suitable base such as sodium hydroxide. Alternatively, iodination can be carried out *via* the copper salt as described earlier.

Compounds of formula V in which R stands for a halogen atom can be manufactured directly by condensing a 1,3-dihalo-propyne with the appropriate nitro-phenol or nitro-thiophenol by a procedure analogous to that described earlier.

Yet another interesting class of novel ethers provided by the invention comprises compounds of the general formula



VI

wherein X, Y, R, *m* and *n* have the significance given earlier. X preferably stands for chlorine and R (when halogen) preferably stands for iodine. The compounds of formula VI are useful as antibacterial/antifungal and insecticidal agents. The compounds in which R stands for a hydrogen atom are particularly good insecticidal agents, especially when used in the formulation of insecticidal compositions in conjunction with carbamate insecticides such as 1-naphthyl-N-methyl-carbamate. The compounds in which R stands for a halogen atom are notable for their antibacterial/antifungal properties. They are useful in the treatment of diseases caused by a wide variety of bacteria and fungi. They are also useful as additives in such materials as paints, leather, textiles and other fibrous materials to inhibit the growth of a variety of fungi such as *Aspergillus niger* and *Staphylococcus aureus*. Compounds of formula VI in which Y stands for an oxygen atom and *m* and *n* each stand for 1 are preferred. The compound 2-nitro-4-chloro-phenyl 3-iodo-propyn(2)-yl ether is specifically distinguishable by its inhibitory effect upon the growth of the fungi *Aspergillus niger*, *P. citrinum* and *Staphylococcus aureus* and the algae *Chlorella vulgaris* and *V. viridis*. The compounds of formula VI can be utilized in the form of conventional pharmaceutical and insecticidal preparations as described earlier in this specification.

The compounds of formula VI, in which R stands for a hydrogen atom can be prepared by condensing an appropriately substituted phenol or thiophenol with a 3-halo-propyne, preferably 3-bromo-propyne, in accordance

with procedures analogous to those described earlier. The halogenation of the terminal carbon can be effected in accordance with any of the usual procedures for the halogenation of acetylenic compounds. Alternatively, compounds of formula VI in which R stands for a halogen atom can be manufactured directly by condensing a 1,3-dihalo-propyne with the appropriately substituted phenol or thiophenol in accordance with procedures analogous to those described earlier.

The following Examples illustrate the process provided by the invention.

EXAMPLE 1.

200 g of 2,3-dichloro-phenol, 160 g of 3-bromo-propyne, 186 g of anhydrous potassium carbonate and 1.0 litres of pure acetone were charged into a 2 litre three-necked round bottom flask equipped with a stirrer and a reflux condenser. After the mixture had been stirred and heated at reflux for 8 hours, it was cooled to room temperature. The solids were filtered off and washed well with 500 ml of acetone. The solvent was evaporated *in vacuo* at 60° C and the residue was dissolved in 700 ml of ethanol. The crystals which formed on chilling in an icewater bath were filtered off and washed well with 500 ml of water. After drying for 48 hours in a vacuum desiccator using anhydrous calcium chloride as the desiccant, there was obtained 2,3-dichloro-phenyl propyn-(2)-yl ether of melting point 47°—49° C.

28.8 g of 2,3-dichloro-phenyl propyn-(2)-yl ether and 300 ml of pure methanol were charged into a 1 litre three-neck round bottom flask equipped with a stirrer, a dropping funnel and a thermometer. To the vigorously stirred solution there were simultaneously added 48 g of iodine in small portions, and 180 ml of a 10% aqueous sodium hydroxide solution, dropwise, over a period of 0.25 hour, while the reaction temperature was kept at 20°—25° C by means of an ice-water bath. After stirring for a further 0.5 hour at room temperature, the resulting precipitate was filtered off and washed well with 200 ml of water. The solids were dried to give 2,3-dichloro-phenyl 3-iodo-propyn-(2)-yl ether of melting point 58°—59° C.

EXAMPLE 2.

50 ml of a 10% aqueous sodium hydroxide solution were placed in a 250 ml flask. After the solution was cooled to 5° C, 6.4 g of bromine were added. A solution of 4.0 g of 2,3-dichloro-phenyl propyn-(2)-yl ether in 30 ml of dioxan were added to the cold yellow solution. After the reaction mixture had been stirred at 5°—10° C for 0.75 hour, the solvents were evaporated *in vacuo* at 60° C. The solids which formed were slurried with 100 ml of water, filtered, washed with 200 ml of water and dried. The crude compound was dissolved in 50 ml of petroleum ether (boiling point = 30°—60° C). After cooling, the crystals were



filtered off and air dried to yield 2,3-dichloro-phenyl 3-bromo-propyn-(2)-yl ether of melting point 68°—69° C.

