THE INTERNUCLEAR CYCLIZATIONS OF AROMATIC SULPHONYL CHLORIDES. TRIBENZ (b, d, f) OXEPIN AND TRIBENZO (b, d, f) THIEPIN*

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Abstract—The thermal and cuprous chloride catalysed decompositions of diphenylether-2-sulphonyl chloride (I), diphenylsulphide-2-sulphonyl chloride (V), biphenyl-2-sulphonyl chloride (IX), 2'-phenyl-diphenylether-2-sulphonyl chloride (XIII), and 2'-phenyl-diphenylsulphide-2-sulphonyl chloride (XVII) at $250-260^{\circ}$ have been examined. In the absence of solvent, intermolecular reactions leading to non-volatile products are generally dominant and in the cases of I and V, the concomitant formation of the appropriate chlorocompounds is an additional factor which leads to poor overall yields of the anticipated internuclear cyclization products, dibenzofuran and dibenzothiophen. The relatively difficult cyclization to biphenylene was not observed in the decomposition of IX and in this case, 2-chloro-biphenyl was the only isolated volatile product. XIII and XVII undergo internuclear cyclizations to give the new compounds tribenz (b, d, f) oxepin (40% yield) and tribenzo (b, d, f) thiepin (24% yield) respectively. In octachloronaphthalene, none of the yields of the cyclization products was improved and in the case of I this solvent promoted the formation of 2-chloro-diphenylether.

THE thermal decompositions of a number of aromatic sulphonyl chlorides $(ArSO_2Cl)$ in an excess of an aromatic hydrocarbon substrate (Ar'H) at temperatures greater than 200° and optionally in the presence of a catalyst have been shown to be useful routes to the biaryls, Ar-Ar'. Thus the decomposition of benzenesulphonyl chloride in biphenyl at 255° leads¹ to the evolution of almost quantitative amounts of sulphur dioxide and hydrogen chloride and to the formation of a mixture of the terphenyl isomers which may be isolated in 78% yield. Similarly, benzenesulphonyl chloride decomposes in boiling naphthalene to give¹ an 80% yield of a mixture of 1- and 2-phenyl naphthalene, and naphthalene-1-sulphonyl chloride and naphthalene-2-sulphonyl chloride decompose in naphthalene at 218° in the presence of cuprous chloride to give² the mixed binaphthyls in 80% and 90% yield respectively. These reactions are comparable with the intermolecular arylations brought about by aromatic diazonium chlorides in the Gomberg-Bachmann-Hey^{3,4} syntheses of biaryls.

The Gomberg reaction has an intramolecular counterpart in the well known Pschorr cyclization,^{5,6} and other corresponding intermolecular and intramolecular arylation reactions such as the decompositions of acylarylnitrosamines have been studied. Now although there are cases where the yields in aromatic sulphonyl halide arylations

^{*} A preliminary account of this work was given at the XIXth International Congress of Pure and Applied Chemistry. London, 10-17th July (1963).

¹ P. J. Bain, E. J. Blackman, W. Cummings, Sheila A. Hughes, E. R. Lynch, E. B. McCall and R. J. Roberts, *Proc. Chem. Soc.* 186 (1962).

² G. M. Badger and C. P. Whittle, Austral. J. Chem. 16, 440 (1963).

³ G. H. Williams, Homolytic Aromatic Substitution Pergamon Press (1960).

⁴ H. Weingarten, J. Org. Chem. 26, 730 (1961).

⁵ D. F. Detar, Organic Reactions IX 409 (1957).

^{*} P. H. Leake, Chem. Rev. 56, 27 (1956).

are not high, for example in the phenylation of dibenzothiophen,⁷ the generally clean character of the reactions suggests that the internuclear cyclizations of appropriately substituted compounds might have preparative advantages. The present paper describes examinations of the thermal and catalytic decompositions of diphenyl ether-2sulphonyl chloride, diphenyl sulphide-2-sulphonyl chloride, biphenyl-2-sulphonyl chloride, 2'-phenyl-diphenyl ether-2-sulphonyl chloride, and of 2'-phenyl-diphenyl sulphide-2-sulphonyl chloride. The new heterocycles, tribenz (b, d, f) oxepin and tribenzo (b, d, f) thiepin, are formed as the result of the internuclear cyclizations of the last two of these compounds.

RESULTS AND DISCUSSION

The decompositions were carried out at 250-260° in a nitrogen atmosphere either in the absence of solvent or in octachloronaphthalene. The choice of diluent was limited by the provision that it should be inert, that it should have an atmospheric b.p. in the region of 250°, and that it should be separable from the possible products of the reactions. The sulphonyl chlorides appear to undergo homolytic dissociation under the conditions used for the intermolecular reactions,^{1,2,7} and although the actual species responsible for the internuclear cyclizations are uncertain, it seems possible that radical species are involved in the side reactions. Hence the provision that the solvent should be inert to such radical species at 250° is a severe one. Even the fully chlorinated aromatic compounds enter into reaction as is indicated, for example, by the observation⁸ that the decomposition of benzenesulphonyl bromide in hexachlorobenzene at 250-260° in the presence of cuprous chloride gives both bromobenzene (68%) and chlorobenzene (17% yield). Consistently, in the present series of decompositions, the presence of octachloronaphthalene generally does not improve the isolated yields of the cyclization products and in the case of diphenylether-2-sulphonyl chloride it promotes the formation of 2-chlorodiphenylether.

Diphenylether-2-sulphonyl chloride (I)



Typical results for the decomposition of diphenylether-2-sulphonyl chloride are in Table 1. In the absence of solvent, the total yield of distillable products is low and is distributed between diphenylether (II), 2-chlorodiphenylether (III), and dibenzofuran (IV). Since the separation of III and IV from this mixture by distillation or by crystallization was not possible, they were separated and isolated by using gas chromatography, and were identified by comparisons of their IR spectra with those of the

⁷ E. B. McCall, A. J. Neale and T. J. Rawlings, J. Chem. Soc. 5288 (1962).

^{*} E. B. McCall, W. Cummings and P. J. Bain, unpublished.

O al sant	Cataluat	SO₃(%)	HCI(%)	Yield (%)°		
Solvent	Catalyst			11	III	IV
	CuCl ^b	96	79	7	17	17
OCN	_	91	16	0	73	10

TABLE 1. THE DECOMPOSITIONS OF DIPHENYLETHER-2-SULPHONYL CHLORIDE AT 250-260°

^a The yields were determined by gas chromatography by using 16 ft \times 3/16 in of 10% Apiezon L on Embacel at 205° and a flame ionization detector.

