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THE REACTION OF 2,4-DINITROBENZENESULPHENYL CHLORIDE WITH ORGANIC MONOSULPHIDES

C. G. MOORE and M. PORTER
The British Rubber Producers' Research Association, Welwyn Garden City, Herts

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Abstract—2,4-Dinitrobenzenesulphenyl chloride (I) reacts with dialkyl, diaralkyl, and alkyl aralkyl monosulphides at ca. 20° in dry acetic acid to give alkyl or aralkyl 2,4-dinitrophenyl disulphides together with alkyl or aralkyl chlorides as major products. The reactivity order with respect to the constitution of the sulphide is: tertiary alkyl > benzyl > secondary alkyl > primary alkyl. With unsymmetrical sulphides, the more branched alkyl group is displaced by the 2,4-dinitrophenylthio group. Monosulphides containing allylically-unsaturated groups react with I both by its addition to the double bond and by fission of a C–S bond in the derived adduct. Based on the response of both the course and rate of reaction to the constitution of the monosulphide and to the nature of the solvent a polar mechanism is proposed, involving an initial electrophilic attack of the sulphenyl chloride on the sulphide sulphur to give a "sulphonium ion" type intermediate which then undergoes cleavage of a preferred C–S bond (dependent on the structures of the alkyl and aralkyl groups) to give the observed products.

AN exchange reaction of arenesulphenyl chlorides with organic disulphides which conforms closely to the stoicheiometry of reaction (1) has been reported recently:[1]

$$\mathrm{ArSCl + RS{\cdot}SR \rightleftharpoons ArS{\cdot}SR + RSCl} \qquad (1)$$

The reaction of 2,4-dinitrobenzenesulphenyl chloride (I) with variously constituted saturated and allylically-unsaturated monosulphides is now described.

This work was undertaken in order to establish a chemical method for determining the amount of olefinic unsaturation in the mono- and polysulphides derived from sulphur-olefin interaction;[2] the principle is to react the unsaturated sulphidic mixture with a known excess of sulphenyl chloride in anhydrous acetic acid under conditions established as leading to quantitative addition of the reagent to olefins[3] and then to determine the unreacted sulphenyl chloride by an iodometric method based on that of Kharasch and Wald.[4] The exchange reaction (1) with disulphides present, and comparable reactions with higher polysulphides, would not interfere since sulphenyl chloride function is not lost in these processes.[1] However, when the method was applied to authentic alkenyl alkyl monosulphides (viz., $\mathrm{CH_2{:}CH{\cdot}CH_2{\cdot}S{\cdot}Bu^t}$ and $\mathrm{Me_2C{:}CH{\cdot}CH(Me){\cdot}S{\cdot}CH_2Ph}$) considerably more than one molar equivalent of the sulphenyl chloride (I) was consumed (see Table), and this finding was followed by the observation that saturated monosulphides also react with I, thus rendering the method invalid.

It has now been established (see Table) that reaction between I and dialkyl,

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[1] C. G. Moore and M. Porter, *J. Chem. Soc.* 2890 (1958).
[2] L. Bateman, C. G. Moore and M. Porter, *J. Chem. Soc.* 2866 (1958).
[3] N. Kharasch, H. L. Wehrmeister and H. Tigerman, *J. Amer. Chem. Soc.* **69**, 1612 (1947); W. L. Orr and N. Kharasch, *Ibid.* **75**, 6030 (1953); and other papers in the same series.
[4] N. Kharasch and M. M. Wald, *Analyt. Chem.* **27**, 996 (1955).

diaralkyl, and cyclic monosulphides is a general one, proceeding according to reaction (2) (Ar = 2,4-dinitrophenyl, here and throughout):

$$\underset{\text{I}}{\text{ArSCl}} + \underset{\text{II}}{\text{R·S·R}} \xrightarrow[20^\circ]{\text{AcOH}} \text{ArS·SR} + \text{RCl} \qquad (2)$$

with the proviso that in some cases elimination of the group R to give olefin and hydrogen chloride, and acetolysis of RCl may be minor competing reactions.

REACTION OF 2,4-DINITROBENZENESULPHENYL CHLORIDE (I) WITH MONOSULPHIDES IN ACETIC ACID AT ca. 20°.