EXAMPLE 3.

5 2.6 g of magnesium turnings and 20 ml of anhydrous ether ~~was~~ placed in a 500 ml three-neck round bottom flask equipped with a stirrer, reflux condenser, dropping funnel and calcium chloride drying tube. A solution of
10 2.5 g of ethyl bromide in 20 ml of anhydrous ether was added dropwise so as to maintain a gentle reflux and the reaction mixture was then heated at reflux for an additional 0.25 hour. A solution of 20.1 g of 2,3-dichloro-phenyl propyn-(2)-yl ether in 50 ml of anhy-
15 drous ether was then added dropwise over a period of 0.25 hour. After the reaction mixture had been heated at reflux for 5 hours, 19.1 g of *paratoluene*-sulphonyl chloride was added in small portions over a period of 0.25 hour
20 and heating at reflux was continued for 17 hours. The reaction mixture was afterwards cooled in an ice-bath and acidified with 100 ml of 3-*N* aqueous hydrochloric acid. The aqueous layer was extracted twice with 150
25 ml of ether. The combined ether extracts were washed twice with 100 ml of water, dried over anhydrous sodium sulphate, filtered and evaporated *in vacuo* at 40° C. The oily residue was poured on to a column containing 300 g of silica gel. The column was washed with six
30 200 ml portions of petroleum ether (boiling point = 30°—60° C) and the bulked eluates were evaporated *in vacuo* at 60° C. The residue was dissolved in 100 ml of petroleum ether (boiling point = 30°—60° C). After chill-
35 ing in an ice-bath, the crystals were filtered off to give 2,3-dichloro-phenyl 3-chloro-propyn-(2)-yl ether of melting point 67°—68° C.

EXAMPLE 4.

A 250 ml flask was charged with 22.5 g of 2,3-dibromo-phenol (obtained from 2-bromo-3-nitro-benzoic acid *via* 2-bromo-3-nitro-benzoyl chloride, 2-bromo-3-nitro-benz-
45 amide, 2-bromo-3-nitro-aniline, 2,3-dibromo-1-nitro-benzene and 2,3-dibromo-aniline), 14 g of potassium carbonate, 12 g of 3-bromo-propyne and 100 ml of acetone. The mixture was stirred and heated to reflux on a steam-
50 bath for 3 hours, then cooled to room temperature. The precipitate of inorganic salt was filtered off. The filter cake was washed with 20 ml of acetone and the acetone solution was
55 distilled under reduced pressure to give an almost white residue of 2,3-dibromo-phenyl propyn-(2)-yl ether melting at 42°—48° C. After recrystallization from petroleum ether (30°—60° C), the product melted at 49°—
60 50° C.

15 g of 2,3-dibromo-phenyl propyn-(2)-yl ether and 90 ml of methanol were placed in a 250 ml flask. The mixture was stirred at
65 room temperature until solution was complete then 14.4 g of iodine and 45 ml of

10% sodium hydroxide solution were simul-
taneously added; the temperature rose to 40°—45° C and a white precipitate was formed. The reaction mixture was allowed to cool to room temperature and then filtered. The filter cake was washed with a 5% solu-
70 tion of potassium iodide and then with water. The dry, semi-white 2,3-dibromo-phenyl 3-iodo-propyn-(2)-yl ether melted at 72°—77° C. After recrystallization from ligroin (60°—
75 90° C), it melted at 82°—84° C.

EXAMPLE 5.

A 1 litre flask was charged with 70 g of 2-nitro-phenol, 65.5 g of 3-bromo-propyne, 76 g of potassium carbonate and 500 ml of acetone. The mixture was stirred and heated to reflux on a steam-bath for 10 hours. The reaction mixture was then cooled to room temperature and the precipitate of inorganic salt was filtered off. The filter cake was washed with 50
80 ml of acetone and the combined washings and filtrate were distilled under reduced pressure. The semi-white residue of 2-nitro-phenyl propyn-(2)-yl ether melted at 72°—74° C. After recrystallization from ethanol, it melted at 74°—76° C.