* 1 mole % based on the sulphonyl chloride was used.

^c OCN denotes octachloronaphthalene; a 25% w/w solution of the sulphonyl chloride was used.

authentic compounds. In octachloronaphthalene a good yield of 2-chloro-diphenylether was obtained. The corresponding cyclization of the diazonium salt derived from diphenylether-2-amine gives dibenzofuran in 45% yield⁹ and, in this and in the Pschorr cyclizations of other amines, the formation of the appropriate chloro-compound by a Gattermann type of reaction is not a feature which is generally observed.⁵ In the present case of diphenylether 2-sulphonyl chloride, the formation of the chloro-compound is competitive with the cyclization to dibenzofuran and this suggests either that the cyclization is inherently difficult or that the decomposition is complex in the absence of a solvent and is complicated in the presence of octachloronaphthalene by solvent participation. In any event, the decomposition as it has been investigated here does not provide a practical alternative to the normal Pschorr types of cyclizations of derivatives of the amine.

Diphenylsulphide-2-sulphonyl chloride (V)



Diphenylsulphide-2-sulphonyl chloride decomposes to give a mixture of products which includes diphenylsulphide (VI) and dibenzothiophen (VIII) and a third component which, by analogy with the case of diphenylether-2-sulphonyl chloride, is assumed to be 2-chloro-diphenylsulphide (VII). These three components are separated cleanly by using gas chromatography and an approximate analysis of the decomposition in the presence of cuprous chloride is in Table 2. The product is evidently as complex as it is for diphenylether-2-sulphonyl chloride and, although it is possible to isolate a small yield of dibenzothiophen from the decomposition in octachloronaphthalene, the reaction is not of preparative value.

⁹ D. F. Detar and S. V. Sagmanli, J. Amer. Chem. Soc. 72, 965 (1950).

Solvent	Catalyst	SO₂(%)	HCI(%)	Yield (%)		
				VI	VII	VIII
	CuCl ^a	69	69	5	17	17º
OCN ^c	—	93	66	_	<u> </u>	17ª

TABLE 2. THE DECOMPOSITIONS OF DIPHENYLSULPHIDE-2-SULPHONYL CHLORIDE AT 250–260°

^a 1 mole % based on the sulphonyl chloride. ^b The yields in this experiment were determined by gas chromatography by using 18 ft \times $\frac{1}{3}$ in of 10% Apiezon L on Embacel at 210° and a flame ionization detector. ^c A 25% w/w solution of the sulphonyl chloride in octachloronaphthalene was used. ^d Isolated yield.

Biphenyl-2-sulphonyl chloride (IX)



There have been only two recorded attempts to convert derivatives of biphenyl-2amine to biphenylene by using intramolecular analogues of intermolecular arylations. Bell¹⁰ decomposed the diazo-compound in the presence of copper and obtained only 2-chlorobiphenyl and 2,2"-azobiphenyl whilst Baker^{11,12} obtained only resinous material on heating the N-acetyl-N-nitroso-derivative. Therefore, in addition to the present study of the decomposition of biphenyl-2-sulphonyl chloride, we have examined the behaviour of the amine under three conditions. In the first, an acetic acid solution of the amine containing sulphuric acid was diazotized with isoamyl nitrite and decomposed in the presence of copper; in the second, an ethanolic hydrogen chloride solution, diazotized with isoamyl nitrite, was decomposed in the presence of copper and sodium hypophosphite, and, in the third, the amine was boiled with isoamyl nitrite in benzene according to the intermolecular arylation conditions recommended by Hwang Hsu¹³ and by Cadogan¹⁴ and also in hexafluorobenzene in an attempt to avoid arylation of the solvent. The reaction mixtures were examined carefully by gas chromatography and by IR spectroscopy, and in no case was biphenylene detected.

- ¹⁰ F. Bell, J. Chem. Soc. 2770 (1928).
- ¹¹ W. Baker, M. P. V. Boarland and J. F. W. McOmie, J. Chem. Soc. 1476 (1954).
- ¹² W. Baker and J. F. W. McOmie, in *Non-Benzenoid Aromatic Hydrocarbons* (Edited D. Ginsburg) p. 43. Interscience (1959).
- 18 Hwang Hsu, Acta Chim. Simica 33, 171 (1959).
- 14 J. I. G. Cadogan J. Chem. Soc. 4257 (1962).

In the decomposition of biphenyl-2-sulphonyl chloride (Table 3), the formation of 2-chloro-biphenyl is favoured compared with the relatively difficult cyclization to biphenylene both in the absence and in the presence of octachloronaphthalene. The formation of a small quantity of dibenzothiophen-5,5-dioxide (XII) in octachloronaphthalene may be owing to competition from a Friedel-Crafts type of reaction since a high recovery of HCl is obtained and the dioxide is the dominant product when the reaction is carried out in impure octachloronaphthalene. However, it is notable that only small amounts of metallic impurities are present in both the purified (82 ppm) and in the impure (118 ppm) solvents compared with the molar proportion of aluminium chloride that is used in the deliberate conversion of the sulphonyl chloride to the dioxide.¹⁵

Solvent	Catalyst	50 (% /)		Yield (%)°	
		30 ₂ (/ ₀)		x	XII
		92	34	45	
	CuCl ^b	92	27	66	
OCN ^c	_	56	52	48	4
OCN [₫]	_	17	93		27

TABLE 3. THE DECOMPOSITIONS OF BIPHENYL-2-SULPHONYL CHLORIDE AT 250-260"

^a The yields given are isolated yields. ^b 1 mole % based on the sulphonyl chloride. ^c A 16.5% w/w solution of the sulphonyl chloride in octachloronaphthalene was used. ^d Impure octachloronaphthalene (Experimental).

2'-Phenyldiphenylether-2-sulphonyl chloride (XIII)



The decomposition of 2'-phenyldiphenylether-2-sulphonyl chloride in the absence of solvent leads to a high recovery of both sulphur dioxide and hydrogen chloride and to the formation of the new heterocycle, tribenz (b, d, f) oxepin (XV). The results in Table 4 show that only relatively small amounts of the alternative cyclization product,

¹⁵ M. Chaix Bull, Soc. Chim. Fr. 53, 700 (1933).