Sulphide	Reaction time (hr)	Moles I consumed per mole of sulphide
Allyl t-butyl	24·0	1·13
	168·0	1·31
Benzyl 4-methylpent-3-en-2-yl	23·5	1·66
	48·0	1·82
	119·0	1·97
Di-n-propyl	140·0	0·057
Di-isopropyl	65·5	0·072
	259·0	0·156
	523·0	0·276
Isopropyl t-butyl	17·0	1·02
	89·0	1·04
Cyclohexyl methyl	25·0	0·041
	47·0	0·264
Diphenyl	97·5	0·00
	288·0	0·00
Dibenzyl	21·5	0·251
	165·5	0·746
Benzyl 2-methylpent-2-yl	25·0	1·13
	122·5	1·20
2-Ethyl-5-isopropyl-2-methylthiacyclopentane	22·0	0·670
	50·0	0·911

The validity of reaction (2) was shown in the case of II (R = CH_2Ph) by allowing equimolar quantities of I and dibenzyl sulphide to react in dry acetic acid at ca. 20°, when benzyl 2,4-dinitrophenyl disulphide was isolated (48 per cent yield after 48 hr reaction), and benzyl chloride, identified as S-benzylisothiuronium picrate (59 per cent yield after 283 hr reaction), was formed. The analogous reaction of I with II (R = isopropyl) gave 2,4-dinitrophenyl isopropyl disulphide (86 per cent yield after 529 hr at ca. 20° and 209 hr at 50°) and there was evidence for the presence of ca. 8 per cent of 2-chloropropyl 2′,4′-dinitrophenyl sulphide, presumably formed by the addition of I to propene,[5] the latter being derived from the displaced isopropyl group in II (R = isopropyl). The fact that monosulphides containing a tertiary alkyl group (e.g. benzyl 2-methylpent-2-yl sulphide) react with more than one molar equivalent of I (see Table) is similarly ascribed to the formation of olefin from the displaced

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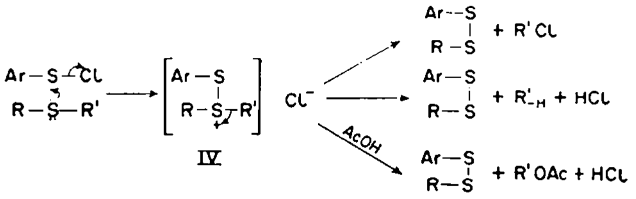
[5] N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.* 71, 2724 (1949).

tertiary alkyl group in the primary reaction and subsequent addition of I to the olefin to give a chloroalkyl 2,4-dinitrophenyl sulphide.

In the reaction of I with unsymmetrical monosulphides III (reaction 3), the group R′ displaced as the chloride is that containing the more substituted α-carbon atom; thus, isopropyl t-butyl sulphide gives 2,4-dinitrophenyl isopropyl disulphide, and benzyl 2-methylpent-2-yl sulphide gives benzyl 2,4-dinitrophenyl disulphide. The

$$\underset{\mathrm{I}}{\mathrm{ArSCl}} + \underset{\mathrm{III}}{\mathrm{R{\cdot}S{\cdot}R'}} \rightarrow \mathrm{ArS{\cdot}SR} + \mathrm{R'Cl} \qquad (3)$$

reaction rate also is markedly dependent on the structure of the saturated monosulphide, the rate increasing with increasing branching on the α-carbon atoms in R- and R′- (see Table). The course and rate of reaction appear, therefore, to depend upon the ease with which the groups R- and R′- in II and III are displaced as carbonium ions, the observed order (see Table) being: $\mathrm{Alk_3C{-}} > \mathrm{PhCH_2{-}} > \mathrm{Alk_2CH{-}} > \mathrm{AlkCH_2{-}} \gg \mathrm{Ph{-}}$ (cf.[6]). These findings, coupled with the fact that the reaction of I with II ($R = CH_2Ph$) is slower in benzene than in acetic acid (see Experimental), suggest that reactions (2) and (3) involve a bimolecular electrophilic attack of the sulphenyl halide on the monosulphide to give a "sulphonium ion" type complex (IV) from which elimination of the cationically most stable group, R′-, occurs to give the observed products (reactions 4, 5, and 6):