53 g of 2-nitro-phenyl propyn-(2)-yl ether and 1000 ml of methanol were placed in a 2 litre flask. The mixture was stirred at room temperature until solution was complete then
95 84 g of iodine and 300 ml of 10% sodium hydroxide solution were simultaneously added. The temperature rose to 40°—45° C and a white precipitate was formed. The reaction mixture was allowed to cool to room tempera-
100 ture and was then filtered. The filter cake was washed with a 5% solution of potassium iodide and then with water. The dry, almost white 2-nitro-phenyl 3-iodo-propyn-(2)-yl ether melted at 94°—96° C. After recrystalli-
105 zation from ethanol, it melted at 96°—98° C.

EXAMPLE 6.

A litre flask was charged with 70 g of 3-nitro-phenol, 65.5 g of 3-bromo-propyne, 76 g of potassium carbonate and 500 ml of ace-
110 tone. The mixture was stirred and heated to reflux on a steam-bath for 10 hours. The reaction mixture was then cooled to room temperature and the precipitate of inorganic salt filtered off. The filter cake was washed
115 with 50 ml of acetone and the combined washings and filtrate were distilled under reduced pressure. The almost white residue of 3-nitro-phenyl propyn-(2)-yl ether melted at 70°—72° C. After recrystallization from
120 ethanol, it melted at 67°—69° C.

53 g of 3-nitro-phenyl propyn-(2)-yl ether and 1000 ml of methanol were placed into a 2 litre flask. The mixture was stirred at room temperature until solution was complete then
125 84 g of iodine and 300 ml of 10% sodium hydroxide solution were simultaneously added. The temperature rose to 40°—45° C and a

white precipitate was formed. The reaction mixture was allowed to cool to room temperature and was then filtered. The filter cake was washed with a 5% solution of potassium iodide and then with water. The dry, semi-white 3-nitro-phenyl 3-iodo-propyn-(2)-yl ether melted at 85°—87° C. After recrystallization from ligroin (60°—90° C), it melted at 88°—90° C.

EXAMPLE 7.

A 2 litre flask was charged with 93 g of 2,4-dinitro-phenol, 65.5 g of 3-bromo-propyne, 44 g of solid sodium hydroxide and 700 ml of water. The mixture was stirred and heated on a steam-bath for 24 hours, then acidified with dilute (1:1) hydrochloric acid and allowed to cool to room temperature. The precipitate was filtered off and washed well with water; the dry reaction product weighed 102 g and melted at 75°—82° C. The crude product was suspended in 350 ml of ethyl acetate. The suspension was washed with two 200 ml portions of a 5% sodium hydroxide solution then with water and the organic layer was dried over sodium sulphate and distilled under reduced pressure. The crude residue of 2,4-dinitro-phenyl propyn-(2)-yl ether melted at 84°—88° C. After recrystallization from ethanol, it melted at 98°—100° C.

66 g of 2,4-dinitro-phenyl propyn-(2)-yl ether and 1200 ml of methanol were placed in a 2 litre flask. The mixture was stirred at 35°—40° C until solution was complete then 84 g of iodine and 300 ml of 10% sodium hydroxide solution were simultaneously added. The temperature rose to 50°—55° C and a white precipitate was formed. The reaction mixture was allowed to cool to room temperature and was then filtered. The filter cake was washed with a 5% solution of potassium iodide and then with water. The dry, semi-white 2,4-dinitro-phenyl 3-iodo-propyn-(2)-yl ether thus obtained melted at 80°—86° C. After recrystallization from ethanol, it melted at 112°—114° C.

EXAMPLE 8.

A 1 litre flask was charged with 37 g of 2,6-dinitro-phenol, 29 g of 3-bromo-propyne, 24 g of potassium bicarbonate and 600 ml of acetonitrile. The mixture was stirred and heated to reflux on a steam-bath for 24 hours. The reaction mixture was then cooled to room temperature and the precipitate of inorganic salt was filtered off. The filter cake was washed with 20 ml of acetonitrile and the combined washings and filtrate were distilled under reduced pressure. The almost white residue of 2,6-dinitro-phenyl propyn-(2)-yl ether melted at 58°—62° C.

22 g of 2,6-dinitro-phenyl propyn-(2)-yl ether and 300 ml of methanol were placed in a 1 litre flask. The mixture was stirred at 30°—35° C until solution was complete then 28 g of iodine and 100 ml of 10% sodium hydroxide solution were simultaneously added.

The temperature rose to 40°—45° C and a white precipitate was formed. The reaction mixture was allowed to cool to room temperature and was filtered. The cake was washed with a 5% solution of potassium iodide and then with water. The dry 2,6-dinitro-phenyl 3-iodo-propyn-(2)-yl ether melted at 90°—94° C.