Solvent	Catalyst	SO2(%)	HCl(%)	Yield (%)		
				XIV	xv	XVI
	<u> </u>	100	99	6	42ª	3
	CuCl ^e	90	92	_	44°	
OCN [₫]	_	95	86	_	43°	

TABLE 4. THE DECOMPOSITIONS OF 2'-PHENYL-DIPHENYLETHER-2-SULPHONYL CHLORIDE AT 250-260°

^a The yields in this experiment were determined by gas chromatography by using 4 ft \times 1^s in of 7.8% Apiezon L on Embacel at 225° and a Pye argon ionisation detector. A 29% yield of tribenz (b, d, f) oxepin was readily isolated from the product. ^b The yields quoted are isolated yields. ^c 1 mole % based on the sulphonyl chloride. ^c A 25% w/w solution of the sulphonyl chloride in octa-chloronaphthalene was used.

4-phenyldibenzofuran (XVI),¹⁶ and of the parent 2-phenyl-diphenyl ether (XIV) are formed. By contrast with the decompositions discussed earlier, the high gas recovery confirms the absence of significant quantities of 2-chloro-2'-phenyldiphenylether and suggests that the cyclization is relatively easy in this case and that it is in competition only with intermolecular arylations leading to polymers. If this is so, the cyclization would be dominant if the decomposition were carried out in an inert solvent but unfortunately the presence of octachloronaphthalene is clearly not beneficial to the reaction and it leads to difficulties in product isolation. In the absence of solvent, simple distillation followed by crystallization serves to recover the pure product. The characterization of the oxepin is dealt with in a later section.

2'-Phenyldiphenylether-2-amine is the precursor to the sulphonyl chloride and it would be an advantage if the amine could be used directly in the preparation of the oxepin. Therefore, we have examined four diazonium cyclization methods. The first method followed that used by Gilman¹⁷ in which the amine is diazotized in acetic acid-sulphuric acid solution and is decomposed in 50% sulphuric acid; only phenolic material was recovered. The other three methods were those used in the attempted conversions of biphenyl-2-amine to biphenylene. In acetic acid-sulphuric acid with isoamyl nitrite followed by decomposition in the presence of copper, a 23% yield of the oxepin was obtained. In ethanolic-hydrogen chloride with isoamyl nitrite and decomposition in the presence of copper and sodium hypophosphite, careful search revealed no oxepin in the product, whilst the Hwang Hsu arylation method in either benzene or in hexafluorobenzene gave maximum yields (gas chromatography) of 10% of the oxepin.

2'-phenyldiphenyl sulphide-2-sulphonyl chloride (XVII)

Although the decomposition of 2'-phenyldiphenylsulphide-2-sulphonyl chloride leads to the formation of tribenzo (b, d, f) thiepin, and although this is readily isolated the reaction is less clear cut than in the case of the corresponding oxygen compound. The gas evolution is less than quantitative and in addition to a relatively greater competition from the alternative cyclization product, 4-phenyldibenzothiophen (XIX),¹⁶ significant quantities of other unidentified substances are evident in the gas

¹⁶ E. B. McCall, A. J. Neale and T. J. Rawlings, J. Chem. Soc. 4900 (1962).

¹⁷ H. Gilman, M. W. Van Ess and D. M. Hayes, J. Amer. Chem. Soc. 61, 643 (1939).



chromatogram of the distilled product. In octachloronaphthalene, the reaction again leads to lowered isolated yields of the cyclization product.

Yield (%) Solvent Catalyst SO₁(%) HCI(%) XVIII XIX CuCl^a 84 96 400.0 14 **OCN^d** 94 85 19.

TABLE 5. THE DECOMPOSITIONS OF 2'-PHENYLDIPHENYLSULPHIDE-2-SULPHONYL CHLORIDE AT 250–260°

* 1 mole % based on the sulphonyl chloride. * The yields were determined by gas chromatography by using 4 ft \times $\frac{1}{3}$ in of 10% Silicone gum rubber on Embacel temperature programmed at 30°/min from 200 to 300° and a catharometer detector. * A 24% yield of tribenzo (b, d, f) thiepin could be isolated readily from a similar product. * A 25% w/w solution was used. * Isolated yield.

The Characterization of the oxepin (XV) and the thiepin (XVIII)

The oxepin was resistant to zinc dust distillation as is typical¹⁸ of aromatic ethers and since no other suitable degradation to compounds of known constitution was available, its structure was confirmed, *inter alia*, by its mass spectrum (Fig. 2). This spectrum shows a very abundant parent ion at m/e 244 and an abundant ion at m/e 216 corresponding to a loss of 28 mass units. The ion at m/e 77 (C_6H_5) is very moderate in the spectrum and this suggests that phenyl groups are not present in the original structure, whilst m/e 94 is indicative of a fragmentation to C_6H_4O . The UV spectra of the oxepin and of the thiepin resemble that of *o*-terphenyl (Fig. 1). This indicates an absence of a major influence of the eight pi electron central rings and is consistent with the observations that have been made on the small effects of the seven membered eight pi and six pi electron central rings on the ultraviolet spectra and the properties

¹⁶ E. Clar, Chem. Ber. 72B 1645 (1939); Z. Valenta, Techniques of Organic Chemistry, IX, part 2; p. 643. Interscience (1963).

¹⁹ J. Meinwald and H. Nozaki, J. Amer. Chem. Soc. 80, 3130 (1958).

²⁰ R. G. Shuttleworth, W. S. Rapson and E. T. Stewart, J. Chem. Soc. 71 (1944); W. S. Rapson, H. M. Schwartz and E. T. Stewart, *Ibid.* 73 (1944).

of tribenzocyclo-octatetraene (XX; Z, CH:CH), tribenzotropone (Z, C:O)^{21.22} and of the tribenzotropylium cation (Z, C⁺).²³



The thiepin undergoes reductive desulphurization²⁴ with Raney nickel W-7 in ethanol at room temperature to give a good yield of *o*-terphenyl (XXII). Surprisingly, we have found that dibenzothiophen is also desulphurized to biphenyl under the same conditions so that the result for the thiepin cannot be taken as evidence for the instability of the seven membered ring. Additional evidence for the structure proposed was found in the sulphur extrusion reaction²⁵ at high temperatures. The thiepin was recovered largely unchanged after 5 hr in diethyl phthalate at 315° in the presence of copper bronze and after this period pyrolysis of the phthalate became significant. Therefore the reaction was carried out in a mixture of the *bis*-phenoxy-terphenyls (XXIII) which are produced in the arylation of a large excess of diphenylether with



benzene-*m*-disulphonyl chloride at 250-260°. This mixture is a very viscous oil at room temperature but it has a high boiling point $(230-260^{\circ}/0.05 \text{ mm})$ and is stable indefinitely at temperatures up to at least 400° in the absence of air. The thiepin was converted to triphenylene (XXI) after 5 hr at 380° in XXIII in the presence of copper bronze.