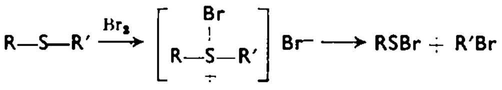


(4)

(5)

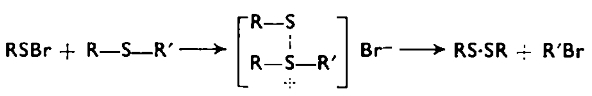
(6)

The reaction paths envisaged above are analogous to those recently proposed for the exchange reaction (1)[1] and for the destructive bromination of unsymmetrical monosulphides (reactions 7 and 8):[7]



$$\mathrm{R{-}S{-}R'} \xrightarrow{\mathrm{Br_2}} \left[\begin{array}{c}\mathrm{Br}\\ |\\ \mathrm{R{-}\overset{+}{S}{-}R'}\end{array}\right]\mathrm{Br^-} \longrightarrow \mathrm{RSBr} + \mathrm{R'Br} \qquad (7)$$

V



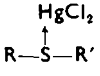
$$\mathrm{RSBr} + \mathrm{R{-}S{-}R'} \longrightarrow \left[\begin{array}{c}\mathrm{R{-}S}\\ |\\ \mathrm{R{-}\overset{+}{S}{-}R'}\end{array}\right]\mathrm{Br^-} \longrightarrow \mathrm{RS{\cdot}SR} + \mathrm{R'Br} \qquad (8)$$

The formation of the intermediate "sulphonium" halides IV and V and their subsequent decomposition by fission of the C–S bonds involving the group R′ which is higher in the cationic stability series conforms to the general pattern of reactivity of sulphides with electrophilic reagents, e.g. their reaction with mercuric chloride and with methyl iodide to give the isolable compounds VI and VII, respectively,

[6] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* pp. 316, 325. Bell, London (1953).

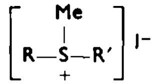
[7] I. L. Knunyants and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1219 (1958).

which undergo decomposition by C–S bond fission involving the group R′ which yields the more stable cation.[8]



$$R-\overset{\overset{HgCl_2}{\uparrow}}{S}-R'$$

VI



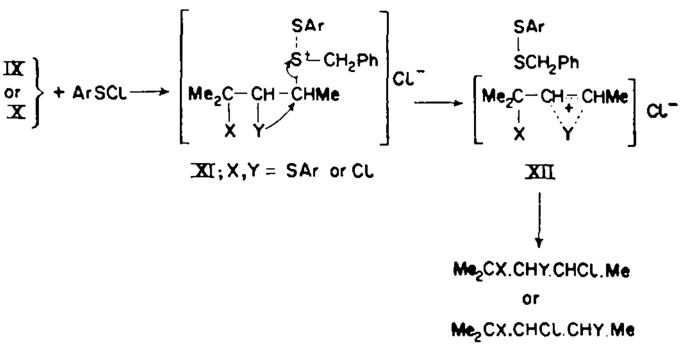
$$\left[R-\underset{+}{\overset{\overset{Me}{|}}{S}}-R'\right]I^-$$

VII

Interaction of the arenesulphenyl chloride (I) with allylically-unsaturated monosulphides involves both addition of I to the double bond and attack on the sulphur atom (as in reactions 2 and 3). For example, benzyl 4-methylpent-3-en-2-yl sulphide (VIII) reacts with ~2 molar equivalents of I to give benzyl 2,4-dinitrophenyl disulphide as one product. Comparison of the data on the above system (see Table) with the kinetics of addition of I to olefins[9] suggests that the reaction involves a fast addition of I to the double bond of VIII to give the adducts IX and/or X (reaction 9), which then undergo a slower reaction with I as indicated below (reaction 10):

$$\mathrm{ArSCl} + \underset{\mathrm{VIII}}{\mathrm{PhCH_2{\cdot}S{\cdot}CHMe{\cdot}CH{:}CMe_2}} \xrightarrow{\text{fast}} \underset{\mathrm{IX}}{\mathrm{PhCH_2{\cdot}S{\cdot}CHMe{\cdot}CH(SAr){\cdot}CMe_2Cl}}$$

$$\text{and/or } \underset{\mathrm{X}}{\mathrm{PhCH_2{\cdot}S{\cdot}CHMe{\cdot}CHCl{\cdot}CMe_2{\cdot}SAr}} \qquad (9)$$



