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THE SYNTHESIS AND ABSORPTION SPECTRA OF THE ISOMERIC DITHIENYL SULPHIDES

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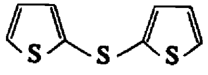
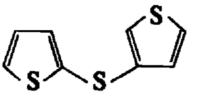
Abstract—The isomeric dithienyl sulphides (I–III) have been prepared by condensation of the appropriate thiophen thiol with a bromothiophen in the presence of cuprous oxide in dimethyl formamide. These sulphides may be oxidized using hydrogen peroxide to the corresponding sulphones (IV–VI). The absorption spectra of these compounds have been recorded.

UNTIL recently only a few sulphides of thiophen were reported in the literature.[1] Alkyl thienyl sulphides have been obtained as by-products in the ring closure of dialkyl succinates with phosphorus trisulphide,[2] and by reaction of olefines with thiophen thiols in the presence of boron trifluoride catalyst.[3] Alkali metal salts of thiophen thiols react readily with alkyl halides to give alkyl thienyl sulphides in good yields.[4–6] Despite such interest, however, only 2,2′-dithienyl sulphide (I) of the three isomeric dithienyl sulphides has been reported previously in the literature. The present paper deals with a general method of synthesis of these three isomeric dithienyl sulphides, 2,2′-, (I); 2,3′-, (II); 3,3′-, (III).


I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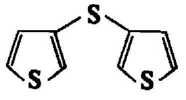
III

2,2′-Dithienyl sulphide (I) has been obtained by reaction of thiophen with sulphur monochloride followed by pyrolysis of the resultant disulphide.[7] This method is based on the known preferential 2-substitution in the thiophen ring.[8] Treatment of 2-thienyl magnesium bromide with excess sulphur also gives I in 55% yield.[9] By analogy with the sulphurization of phenyl magnesium bromide,[10] this reaction presumably proceeds through the 2,2′-dithienyl disulphide. Such a method, however, is not applicable to the synthesis of the other isomeric sulphides (II and III) since the required Grignard reagents based on 3-halogenothiophens are not readily prepared.[11]

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[1] H. D. Hartough, *Thiophene and its Derivatives* Chapt. XIII. Interscience, New York (1952).
[2] W. Steinkopf and P. Leonhardt, *Liebigs Ann.* **495**, 166 (1932).
[3] H. D. Hartough, *Thiophene and its Derivatives* p. 433. Interscience, New York (1952).
[4] W. H. Houff and R. D. Schuetz, *J. Amer. Chem. Soc.* **75**, 2072, 6316 (1953).
[5] S. Gronowitz and P. Moses, *Acta Chem. Scand.* **16**, 155 (1962).
[6] R. W. Higgins and R. Garrett *J. Org. Chem.* **27**, 2168 (1962).
[7] E. Koft, U.S. Pat. 2, 571, 370 (1951).
[8] H. D. Hartough, *Thiophene and its Derivatives* p. 144. Interscience, New York (1952).
[9] F. Challenger and J. B. Harrison, *J. Inst. Petroleum* **21**, 135 (1935).
[10] M. S. Kharasch and O. Reinmuth. *Grignard Reactions of Non-Metallic Substances* p. 1275. Constable, London (1954).
[11] S. Gronowitz, *Advances in Heterocyclic Chemistry* Vol. 1. p. 41. Academic Press, New York (1963).

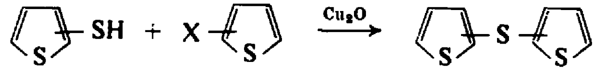
A number of sulphides have been prepared in good yields by the reaction of cuprous mercaptides with alkyl and aryl halides in a heated quinoline–pyridine mixture.[12,13] Reifschneider[14,15] has recently obtained a number of similar derivatives by interaction of aryl thiols with halides in the presence of cuprous oxide in a similar reaction medium. Bacon and Hill[16] have shown that cuprous oxide promotes substitution reactions between aryl halides and nucleophiles (e.g. phenols and thiols). These authors postulate that the first step in the reaction with a thiol is conversion to the cuprous salt which then reacts with the halide to give the desired sulphide.

$$2RSH + Cu_2O \rightarrow 2RSCu + H_2O$$

$$2RSCu + 2ArX \rightarrow 2RSAr + Cu_2X_2$$

While a number of organic solvents were tried, including the quinoline–pyridine mixture, dimethyl formamide in the presence of an alkali metal hydroxide was found to give the best results.