- ²¹ E. D. Bergmann and J. Klein, J. Org. Chem. 23, 512 (1958).
- ²² M. Stiles and A. J. Libby J. Org. Chem. 22, 1243 (1957), 24, 268 (1959); M. Stiles and A. J. Sisti *Ibid.* 26, 3639 (1961).
- ²³ G. Naville, H. Strauss and E. Heilbronner, Helv. Chim. Acta 43, 1221 (1960).
- ²⁴ G. R. Pettit and E. E. van Tamelen, Org. Reactions 12, 356 (1962).
- ²⁶ R. H. B. Galt and J. D. Loudon, J. Chem. Soc. 885 (1959).







Fig. 2

EXPERIMENTAL

The UV spectra EtOH solutions) were obtained by using a Unicam SP 700 spectrometer and the IR spectra (CCl₄ and CS₂ solutions except where stated) by using a Grubb-Parsons S4 spectrometer. The mass spectra were determined and interpreted by Dr. R. I. Reed of Glasgow University. The gas chromatographic analyses were carried out by ignoring mass sensitivity and injection errors except where indicated and these and the UV and IR spectra were supplied by Mr. R. A. Lidgett of these laboratories. The authentic sample of biphenylene was supplied by Dr. J. F. W. McOmie of Bristol University.

Octachloronaphthalene was prepared by the chlorination of naphthalene according to a published method.²⁴ It was purified by sublimation at 180°/0·1 mm and then recrystallized three times from benzene to give colourless crystals having m.p. 200–202°. (Found: C, 29·82; H, 0; Cl, 70·20. Calc. for $C_{10}Cl_{1}$: C, 29·75; Cl, 70·25%). Spectrographic analyses showed the presence of 82 ppm of metallic impurities with a predominance of Al(20), Cu(20), Fe(10), Ca(10), Na(10) and Si(5 ppm). It is notable that we have found that the courses of the decompositions of the sulphonyl chlorides are very sensitive to the purity of the octachloronaphthalene used. Thus, for example, the omission of the sublimation from the purification gave yellow crystals with m.p. 192–193° and the use of this as a solvent promoted the formation of dibenzothiophen-5,5-dioxide from biphenyl-2-sulphonyl chloride. This impure octachloronaphthalene contained 118 ppm of metallic impurities with Al(20), Cu(10), Fe(10), Ca(10), Na(10), and Si(50 ppm) predominant.

General method for the preparations of the sulphonyl chlorides

All the sulphonyl chlorides were prepared from the corresponding amines by a modification of the Sandmeyer reaction that has been described by Meerwein.³⁷ In general, it was found that the compounds decomposed on attempted distillation and they were all isolated by crystallization. The general procedure is illustrated by the preparation of 2'-phenyldiphenylsulphide-2-sulphonyl chloride; this method was followed closely in all cases.

2'-Phenyldiphenylsulphide-2-amine (32 g 0.116 mole) was dissolved in glacial acetic acid (79 ml) and conc. HCl (26 ml) added. The vigorously stirred solution was diazotised at $0-5^{\circ}$ with NaNO₂ (9.25 g, 0.135 mole) in water (19.5 ml) and the diazonium salt solution poured into a mixture of 30% SO₃-glacial acetic acid (70 ml) and benzene (70 ml) in which CuCl₃:2H₃O (5.7 g) had been suspended and which was at 10° initially. When the vigorous N₃ evolution had subsided, the mixture was heated to 40° and it was maintained at this temp by the heat of the reaction or by subsequent external heating for 3 hr. It was then poured into water (1000 ml) and the resultant oil was extracted into ether, dried (Na₃SO₄) and the ether removed *in vacuo*. The oil crystallized from dry petrol (b.p. 80-100°) as yellow crystals m.p. 79-80° (15.5 g, 36%) of the sulphonyl chloride.

General method for the decompositions

The sulphonyl chloride (5-10 g) alone or intimately mixed with octachloronaphthalene and with CuCl where indicated was contained in a glass vessel under a N₂ atm. The contents were stirred and the vessel was plunged into a high temp salt bath (HTS)³⁴ held at 250-260°. After 10 min the temp of the reactants reached 250° and the reaction was allowed to proceed at this temp until the evolution of SO₂ and HCl had ceased (2-5 hr). The gases evolved were led through a sintered glass gas distributor into NaOH aq. HCl was determined after expulsion of SO₂ by titration with AgNO₃ and SO₃, after oxidation with I₂, by back titration with Na₃S₂O₃. The sulphonyl chloride contents of the starting compounds were determined by using the method of Jensen and Brown³⁴ except that tetrahydrofuran was used as the solvent instead of EtOH to give improved end-points.

Diphenylether-2-sulphonyl chloride (I)

2-Nitro-diphenylether (50.3 g, 0.234 mole), obtained in 80% yield from o-chloronitrobenzene by the method of Brewster and Groening,⁵⁰ in EtOH (500 ml) was hydrogenated at room temp by using

- ²⁸ V. Shvemberger and V. Gordon, J. Gen. Chem. USSR. 2, 921 (1932).
- ¹⁷ H. Meerwein, G. Dittmar, L. Gollner, K. Hafner, F. Mensch, and O. Steinfort, *Chem. Ber.* 90, 841 (1957).
- ²⁶ W. E. Kirst, W. M. Nagle and J. B. Castner, Trans. Amer. Inst. Chem. Eng. 36, 371 (1940).
- ²⁸ E. R. Jensen and H. C. Brown, J. Amer. Chem. Soc. 80, 4038 (1958).
- ²⁰ R. Q. Brewster and T. Groening, Org. Syntheses. Coll. Vol. II, p. 445.

5% Pd—C (5 g). Distillation of the product gave an oil b.p. $100-105^{\circ}/0.25$ mm which solidified to give colourless crystals, m.p. 43-45° (38.2 g, 88%) of diphenylether-2-amine. Jones and Cook³¹ and Suter³² gave m.p. 43-45° and m.p. 44-45°, b.p. 172-173°/14 mm for the products from SnCl₂ and Fe-HCl reductions respectively.