(10)

Two features of this reaction require comment: firstly, that it is the secondary alkyl group in XI, and not the benzyl group, which undergoes displacement by C–S bond fission, contrary to the general pattern observed previously for saturated monosulphides (Table and p. 60); and secondly, that the reaction of I with IX and/or X is much faster than its reaction with other monosulphides containing displaceable secondary alkyl groups. Both features are explicable in terms of participation of the groups ArS- or Cl- vicinal to the C–S bond in XI, giving anchimeric assistance to a preferred cleavage of the designated secondary alkyl C–S bond in XI with the formation of the mesomeric cation in XII.[10]

The addition products of I to olefins are substituted monosulphides which in principle should react further with the sulphenyl halide as in reaction (10); that

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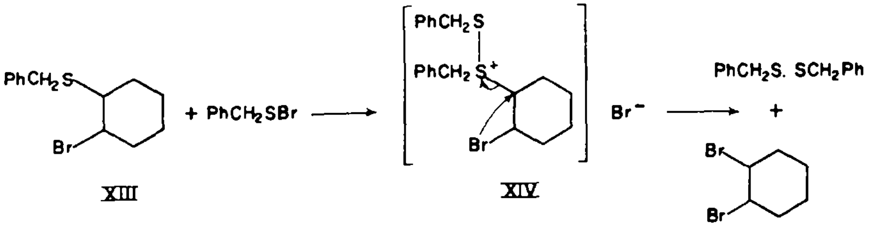
[8] D. S. Tarbell and D. P. Harnish, *Chem. Rev.* **49**, 1 (1951); J. Goerdeler, in Houben-Weyl *Methoden der Organischen Chemie* Vol. 9, pp. 175 *et seq.* Georg Thieme, Stuttgart (1955).

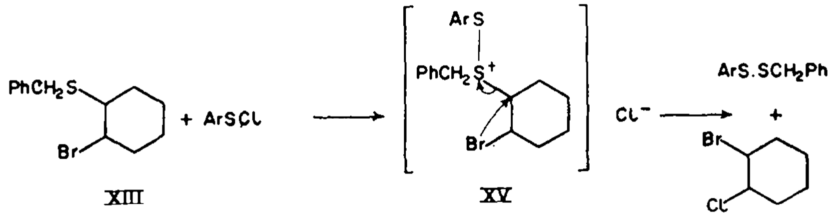
[9] W. L. Orr and N. Kharasch, *J. Amer. Chem. Soc.* **75**, 6030 (1953); **78**, 1201 (1956); D. R. Hogg and N. Kharasch, *Ibid.* **78**, 2728 (1956).

[10] A. Streitwieser, *Chem. Rev.* **56**, 571 (1956).

this is not observed experimentally[3] is now ascribed to the electron-withdrawing 2,4-dinitrophenyl group in the product, $\overleftarrow{\mathrm{ArS}}{\cdot}\mathrm{CR_2{\cdot}CR_2{\cdot}Cl}$, deactivating the sulphide sulphur towards electrophilic attack by a second sulphenyl chloride molecule. Support for this argument is found in the reactivity of phenylmethanesulphenyl bromide towards cyclohexene. Reaction of equimolar amounts of these compounds in benzene gave the anticipated product XIII. However, reaction of the sulphenyl bromide (2 moles) with the olefin (1 mole) gave a small amount of dibenzyl disulphide as an additional product, whose formation is consistent with reaction (11). Confirmatory evidence for this is the fact that reaction of XIII with I in acetic acid yielded benzyl 2,4-dinitrophenyl disulphide as one product (reaction 12):

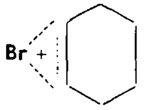


(11)



(12)

The preferential cleavage of the designated secondary cycloalkyl group in XIV and XV is attributed to anchimeric assistance of the neighbouring bromine atom, leading to the intermediate mesomeric cyclic bromonium ion XVI (cf. p. 61).