EXAMPLE 9.

A 2 litre flask was charged with 87 g of 2-nitro-4-chloro-phenol, 65.5 g of 3-bromo-propyne, 44 g of solid sodium hydroxide and 700 ml of water. The mixture was stirred and heated on a steam-bath for 24 hours. The reaction mixture was then acidified with dilute (1:1) hydrochloric acid and allowed to cool to room temperature. The precipitate was filtered off and washed well with water. The crude product was suspended in 350 ml of ethyl acetate. The suspension was washed with two 200 ml portions of a 5% solution of sodium hydroxide then with two 100 ml portions of distilled water and the organic layer was dried over sodium sulphate and distilled under reduced pressure. The crude residue of 2-nitro-4-chloro-phenyl propyn-(2)-yl ether melted at 75°—85° C. After recrystallization from ethanol, it melted at 85°—86° C.

64 g of 2-nitro-4-chloro-phenyl propyn-(2)-yl ether and 1200 ml of methanol were placed in a 2 litre flask. The mixture was stirred at 35°—40° C until solution was complete then 84 g of iodine and 300 ml of 10% sodium hydroxide solution were simultaneously added. The temperature rose to 50°—55° C and a white precipitate was formed. The reaction mixture was allowed to cool to room temperature and was then filtered. The filter cake was washed with a 5% solution of potassium iodide and then with water. The dry 2-nitro-4-chloro-phenyl 3-iodo-propyn-(2)-yl ether melted at 110°—115° C. After recrystallization from ethanol, it melted at 116°—117° C.

EXAMPLE 11.

A 500 ml flask was charged with 18.5 g of 2-nitro-4-chloro-6-iodo-phenol, 8.2 g of 3-bromo-propyne, 9.2 g of potassium carbonate and 200 ml of acetone. The mixture was stirred and heated to reflux on a steam-bath for 30 hours. The reaction mixture was then cooled to room temperature and the precipitate of inorganic salt was filtered off and the acetone solution distilled off under reduced pressure. The almost white residue of 2-nitro-4-chloro-6-iodo-phenyl propyn-(2)-yl ether melted at 81°—86° C. After recrystallization from ligroin, it melted at 91°—93° C.

15 g of 2-nitro-4-chloro-6-iodo-phenyl propyn-(2)-yl ether and 170 ml of methanol were placed in a 500 ml flask. The mixture was stirred at 30°—35° C until solution was complete then 13.7 g of iodine and 40 ml of 10% sodium hydroxide solution were simultaneously added. The temperature rose to 40°—45° C

and a white precipitate was formed. The reaction mixture was allowed to cool to room temperature and then filtered. The cake was washed with a 5% solution of potassium iodide and then with water. The dry semi-white 2-nitro-4-chloro-6-iodo-phenyl 3-iodo-propyn-(2)-yl ether was recrystallized from ethanol and melted at 115°—116° C.

EXAMPLE 12.

10 A) The preparation of the starting material:

A 500 ml flask was charged with 17.1 g of 3-bromo-propyne and 50 ml of pure methanol. To the vigorously stirred solution, which was cooled to 15°—20° C, there were added simultaneously 48 g of iodine, in small portions, and 180 ml of a 10% aqueous sodium hydroxide solution, dropwise, over a period of 0.25 hour while the reaction temperature was kept at 20° C. After stirring for a further hour at room temperature, the reaction mixture was diluted with 100 ml of ether and 50 ml of water. The aqueous layer was separated and extracted with three 75 ml portions of ether. The combined ether extracts were washed once with 100 ml of water, dried over anhydrous sodium sulphate and evaporated to yield 1-iodo-3-bromo-propyne.

B) The process:

A 250 ml flask was charged with 8.9 g of 2,3-dichloro-thiophenol, 14.7 g of 1-iodo-3-bromo-propyne, 8.3 g of potassium carbonate and 150 ml of acetone. After the reaction mixture had been stirred and heated at reflux for 8 hours, the solids were filtered off and the filtrate was evaporated *in vacuo* at 60° C. The residue was taken up in 250 ml of petroleum ether (30°—60° C) and chromatographed on 150 g of silica gel. After taking a total of 1 litre of petroleum ether (30°—60° C) eluates, which were discarded, the column was eluted with eight 200 ml portions of a mixture of benzene/(petroleum ether) (1:10) which were combined and evaporated. The residue was crystallized from 50 ml of petroleum ether (30°—60° C) to give 2,3-dichloro-phenyl 3-iodo-propyn-(2)-yl thioether of melting point 72°—74° C.