Diphenylether-2-amine (24 g, 0.13 mole) when subjected to the general Meerwein procedure gave an oil (25 g) which could not be crystallized when first obtained and could not be purified by distillation even at low press. Thus the crude oil when distilled gave a colourless oil, b.p. $168-170^{\circ}/0.2$ mm with a Jensen-Brown analyses of 95% and a poor microanalysis. Subsequent re-distillation through a Vigreux column gave a colourless oil b.p. $138^{\circ}/0.05$ mm with a Jensen-Brown analysis of 96.6%. After several months the oil crystallized when vacuum was applied and it crystallized from petrol (b.p. $60-80^{\circ}$) as colourless flakes m.p. $53-54^{\circ}$ of *diphenylether-2-sulphonyl chloride* (Found: C, 53.42; H, 3.48; Cl, 12.40; S, 11.70; C₁₉H₉CIO₃S requires: C, 53.63; H, 3.38; Cl, 13.30; S, 11.93%). It had Jensen-Brown analysis, 99.4%, and formed N-*phenyldiphenylether-2-sulphonamide* m.p. $171-172^{\circ}$ (Found: C, 66.15; H, 5.09; N, 4.25; S, 10.25. C₁₉H₁₅NO₃S requires: C, 66.44; H, 4.65; N, 4.31; S, 9.84%).

The decompositions of diphenylether-2-sulphonyl chloride

(1) No solvent; cuprous chloride catalyst. The decomposition of the sulphonyl chloride (5:27 g, 0:02 mole) in the presence of CuCl (0:019 g, 0:0002 mole) was complete in 1:5 hr at 250-260° and SO₂ (96%) and HCl (79%) were evolved. Simple distillation of the reaction mixture gave a colourless oil (1:5 g), b.p. 75-77°/0·1 mm. Gas chromatography using 2 ft \times $\frac{1}{16}$ in of 5% Silicone gum rubber on Embacel programmed from 100-300° at 75°/min indicated that 53% of the distillate was dibenzo-furan. This could not be isolated and more efficient gas chromatography (footnote to table 1) resolved the supposed dibenzofuran into two components. All the three products were isolated by preparative scale gas chromatography and were identified by comparisons of the IR spectra of the eluants with those of authentic samples. For this purpose, 2-chlorodiphenylether was prepared from diphenylether-2-amine by a Sandmeyer reaction closely similar to that described for 2-chlorobiphenyl.¹⁴ It had m.p. 45-47° (Huang,¹⁴ 47-48°). (Found: C, 70.4; H, 4.25; Cl, 17.22; calc. for C₁₂H₉CIO: C, 70.4; H, 4.43; Cl, 17.33%).

(2) Solvent octachloronaphthalene; no catalyst. The sulphonyl chloride (4 g, 0.015 mole) in octachloronaphthalene (12 g) at 250-260° gave SO₂ (91%) and HCl (16%) after 6 hr. The reaction mixture was extracted thoroughly with hot EtOH and the extract distilled to yield a colourless oil, b.p. 99°/0.2 mm (2.5 g) which was analysed by gas chromatography (Table 1). The oil solidified and crystallized from EtOH as colourless crystals of 2-chlorodiphenylether (1.52 g, 50%; m.p. and mixed m.p., $45-46^{\circ}$).

Diphenylsulphide-2-sulphonyl chloride (V)

2-Nitrodiphenylsulphide (174 g, 0.76 mole) obtained in 89% yield from *ortho*-chloronitrobenzene by the method of Roberts and Turner³⁴ was reduced with Fe powder (523 g), glacial acetic acid (3.5 ml) and water (3500 ml) at 85–90° for 12 hr. Diphenylsulphide-2-amine was obtained as a yellow oil (105 g, 69%) which crystallized and had m.p. 31–32°. (Found: C, 72·1; H, 5·76; N, 6·71; S, 15·6. Calc. for $C_{13}H_{11}NS$: C, 71·6; H, 5·51; N, 6·96; S, 15·9%).

Diphenylsulphide-2-amine (90 g, 0.45 mole) gave a brown oil (124 g) by the Meerwein procedure but attempted distillation led to decomposition at ca. 210°. The oil solidified on standing and crystal-lized from petrol (b.p. 40–60°) as colourless crystals m.p. 53–55° (71 g, 56%) of diphenylsulphide-2-sulphonyl chloride (Found: C, 50.86; 50.98; H, 4.09; 3.86; Cl, 12.25; 12.31; S, 22.08; 22.50. $C_{12}H_{0}$ ClO₂S₂ requires: C, 50.61; H, 3.19; Cl, 12.45; S, 22.52%). It had Jensen-Brown analysis, 99.5% and formed N-phenyldiphenylsulphide-2-sulphonamide, m.p. 156–157°. (Found: C, 63.91, 64.01; H, 4.47, 4.68; N, 4.15, 3.97; S, 18.28, 18.51. $C_{18}H_{18}NO_{8}S_{2}$ requires: C, 63.32; H, 4.43; N, 4.10; S, 18.78%).

³¹ H. I. Jones and A. N. Cook, J. Amer. Chem. Soc. 38, 1534 (1916).

32 C. M. Suter, J. Amer. Chem. Soc. 51, 2583 (1929).

³³ D. A. Shirley, Preparation of Organic Intermediates p. 48. J. Wiley (1951).

³⁴ E. Roberts and E. E. Turner, J. Chem. Soc. 1207 (1926).

³⁵ A. Lüttringhaus and D. Ambros, Chem. Ber. 89, 463 (1956).

The decompositions of diphenylsulphide-2-sulphonyl chloride

(1) No solvent; cuprous chloride catalyst. The sulphonyl chloride (5.4 g, 0.019 mole) with CuCl (0.019 g, 0.00019 mole) gave SO₂ (69%) and HCl (69%) after 2 hr at 250-260°. Distillation recovered a pale yellow oil b.p. 119-130°/0·1 mm (1.45 g) which was analysed by gas chromatography (Table 2).

(2) Solvent octachloronaphthalene; no catalyst. The sulphonyl chloride (4.8 g, 0.017 mole) and octachloronaphthalene (14.5 g) gave SO₂ (93%) and HCl (66%) after 5 hr at 250-260°. The reaction mixture was extracted into EtOH and distilled to give an oil, b.p. 120-150°/0.5 mm (1.6 g) which after several crystallizations from EtOH gave dibenzothiophen (0.5 g, 17%; m.p. and mixed m.p. 98-99.5°; IR spectrum).