XVI

EXPERIMENTAL

Materials. All monosulphides and the unsymmetrical disulphides were analytically pure, being purified commercial samples or materials prepared in these laboratories and described elsewhere. British Drug Houses, "dry acetic acid" (water content, 0·01–0·1 %) was used throughout.

Reaction of 2,4-dinitrobenzenesulphenyl chloride (I) *with monosulphides*

Analytical procedure (cf.[4]). To a solution of the sulphide (in amount calculated to allow ca. 25 % excess of I) in acetic acid (10 ml) was added a standard solution of I in acetic acid (10·00 ml of 0·1 M) and the mixture allowed to stand at ca. 20° for the desired time. Dry iodate-free sodium iodide (1·5 g) was then added and the mixture shaken for 1·5 min, after which distilled water (100 ml) was added, followed by a measured excess of standard aq sodium thiosulphate. After shaking the mixture for

0·5 min the excess of thiosulphate was determined by titration against standard aq iodine. The extents of reaction (expressed as moles of I reacted per mole of sulphide reactant) as a function of time are detailed in the Table.

Isolation of disulphide products. In general, the products from two determinations above were combined, any iodine present was destroyed by aq sodium thiosulphate and the solid material filtered off, washed with water, twice extracted with boiling ethanol, and the combined extracts crystallized. Specific examples of the disulphide products formed are given below.

(1) From the reaction of isopropyl t-butyl sulphide with I was isolated 2,4-dinitrophenyl isopropyl disulphide (63%), m.p. 61·5–62° (Found: C, 39·45; H, 3·75; S, 23·1. Calc. for $C_9H_{10}O_4N_2S_2$: C, 39·4; H, 3·7; S, 23·4%).

(2) From reaction of I with benzyl 4-methylpent-3-en-2-yl sulphide was isolated benzyl 2,4-dinitrophenyl disulphide (59%), m.p. 110·5–111·5, mixed m.p. 110·5–112·5° (Found: C, 48·6, 48·7; H, 3·55, 3·4; S, 19·8. Calc. for $C_{13}H_{10}O_4N_2S_2$: C, 48·4; H, 3·1; S, 19·9 %).

(3) Reaction of dibenzyl sulphide (180 mg, 0·84 mmole) with an acetic acid solution of I (75 ml of 0·01 M) for 48 hr, followed by removal of the solvent *in vacuo* at room temp and two crystallizations of the residue from ethanol yielded benzyl 2,4-dinitrophenyl disulphide (130 mg, 48%), m.p. and mixed m.p. 111–112° (Found: C, 48·6; H, 3·3; S, 19·9%).

(4) Reaction of benzyl 2-methylpent-2-yl sulphide (208 mg, 1 mmole) in acetic acid (10 ml) with a solution of I (100 ml of 0·01 M) for 20 hr and subsequent isolation as in (3) gave benzyl 2,4-dinitrophenyl disulphide (158 mg, 49%), m.p. 111–112°, mixed m.p. 111–112·5° (Found: C, 48·45; H, 3·2; S, 20·0%).

Reaction of (I) *with dibenzyl sulphide in benzene*

A mixture of I (235 mg, 1 mmole) and the sulphide (215 mg, 1 mmole) in benzene (9·5 ml) was allowed to react for 14 days at ca. 20°. Removal of the solvent *in vacuo*, extraction of the residue with cold anhydrous ether and crystallization of the insoluble portion from ethanol gave benzyl 2,4-dinitrophenyl disulphide (118 mg, 37%), m.p. 110·5–112° (Found: C, 48·65; H, 3·2; S, 20·2%).

Reaction of (I) *with dibenzyl sulphide. Identification of benzyl chloride*

(1) *Control experiment.* A mixture of benzyl chloride (0·652 g, 5 mmoles) and thiourea (0·386 g, 5 mmoles) in ethanol (1·2 ml) was refluxed for 0·5 hr, the solution then cooled and added slowly with stirring to a conc aqueous-ethanolic solution of sodium picrate (1·26 g, 5 mmoles) to give S-benzylisothiuronium picrate (1·584 g, 80%), m.p. 182–183° (from benzene) (Cope *et al.*[11] give m.p. 187–188·5°; however, recrystallization of the above sample from various solvents did not raise the m.p.).