From all these results it is apparent that the condensation of a thiophen thiol with a halogenothiophen in the presence of cuprous oxide offers a general method for the synthesis of the three isomeric dithienyl sulphides.



(where X is Cl, Br or I)

The results are summarized in Table 1.

TABLE 1. THE REACTION OF THIENYL HALIDES WITH THIOPHEN THIOLS PROMOTED BY CUPROUS OXIDE IN ORGANIC SOLVENTS

Thienyl halide and conc. (g mole)	Thiophen thiol and conc. (g mole)	Cu_2O (g mole)	Solvent	Temp (°C)	Time (hr)	Dithienyl sulphide	%age yield
2-C_4H_3SCl 0·027	2-$C_4H_3S.SH$ 0·027	0·031	Quinoline/ pyridine	110–120	19	I	12·5
2-C_4H_3SBr 0·027	2-$C_4H_3S.SH$ 0·027	0·031	Quinoline/ pyridine	110–120	19	I	34·0
2-C_4H_3SCl 0·10	2-$C_4H_3S.SH$ 0·10	0·050	Dimethyl Formamide	126	24	I	8·6
2-C_4H_3SBr 0·10	2-$C_4H_3S.SH$ 0·10	0·050	Dimethyl Formamide	130	24	I	62·0
2-C_4H_3SI 0·10	2-$C_4H_3S.SH$ 0·10	0·050	Dimethyl Formamide	130	24	I	51·5
2-C_4H_3SBr 0·20	3-$C_4H_3S.SH$ 0·20	0·10	Dimethyl Formamide	140	24	II	73·5
3-C_4H_3SBr 0·10	2-$C_4H_3S.SH$ 0·10	0·050	Dimethyl Formamide	140	24	II	63·0
3-C_4H_3SBr 0·10	3-$C_4H_3S.SH$ 0·10	0·050	Dimethyl Formamide	140	24	III	48·0

The results show that the reaction of thiophen thiols with halogenothiophens promoted by cuprous oxide in dimethyl formamide offers a general method for the synthesis of the three isomeric dithienyl sulphides (I-III) in good yields. Of the

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[12] R. Adams, W. Reifschneider and M. D. Nair, *Croatica Chem. Acta* **29**, 277 (1957).

[13] R. Adams and A. Ferretti, *J. Amer. Chem. Soc.* **81**, 4927 (1959).

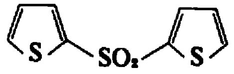
[14] W Reifschneider, U.S. Pat. 3,098,104 (1963)

[15] W Reifschneider, U.S. Pat. 3,102,916 (1964).

[16] R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.* 1108 (1964).

halogenothiophens, the bromo derivative is the preferred reactant. The use of quinoline-pyridine as reaction medium leads to a reduction in the yield of final product.

The three isomers (I–III) may be characterized as their respective sulphones (IV–VI) by oxidation using hydrogen peroxide in glacial acetic acid.



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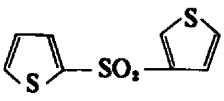

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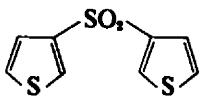

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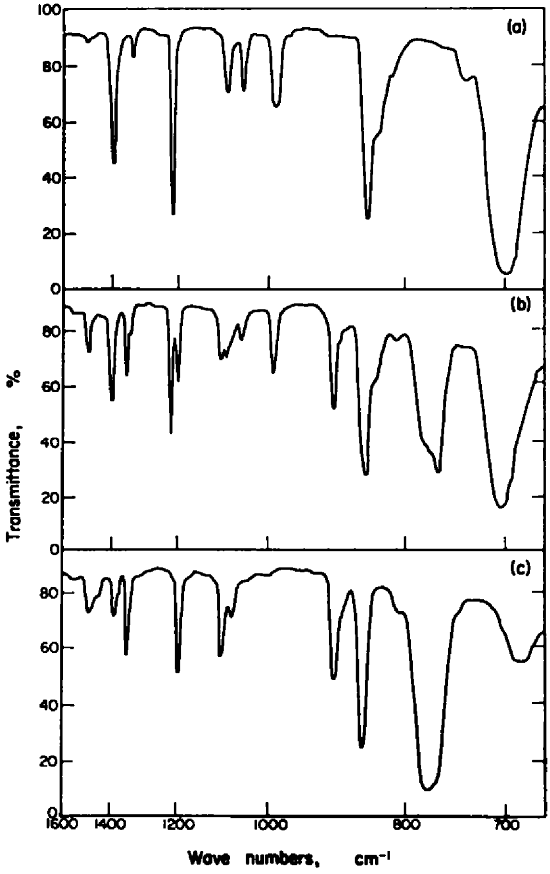