Biphenyl-2-sulphonyl chloride (IX)

Biphenyl-2-amine (64.7 g, 0.38 mole) gave an oil by the Meerwein procedure which crystallized from petrol (b.p. 80-100°) as colourless plates, m.p. $102-104^\circ$ (51 g, 53%) of biphenyl-2-sulphonyl chloride. (Found: C, 57.49, 57.71; H, 3.73, 3.93; Cl, 14.48, 14.30; S, 12.72, 12.46. Calc. for C₁₄H₂ClO₂S: C, 57.03; H, 3.59; Cl, 14.04; S, 12.69%). It had Jensen-Brown analysis, 99%.

The decompositions of biphenyl-2-sulphonyl chloride

(1) No solvent; no catalyst. The sulphonyl chloride (5 g, 0.02 mole) gave SO₂ (92%) and HCl (34%) after 6 hr at 250-260° and distillation of the reaction mixture gave a colourless oil b.p. 70°/0.05 mm (1.7 g, 45%) having an IR spectrum identical with that of 2-chlorobiphenyl. Biphenylene was not detected in the spectrum. The chloro- compound was prepared from biphenyl-2-amine (Ref. 33) and had b.p. 142-144°/15 mm, m.p. 29-30°. (Found: C, 76.8; H, 4.65; Cl, 18.5; Calc. for $C_{12}H_9Cl$; C, 76.4; H, 4.81; Cl, 18.8%).

(2) No solvent; cuprous chloride catalyst. The sulphonyl chloride (5 g, 0.02 mole) with CuCl (0.02 g, 0.0002 mole) gave SO₂ (92%) and HCl (27%) after 2 hr, at 250-260°. Distillation gave 2-chlorobiphenyl (2.5 g, 66%); biphenylene was not detected by gas chromatography (2 ft $\times \frac{3}{16}$ in of 5% Silicone gum rubber on Embacel programmed 100-270° at 15°/min).

(3) Solvent octachloronaphthalene; no catalyst. The sulphonyl chloride (5 g, 0.02 mole) in octachloronaphthalene (25 g) gave SO₂ (56%) and HCl (52%) after 5 hr at 250–260°. The reaction mixture was extracted with hot EtOH and the extract distilled to give 2-chlorobiphenyl, b.p. 136–142°/16 mm (1.8 g, 48%; m.p. and mixed m.p. 29–31°; IR spectrum) and a crystalline residue which crystallized from glacial acetic acid as dibenzothiophen-5,5-dioxide, m.p. 232–235° (0.16 g, 4%; IR spectrum, nujol). Sublimation of the octachloronaphthalene residue failed to recover further product.

(4) Solvent impure octachloronaphthalene; no catalyst. The sulphonylchloride ((5 g, 0.02 mole) in impure octachloronaphthalene (25 g) gave SO_4 (17%) and HCl (93%) after 5 hr at 250–260°. Sublimation of the reaction mixture at 250° and atm. press. gave a yellow solid which crystallized from benzene as colourless needles of dibenzothiophen-5,5-dioxide (1.2 g, 27%; m.p. and mixed m.p., 238–240°; IR spectrum, nujol). Continued sublimation gave a product containing substantial quantities of octachloronaphthalene which could not be purified by recrystallization.

The attempted cyclizations of biphenyl-2-amine

(1) Biphenyl-2-amine (8.5 g, 0.05 mole) in acetic acid (375 ml.) containing H_2SO_4 (5.3 ml) was treated with isoamyl nitrite (13.3 ml) in acetic acid (62.5 ml) and the diazonium solution decomposed with Cu (6.4 g) as described in Ref. 5, p. 439. No biphenylene could be detected in the IR spectrum of the oil obtained after removal of the acetic acid. The oil solidified and gave colourless flakes of biphenyl (2.5 g, 33%; m.p. and mixed m.p.; IR spectrum).

(2) Biphenyl-2-amine (18.9 g, 0.11 mole) in 15% ethanolic HCl (300 ml) was diazotized with isoamyl nitrite (40 ml) and decomposed with Cu (2 g) and NaHPO₂ (100 g in 100 ml of dil. H₂SO₄) as in Ref. 5, p. 437. After reaction (vigorous N₂ evolution initially) the solution was extracted into ether, washed dried, and the ether removed to give an oil (3 g) in which no biphenylene could be detected by gas chromatography or in the IR spectrum.

(3) Biphenyl-2-amine (0.65 g, 0.0038 mole) isoamyl nitrite (0.67 g, 0.0057 mole) and benzene (100 ml) were heated under reflux for 24 hr. Removal of the benzene by distillation left a brown oil which was examined by gas chromatography (4 ft $\times \frac{1}{34}$ in of 10% Apiezon L on Embacel at 125°; Pye argon ionization detector). No biphenylene was detected. Similarly the amine (1 g, 0.0059 mole), isoamyl nitrite (1 g, 0.008 g mole) and hexafluorobenzene (25 ml) were heated under reflux for 24 hr and no biphenylene was detected in the product after removal of the hexafluorobenzene.

2'-Phenyldiphenylether-2-sulphonyl chloride (XIII)

An adaptation of the method of Brewster and Groening³⁰ using 2-phenyl-phenol (290 g, 1·7 mole) and o-chloronitrobenzene (158 g, 1·0 mole) gave 2-nitro-2'-phenyldiphenylether as a yellow oil (264 g, 91%) b.p. 185-186°/0·5 mm (Found: C, 74·08, 75·41; H, 4·47, 5·14; N, 5·09, 5·87. C₁₈H₁₃NO₃ requires: C, 74·22; H, 4·50; N, 4·81%). The nitrocompound was reduced according to the method described by Suter³² for the reduction of 2-nitrodiphenylether and also by catalytic hydrogenation with 5% Pd-C to give 2'-phenyldiphenylether-2-amine, m.p. 88·5-90°, in 60% and 90% yield respectively. (Found: C, 81·72, 82·94; H, 5·97; 6·08; N, 5·42, 5·27; M, 260. C₁₈H₁₈NO requires: C, 82·73; H, 5·79; N, 5·36%; M, 261). The amine formed N-(2-2'-biphenylyloxyphenyl)-phthalimde as colourless plates, m.p. 217-218°. (Found: C, 79·7; H, 4·36; N, 3·75. C₂₆H₁₇NO₃ requires: C, 79·8; H, 4·38; N, 3·58%).