EXAMPLE 13.

A 1 litre flask was charged with 23 g of 4-nitro-thiophenol, 55 g of 1-iodo-3-bromo-propyne (prepared as described in Example 12A), 27.9 g of potassium carbonate and 400 ml of acetone. After the reaction mixture had been stirred and heated at reflux for 8 hours, it was cooled to room temperature. The solids were slurried in 500 ml of petroleum ether (boiling point=30°—60° C), filtered and washed with 500 ml of petroleum ether. The solids were dissolved in 400 ml of hot ethanol and the insolubles were filtered off. After the solution had been chilled, the crystals were filtered off to give 4-nitro-phenyl 3-iodo-

propyn-(2)-yl thioether of melting point 174°—175° C.

EXAMPLE 14.

A 500 ml flask was charged with 31 g of 4-nitro-thiophenol and 84 ml of a 10% aqueous sodium hydroxide solution. 26 g of 3-bromo-propyne were added dropwise to the stirred solution over a period of 0.25 hour, the reaction temperature being kept between 25° C and 30° C. After stirring for 1 hour at room temperature, the precipitate was filtered off, washed with 200 ml of water and dried in a vacuum over at 50° C to yield 4-nitro-phenyl propyn-(2)-yl thioether of melting point 95°—97° C.

EXAMPLE 15.

A 500 ml flask was charged with 20 g of 2-nitro-4-chloro-thiophenol and 55 ml of a 10% aqueous sodium hydroxide solution. 13 g of 3-bromo-propyne were added dropwise to the stirred solution over a period of 0.25 hour, the reaction temperature being kept between 25° C and 30° C. After stirring for 1 hour at room temperature, the precipitate was filtered, washed with 200 ml of water and dried to yield 2-nitro-4-chloro-phenyl propyn-(2)-yl thioether of melting point 134°—136° C.

EXAMPLE 16.

A 250 ml flask was charged with 20.7 g of 2-bromo-3-chloro-phenol (obtained from 2-bromo-3-nitro-aniline *via* 2-bromo-3-chloro-nitro-benzene and 2-bromo-3-chloro-aniline), 14 g of potassium carbonate, 13.2 g of 3-bromo-propyne and 100 ml of acetone. The mixture was stirred and heated to reflux on a steam-bath for 8 hours. The reaction mixture was then cooled to room temperature and the precipitate of inorganic salt was filtered off. The filter cake was washed with 20 ml of acetone and the acetone solution was distilled under reduced pressure. The oily residue of 2-bromo-3-chloro-phenyl propyn-(2)-yl ether distilled at 72°C/0.04 mm.

13 g of 2-bromo-3-chloro-phenyl propyn-(2)-yl ether and 100 ml of methanol were placed in a 250 ml flask. The mixture was stirred at room temperature until solution was complete then 30.8 g of iodine and 90 ml of 10% sodium hydroxide solution were simultaneously added. The temperature rose to 40°—45° C and a white precipitate was formed. The reaction mixture was allowed to cool to room temperature and was filtered. The filter cake was then washed with a 5% solution of potassium iodide and then with water. The dry, off-white 2-bromo-3-chloro-phenyl 3-iodo-propyn-(2)-yl ether melted at 60°—68° C. A small sample was recrystallized from ligroin (60°—90° C) and melted at 81°—82° C.

EXAMPLE 17.

A 250 ml flask was charged with 8 g of cuprous chloride, 20 g of ammonium carbonate and 40 ml of water. The mixture was

stirred and heated to 50° C in order to dissolve the solids. A solution of 9.1 g of 2-nitro-4-chloro-phenyl propyn-(2)-yl thioether (prepared as described in Example 15) in 40 ml of dioxan was added dropwise to the warm solution over a period of 0.25 hour. After the reaction mixture had been stirred vigorously for 0.5 hour, the precipitate was filtered off, washed with 200 ml of water and transferred, with 200 ml of water, to a 500 ml flask. A solution of 10 g of iodine, 10 g of potassium iodide and 30 ml of water were added at once to the slurry. After the reaction mixture had been stirred for 1 hour, the solids were filtered off and washed four times with 150 ml of water. The remaining solids were washed three times with 200 ml of hot benzene. The benzene extracts were evaporated at 60° C under reduced pressure. The residue was slurried with 200 ml of ethanol and filtered to yield 2-nitro-4-chloro-phenyl 3-iodo-propyn-(2)-yl thioether of melting point 167°—168° C.