(2) *Examination of reaction products.* A solution of I (1·174 g, 5 mmoles) and the sulphide (1·071 g, 5 mmoles) in acetic acid (15 ml) was caused to react for 283 hr at ca. 20°. Evaporative distillation of the product at 10^{-2} mm, addition of the distillate to water and neutralization of the acid with aq sodium hydroxide, followed by extraction with benzene and removal of solvent gave a residue which on treatment with thiourea as in (1) gave S-benzylisothiuronium picrate (1·17 g, 59%), m.p. and mixed m.p. 182–183° (from aq ethanol) (Found: C, 42·2; H, 3·3; S, 8·35. Calc. for $C_{14}H_{13}O_7N_5S$: C, 42·55; H, 3·3; S, 8·1%).

Reaction of (I) *with di-isopropyl sulphide*

The reactants (0·01 mole of each) in acetic acid (20 ml) were caused to react at ca. 20° for 529 hr and then at 50° for 209 hr, conditions leading to ca. 97% reaction of I. Separation of volatile material by low-pressure evaporative distillation at room temp left a crystalline residue (2·67 g) which, on extraction with hot ethanol, gave an insoluble residue (78 mg) of bis(2,4-dinitrophenyl) disulphide. Fractional crystallization of the ethanolic extract gave: (i) 2,4-dinitrophenyl isopropyl disulphide (1·97 g), m.p. and mixed m.p. 60·5–61·5° (Found: C, 39·6; H, 3·6; S, 23·7. Calc. for $C_9H_{10}O_4N_2S_2$: C, 39·4; H, 3·7; S, 23·4%); and (ii) a red oil (0·60 g) which partially solidified on standing (Found: C, 39·7; H, 3·55; Cl, 4·55; S, 19·0, 19·3. Calc. for a 64 : 36 wt % mixture of 2,4-dinitrophenyl isopropyl disulphide and 2-chloropropyl 2′,4′-dinitrophenyl sulphide: C, 39·3; H, 3·55; Cl, 4·6; S, 19·1%). The disulphide accounts for 85·7% and the chloromonosulphide for 8·1% of incident I.

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[11] A. C. Cope, T. T. Foster and P. H. Towle, *J. Amer. Chem. Soc.* **71**, 3929 (1949).

Reaction of phenylmethanesulphenyl bromide with cyclohexane

(1) The sulphenyl bromide, prepared in benzene solution (50 ml) from toluene-ω-thiol (0·02 mole) and N-bromosuccinimide (0·02 mole) by Emde's method,[12] was added (without isolation) to cyclohexene (0·02 mole) in benzene (5 ml) and the mixture allowed to stand for 15 days. Removal of solvent at low pressure gave a pale yellow liquid residue, undistillable at 0·1 mm (bath temp 150°), but which, on short-path distillation at $< 10^{-3}$ mm (bath temp 70–80°), gave a yellow liquid distillate, unstable towards moist air, which consisted mainly of *benzyl 2-bromocyclohexyl sulphide* (XIII) (Found: C, 54·8; H, 5·75; S, 12·8; Br, 23·2. $C_{13}H_{17}SBr$ requires: C, 54·75; H, 6·0; S, 11·25; Br, 28·0%). No dibenzyl disulphide was isolable from the reaction product.

(2) Reaction of the sulphenyl bromide with a 0·5 molar proportion of cyclohexane under the conditions in (1) above gave the adduct XIII and dibenzyl disulphide (50 mg), m.p and mixed m.p. 68·5–70° (Found: C, 68·3; H, 5·85. Calc. for $C_{14}H_{14}S_2$: C, 68·25; H, 5·7%). Confirmation that the dibenzyl disulphide resulted directly from interaction of the adduct XIII with excess sulphenyl bromide was obtained by allowing XIII to react with the sulphenyl chloride I in acetic acid for 14 days at ca. 20° when benzyl 2,4-dinitrophenyl disulphide, m.p. 110–112° (Found: C, 48·4; H, 3·2; S, 20·3%) was obtained.

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[12] H. Emde, Ger. Pat. 804572 (1951); *Chem. Abstr.* **46**, 529 (1952).