The amine (212 g, 0.62 mole) gave an oil by the Meerwein procedure and this oil was purified by extraction into petrol (b.p. 60-80°) to give a product (167 g) with Jensen-Brown analysis, 75%. Complete decomposition occurred on attempted distillation and repeated crystallizations from petrol (b.p. 60-80°) were necessary to give pure 2'-phenyldiphenylether-2-sulphonyl chloride as colourless crystals, m.p. 76-77°. (Found: C, 63·3, 63·5; H, 3·95, 3·71; Cl, 10·19, 10·32; S, 9·29, 9·08. C₁₈H₁₃ClO₃S requires: C, 62·7; H, 3·80; Cl, 10·28; S, 9·30%). It formed N,2'-diphenyldiphenylether-2-sulphon-amide m.p. 155-156°. (Found: C, 72·4; H, 5·17; N, 3·53; S, 8·0. C₂₄H₁₉NO₃S requires: C, 71·8; H, 4·77; N, 3·49; S, 8·0%).

The decompositions of 2'-phenyldiphenylether-2-sulphonyl chloride

(1) No solvent; no catalyst. The sulphonyl chloride (5 g, 0.0145 mole) gave SO₂ (100%) and HCl (99%) after 4.5 hr at 250-260°. Distillation of the reaction mixture gave a pale yellow oil, b.p. 180-195° 0.5 mm (2.0 g) which was analysed by gas chromatography. (Table 4). For the purpose of identification, XIV was prepared from bromobenzene by an Ullmann reaction and had m.p. 48-49° (Refs. 9 and 35 give m.p. 49°). Repeated crystallizations of the oil from ethanol recovered *tribenz* (b, d, f) oxepin as colourless crystals, m.p. 115-116° (1.03 g, 29%). (Found: C, 88.4, 88.4; H, 5.12, 5.37; M (mass spectrum), 244. C₁₈H₁₂O requires C, 88.5; H, 4.95%. M 244) λ_{max} 241 (45,000) and 263 m μ (E, 16,700).

(2) No solvent; cuprous chloride catalyst. The sulphonyl chloride (5.40 g, 0.016 mole) and CuCl (0.016 g, 0.00016 mole) gave SO₂ (90%) and HCl (92%) after 2 hr at 250-260°. Distillation gave an oil b.p. 146-147°/0.1 mm (2.6 g) which solidified and a single crystallization from EtOH gave colourless flakes of tribenz (b, d, f) oxepin m.p. 114-116° (1.68 g, 44%; mixed m.p. and IR spectrum).

(3) Solvent octachloronaphthalene; no catalyst. The sulphonyl chloride (5 g, 0.015 mole) in octachloronaphthalene (15 g) gave SO₂ (95%) and HCl (86%) after 5 hr at 250-260°. The reaction mixture was extracted thoroughly with hot EtOH and the extract distilled to give a brown oil, b.p. 180-195°/0.1 mm (3.2 g). Three successive crystallizations from EtOH were necessary to recover tribenz (b, d, f) oxepin, m.p. 115-116° (1.5 g, 43%).

The attempted cyclizations of 2'-phenyldiphenylether-2-amine

(1) The amine (10 g, 0.038 mole) in glacial acetic acid was diazotized with a nitrosyl sulphuric acid solution (from NaNO₂ 2.9 g, 0.04 mole and H₂SO₄, 20.5 ml) and then added gradually to boiling 50% H₂SO₄ (150 ml). A brown oil (0.1 g) containing substantial phenolic material (IR) was recovered from the steam distillate. The residue was extracted into ether, washed, dried (Na₂SO₄) and distilled to give an oil, b.p. 154–156°/0.01 mm (1.7 g) also containing substantial phenolic material.

(2) The amine (26 g, 0.1 mole) in glacial acetic acid (750 ml) containing H_2SO_4 (10.5 ml) was diazotized with isoamyl nitrite (26.5 ml) in acetic acid (125 ml) and decomposed with Cu (12.8 g) as described in Ref. 5, p. 439. Removal of the acetic acid left a tarry residue which was exhaustively extracted with hot benzene to recover an oil (7.8 g) which solidified and crystallized from petrol (b.p. 60-80°) as tribenz (b, d, f) oxepin (5.5 g, 23%; m.p. and mixed m.p. 112-114°; IR spectrum).

(3) The amine (14.6 g, 0.056 mole) in 15% ethanolic HCl (150 ml) was diazotized with isoamyl nitrite (20 ml) and decomposed with Cu (1 g) and Na₂HPO₂ (50 g in 50 ml dil H₂SO₄). After reaction (vigorous N₂ evolution initially), ether extraction recovered an oil (14.8 g) which contained only small quantities of the oxepin and of 4-phenyldibenzofuran (IR spectrum; gas chromatography).

(4) The amine (1 g, 0.0038 mole), isoamyl nitrite (0.67 g, 0.0057 mole) and benzene (100 ml) were heated under reflux for 24 hr. Removal of the benzene gave an oil (1.2 g) which was analysed by gas chromatography by using a Pye argon chromatograph and 4 ft $\times \frac{1}{16}$ in of 10% Apiezon L on Gas Chrom. P. at 225°. Comparison of the reaction mixture with a test mixture of known composition, and neglecting injection errors, indicated the presence of tribenz (b, d, f) oxepin (10% yield) and 4-phenyl-dibenzofuran (1%). Similarly, the amine (1 g) in hexafluorobenzene (25 ml) with isoamyl nitrite (0.67 g) after 24 hr under reflux gave an oil which contained a maximum 10% yield of the oxepin.

2'-Phenyldiphenylsulphide-2-sulphonyl chloride (XVIII)

Compound IX (141 g, 0.56 mole) was reduced with Zn-H₂SO₄ (Bourgeois³⁶) and the biphenyl-2thiol isolated by steam distillation, extraction into ether and subsequent distillation, b.p. 100–102°/ 0.25 mm, m.p. 38–39° (74 g, 70%). A mixture of the biphenyl-2-thiol (72.7 g, 0.39 mole) and EtONa (0.39 mole) in EtOH (100 ml) was dried and the residue in water (125 ml) added gradually to ochloronitrobenzene (62 g, 0.39 mole) in N,N-dimethylformamide (250 ml). After 2 hr at 100° the mixture was poured into water, extracted into ether, washed and dried (Na₂SO₄). Removal of the ether left an oil which solidified and crystallized from EtOH as yellow crystals, m.p. 93–94° (96 g, 80%) of 2-*nitro*-2'-*phenyldiphenylsulphide*. (Found: C, 70·4; H, 4·19; N, 4·48; S, 10·35. C₁₈H₁₈NO₂S requires: C, 70·3; H, 4·26; N, 4·56; S, 10·35%). This nitro-compound (96 g, 0·3 mole) was reduced by the procedure described for 2-nitrodiphenylsulphide and gave 2'-*phenyldiphenylsulphide*-2-*amine* as a pale yellow oil, b.p. 170–172°/0·04 mm (59·5 g, 73%) which did not crystallize. (Found: C, 78·0; H, 5·38; N, 5·02; S, 11·74. C₁₈H₁₈NS requires: C, 77·9; H, 5·45; N, 5·05; S, 11·56%).