EXAMPLE 18.

A 500 ml flask was charged with 40.8 g of 2,4-dinitro-thiophenol and 96 ml of a 10% aqueous solution of sodium hydroxide. 26 g of 3-bromo-propyne were added to the stirred solution over a period of 0.25 hour, the reaction temperature being kept between 25° C and 30° C. After stirring for 1 hour at room temperature, the precipitate was filtered off and washed with 200 ml of water. The solids were crystallized from 100 ml of benzene to yield 2,4-dinitro-phenyl propyn-(2)-yl thioether of melting point 122°—124° C.

A 250 ml flask was charged with 8 g of cuprous chloride, 20 g of ammonium carbonate and 40 ml of water. The mixture was stirred and heated to 50° C in order to dissolve the solids. A solution of 9.6 g of 2,4-

dinitro-phenyl propyn-(2)-yl thioether in 50 ml of dioxan was added dropwise to the warm solution over a period of 0.25 hour. After the reaction mixture had been stirred vigorously for 0.5 hour, the precipitate was filtered off, washed with 200 ml of water and transferred, with 200 ml of water, to a 500 ml three-neck round bottom flask equipped with a stirrer. A solution of 10 g of iodine, 10 g of potassium iodide and 30 ml of water was added at once to the slurry. After the reaction mixture had been stirred for 1 hour, the solids were filtered off and washed four times with 150 ml of water. The remaining solids were washed three times with 200 ml of hot benzene. The benzene extracts were evaporated at 60° C under reduced pressure. The residue was slurried with 200 ml of ethanol and filtered to yield 2,4-dinitro-phenyl 3-iodo-propyn-(2)-yl thioether.

2,4 - Dinitro - phenyl 3 - iodo - propyn-(2)-yl thioether was also prepared as follows:

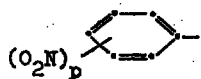
A 250 ml flask was charged with 10.2 g of 2,4-dinitro-thiophenol, 14.7 g of 1-iodo-3-bromo-propyne, 8.3 g of potassium carbonate and 150 ml of acetone. After the reaction mixture had been stirred and heated at reflux for 8 hours, the solids were filtered off and the filtrate was evaporated *in vacuo* at 60° C. The residue was crystallized to give 2,4-dinitro-phenyl 3-iodo-propyn-(2)-yl thioether.

WHAT WE CLAIM IS:—

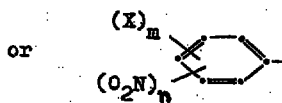
1) Compounds of the general formula



wherein Y stands for an oxygen or sulphur atom, R stands for a hydrogen or halogen atom and Ar stands for a grouping of the formula



Ia



Ib

or, except where R stands for a hydrogen atom, a grouping of the formula



Ic

— in which groupings X stands for a halogen atom, p stands for an integer of from 1 to 5 (the nitro group in the grouping of formula Ia being in the *ortho*- or *para*-position where p stands for 1, Y stands for an oxygen atom and R stands for a hydrogen or iodine atom) and m and n each stand for integers of from 1 to 4 according to the availability of position or positions.

stirred and heated to 50° C in order to dissolve the solids. A solution of 9.1 g of 2-nitro-4-chloro-phenyl propyn-(2)-yl thioether (prepared as described in Example 15) in 40 ml of dioxan was added dropwise to the warm solution over a period of 0.25 hour. After the reaction mixture had been stirred vigorously for 0.5 hour, the precipitate was filtered off, washed with 200 ml of water and transferred, with 200 ml of water, to a 500 ml three-neck round bottom flask equipped with a stirrer. A solution of 10 g of iodine, 10 g of potassium iodide and 30 ml of water were added at once to the slurry. After the reaction mixture had been stirred for 1 hour, the solids were filtered off and washed four times with 150 ml of water. The remaining solids were washed three times with 200 ml of hot benzene. The benzene extracts were evaporated at 60° C under reduced pressure. The residue was slurried with 200 ml of ethanol and filtered to yield 2-nitro-4-chloro-phenyl 3-iodo-propyn-(2)-yl thioether of melting point 167°—168° C.

EXAMPLE 18.

A 500 ml flask was charged with 40.8 g of 2,4-dinitro-thiophenol and 96 ml of a 10% aqueous solution of sodium hydroxide. 26 g of 3-bromo-propyne were added to the stirred solution over a period of 0.25 hour, the reaction temperature being kept between 25° C and 30° C. After stirring for 1 hour at room temperature, the precipitate was filtered off and washed with 200 ml of water. The solids were crystallized from 100 ml of benzene to yield 2,4-dinitro-phenyl propyn-(2)-yl thioether of melting point 122°—124° C.

A 250 ml flask was charged with 8 g of cuprous chloride, 20 g of ammonium carbonate and 40 ml of water. The mixture was stirred and heated to 50° C. in order to dissolve the solids. A solution of 9.6 g of 2,4-

dinitro-phenyl propyn-(2)-yl thioether in 50 ml of dioxan was added dropwise to the warm solution over a period of 0.25 hour. After the reaction mixture had been stirred vigorously for 0.5 hour, the precipitate was filtered off, washed with 200 ml of water and transferred, with 200 ml of water, to a 500 ml three-neck round bottom flask equipped with a stirrer. A solution of 10 g of iodine, 10 g of potassium iodide and 30 ml of water was added at once to the slurry. After the reaction mixture had been stirred for 1 hour, the solids were filtered off and washed four times with 150 ml of water. The remaining solids were washed three times with 200 ml of hot benzene. The benzene extracts were evaporated at 60° C under reduced pressure. The residue was slurried with 200 ml of ethanol and filtered to yield 2,4-dinitro-phenyl 3-iodo-propyn-(2)-yl thioether.

2,4 - Dinitro - phenyl 3 - iodo - propyn-(2)-yl thioether was also prepared as follows:

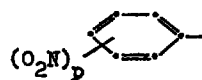
A 250 ml flask was charged with 10.2 g of 2,4-dinitro-thiophenol, 14.7 g of 1-iodo-3-bromo-propyne, 8.3 g of potassium carbonate and 150 ml of acetone. After the reaction mixture had been stirred and heated at reflux for 8 hours, the solids were filtered off and the filtrate was evaporated *in vacuo* at 60° C. The residue was crystallized to give 2,4-dinitro-phenyl 3-iodo-propyn-(2)-yl thioether.

WHAT WE CLAIM IS:—

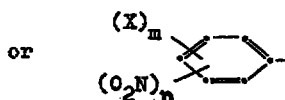
1) Compounds of the general formula



wherein Y stands for an oxygen or sulphur atom, R stands for a hydrogen or halogen atom and Ar stands for a grouping of the formula



Ia



Ib

or, except where R stands for a hydrogen atom, a grouping of the formula



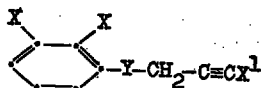
Ic

— in which groupings X stands for a halogen atom, p stands for an integer of from 1 to 5 (the nitro group in the grouping of formula Ia being in the *ortho*- or *para*-position where p stands for 1, Y stands for an oxygen atom and R stands for a hydrogen or iodine atom) and m and n each stand for integers of from 1 to 4 according to the availability of position or positions.





2) Compounds of the general formula



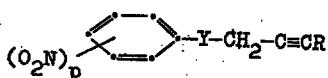
wherein X and Y have the significance given in claim 1 and X¹ stands for a halogen atom.

3) Compounds as set forth in claim 2, wherein Y stands for an oxygen atom.

4) 2,3-Dichloro-phenyl 3-iodo-propyn(2)-yl ether.

5) 2-Bromo-3-chloro-phenyl 3-iodo-propyn(2)-yl ether.

6) Compounds of the general formula



wherein Y, R and p have the significance given in claim 1.

7) Compounds as set forth in claim 6, wherein Y stands for an oxygen atom.

8) Compounds as set forth in claim 7, wherein R stands for a halogen atom and p stands for 1 or 2.

9) 2-Nitro-phenyl propyn(2)-yl ether.

10) 3-Nitro-phenyl propyn(2)-yl ether.

11) 2,4-Dinitro-phenyl propyn(2)-yl ether.

12) 2,6-Dinitro-phenyl propyn(2)-yl ether.

13) 2,4-Dinitro-phenyl propyn(2)-yl thioether.

14) 2,4-Dinitro-phenyl 3-iodo-propyn(2)-yl thioether.

15) 2-Nitro-phenyl 3-iodo-propyn(2)-yl ether.

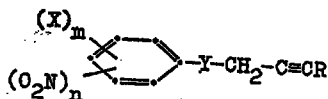
16) 3-Nitro-phenyl 3-iodo-propyn(2)-yl ether.