The amine (59.5 g, 0.22 mole) gave an oil by the Meerwein procedure which crystallized from petrol (b.p. 60-80°) to give yellow crystals, m.p. 78-79° (24 g, 30%) of 2'-phenyldiphenylsulphide-2-sulphonyl chloride. (Found: C, 60.5; 60.5; H, 3.54, 3.48; Cl, 9.89, 9.90; S, 17.9, 17.7. $C_{18}H_{13}ClO_2S_2$ requires: C, 59.9; H, 3.63; Cl, 9.83; S, 17.7%). It formed N,2'-diphenyldiphenylsulphide-2-sulphon-amide, m.p. 200°. (Found: C, 69.2; H, 4.43; N, 3.31; S, 15.5. $C_{24}H_{19}NO_2S_3$ requires: C, 69.0; H, 4.59; N, 3.36; S, 15.4%).

The decompositions of 2'-phenyldiphenylsulphide-2-sulphonyl chloride

A series of decompositions in the presence and absence of octachloronaphthalene and with and without CuCl as a catalyst were carried out and the crude reaction mixtures examined by gas chromatography. The highest yield of tribenzo (b, d, f) thiepin was obtained by using CuCl in the absence of solvent and, except in the case described below for the decomposition in octachloronaphthalene, this method was used in all subsequent work. Thus, the sulphonyl chloride (10 g, 0.028 mole) and CuCl (0.027 g, 0.00028 mole) gave SO₂ (80%) and HCl (94%) after 2 hr at 250-260°. Distillation gave a pale yellow oil, b.p. 163-166°/0.05 mm (5.2 g) which crystallized from EtOH as colourless needles m.p. 117-118° (1.7 g, 24%) of *tribenzo* (b, d, f) *thiepin*. (Found: C, 82-8; H, 4-64; S, 12-2° M(Mechrolab osmometer), 254; M(mass spectrum), 260. C₁₈H₁₈S requires: C, 83·1; H, 4·60; S, 12·3%, M, 260). λ_{max} 236 (46,000) and 251 m μ (24,600). It formed the *dioxide*, m.p. 200-201s after treatment with H₄O₂ in boiling acetic acid. (Found: C, 73·6; H, 3·91; S, 11·5. C₁₈H₁₂O₂S₂ requires: C, 74·0; H, 4·11; S, 11·0%).

In octachloronaphthalene (15 g) the sulphonyl chloride (5 g, 0.014 mole) gave SO₂ (94%) and HCl (85%) after 5 hr at 250-260°. The product was extracted into EtOH and distilled to give a yellow oil which required 3 crystallizations from EtOH to give moderately pure tribenzo (b, d, f) thiepin (0.66 g, 19%; m.p. and mixed m.p. 114-116°).

Reductive desulphurization of the thiepin

After the thiepin (0.5 g) and Raney Ni W-7 (2 g) had been boiled in EtOH (10 ml) for 5 hr, a colourless oil (0.42 g) was recovered which crystallized from MeOH as colourless needles, m.p. 46-48° (0.26 g) of partly hydrogenated *o*-terphenyl (IR spectrum). Therefore, the thiepin (0.5 g) in EtOH (20 ml) was shaken at room temp with Raney Ni W-7 (1.5 g) for 16 hr and an oil (0.43 g) was recovered which crystallized from MeOH as *o*-terphenyl (m.p., mixed m.p., 52-54°; IR spectrum; 0.3 g, 68%). Dibenzothiophen (0.2 g) with W-7 (1 g) in EtOH (5 ml) was treated similarly and gave

³⁶ E. Bourgeois, Ber. Dtsch. Chem. Ges. 28, 2312 (1895).

partly hydrogenated biphenyl (m.p. 66-68°; IR spectrum) Badger³⁷ and others³⁸ report the formation of high yields of pure biphenyl by using W-7 in boiling EtOH and therefore the W-7 used here may be more active than is usual although it was made by a standard procedure.³⁹

Sulphur extrusion from the thiepin

The thiepin (0.20 g) was recovered unchanged from diethyl phthalate (2.5 ml) and Cu-bronze (0.33 g) after 30 min at 315° and therefore the reaction time was extended to 5 hr. Extraction of the cooled reactants with boiling benzene and filtration of the extract through charcoal left a diethyl phthalate solution from which crude phthalic anhydride (0.2 g) m.p. 124–130° crystallized. This was removed and the filtrate was taken into ether, washed with dil. NaOH aq, and with water, dried (MgSO₄) and distilled to recover diethyl phthalate and to leave crude thiepin as an oil. This crude oil with Cu-bronze (0.33 g) in the mixed bis-phenoxyterphenyls (2.5 g) was maintained at 380° for 5 hr. Distillation gave an oily solid b.p. $160^{\circ}/0.2$ mm which, after removal of adhering oil, crystallized from EtOH as colourless needles (0.005 g) of triphenylene (m.p. and mixed m.p. 192–193°; IR spectrum, nujol).

The mixed bis-phenoxyterphenyls (XXIII) were prepared from benzene-m-disulphonyl chloride (13.8 g, 0.05 mole) and diphenylether (255 g, 1.5 moles) with CuCl (0.05 g, 0.0005 mole) which were heated at 250-260° for 5 hr. SO₂ (94%) and HCl (97%) were evolved and distillation gave a pale yellow oil, b.p. 230-266°/0.05 mm (14.9 g, 72%). (Found: C, 86.60; H, 5.43; Cl, 0; S, 0. M (Mechrolab osmometer), 400. C₂₀H₂₂O₂ requires: C, 86.93; H, 5.35%. M, 414).

³⁷ G. M. Badger and W. H. F. Sasse, J. Chem. Soc. 3862 (1957).

- ³⁴ F. F. Blicke and D. G. Sheets, J. Amer. Chem. Soc. 71, 4010 (1949); G. E. Wiseman and E. S. Gould, *Ibid.* 76, 1706 (1954).
- ³⁹ H. R. Billica and H. Adkins, Org. Syntheses. Coll. Vol. III, p. 176ff.