17) 2,4-Dinitro-phenyl 3-iodo-propyn(2)-yl ether.

18) 2,6-Dinitro-phenyl 3-iodo-propyn(2)-yl ether.

19) 4-Nitro-phenyl 3-iodo-propyn(2)-yl thioether.

20) Compounds of the general formula



wherein X, Y, R, n and m have the significance given in claim 1.

21) 2-Nitro-4-chloro-phenyl 3-iodo-propyn(2)-yl ether.

22) 2-Nitro-4-chloro-phenyl propyn(2)-yl ether.

23) 2-Nitro-4-chloro-phenyl 3-iodo-propyn(2)-yl thioether.

24) A process for the manufacture of the compounds claimed in claim 1, which process

comprises *either* reacting a compound of the general formula

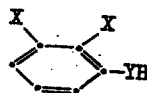


, wherein Y and Ar have the significance given in claim 1, with a 3-halo-propyne and, where required, halogenating the reaction product of the formula



, wherein Y and Ar have the significance given in claim 1, *or* condensing a compound of the general formula first written in this claim with a 1,3-dihalo-propyne.

25) A process as set forth in claim 24, wherein a compound of the general formula



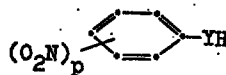
, wherein X and Y have the significance given in claim 1, is reacted with a 3-halo-propyne and the reaction product is halogenated.

26) A process as set forth in claim 25, wherein a 2,3-dihalo-phenol is reacted with a 3-bromo-propyne in the presence of a base and the reaction product is halogenated by treatment with a halogen in the presence of a base.

27) A process as set forth in claim 25 or claim 26, wherein 2,3-dichloro-phenol is reacted with 3-bromo-propyne and the resulting 2,3-dichloro-phenyl propyn(2)-yl ether is iodinated.

28) A process as set forth in claim 24, wherein a compound of the formula written in claim 25 is condensed with a 1,3-dihalo-propyne in the presence of a base.

29) A process as set forth in claim 24, wherein a compound of the general formula



, wherein Y and p have the significance given in claim 1, is reacted with a 3-halo-propyne.

30) A process as set forth in claim 29, wherein the product obtained according to the process of said claim is halogenated.

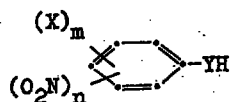
31) A process as set forth in claim 24, wherein a compound of the formula written in claim 29 is condensed with a 1,3-dihalo-propyne in the presence of a base.

32) A process as set forth in any one of claims 29 to 31 inclusive, wherein a starting compound is used in which p stands for 1 or 2 and Y stands for an oxygen atom and wherein said compound is *either* reacted with a 3-halo-propyne and the reaction product brominated

or iodinated or condensed with a 1-(bromo or iodo)-3-halo-propyne in the presence of a base.

33) A process as set forth in claim 9 wherein 2,4-dinitro-phenol is the starting compound used.

34) A process as set forth in claim 24, wherein a compound of the general formula



, wherein X, Y, m and n have the significance given in claim 1, is reacted with a 3-halo-propyne.

35) A process as set forth in claim 34, wherein the product obtained according to the process of said claim is halogenated.

36) A process as set forth in claim 24, wherein a compound of the formula written in claim 34 is condensed with a 1,3-dihalo-propyne.

37) A process as set forth in claim 34, claim 35 or claim 36, wherein a starting compound is used in which m and n each stand for 1.

38) A process for the manufacture of the compounds claimed in claim 1, substantially as described with reference to the Examples.

39) Compounds as set forth in claim 1, when manufactured by the process claimed in any one of claims 24 to 38 inclusive.

40) A composition of matter comprising a compound as set forth in claim 1 in association with a compatible carrier.

41) A composition of matter comprising a compound as set forth in claim 3 in association with a compatible carrier.

42) A composition as set forth in claim 41, wherein said compound is 2,3-dichloro-phenyl 3-iodo-propyn-(2)-yl ether.

43) A composition of matter comprising a compound as set forth in claim 7 in association with a compatible carrier.

44) A composition as set forth in claim 43, wherein said compound is 2,4-dinitro-phenyl 3-iodo-propyn-(2)-yl ether.

45) A composition as set forth in claim 43, wherein said compound is 2,6-dinitro-phenyl 3-iodo-propyn-(2)-yl ether.

46) An oil-base paint or water-base paint containing from 0.2 per cent to 2.0 per cent by weight of a compound as set forth in claim 7.

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