FIG. 1. The IR spectra of the isomeric dithienyl sulphides
(a) 2,2′-dithienyl sulphide (I)
(b) 2,3′-dithienyl sulphide (II)
(c) 3,3′-dithienyl sulphide (III).

This reaction proceeds smoothly giving at least an 80% yield of the desired sulphone.

The IR spectra of the sulphides (Fig. 1) and sulphones (Fig. 2) show the characteristic ring frequencies of the thiophen nucleus in the region 1600–1000 cm^{-1} (6·2–10·0 μ). The monosubstitution pattern is shown in the 900–750 cm^{-1} (11·1–13·3 μ) region.

Thus, the 2-thienyl group has a characteristic doublet about 840 cm^{-1} (11·9 μ)[17] whereas the 3-thienyl group is identified[18] by two bands of medium intensity at 895 and 855 cm^{-1} (11·2 and 11·7 μ) and a strong band at 775 cm^{-1} (12·9 μ). Absorption due to the sulphone group (Fig. 2) is shown[19] by two strong bands at about 1320 and 1140 cm^{-1} (7·6 and 8·8 μ). No absorption due to the sulphide group is found in Fig. 1 since this normally occurs outwith the region scanned.[20]

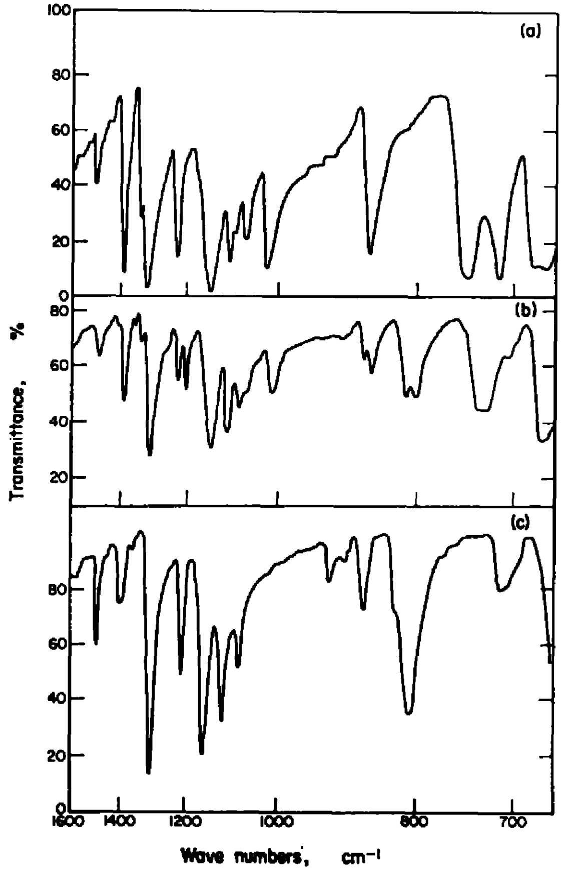

Fig. 2. The IR spectra of the isomeric dithienyl sulphones
(a) 2,2′-dithienyl sulphone (IV)
(b) 2,3′-dithienyl sulphone (V)
(c) 3,3′-dithienyl sulphone (VI)

The UV spectra of the three isomers (I–III) are shown in Fig. 3 and cover the region above 190 mμ. The 2-thienyl group (as in I) gives a characteristic absorption pattern consisting of three bands, at 200, 238 and 264 mμ whereas the 3-thienyl group (as in III) possesses only two bands, at 212 and 272 mμ. II shows a spectrum expected

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[17] A. R. Katritzky and A. J. Boulton *J. Chem. Soc.* 3500 (1959).

[18] S. Gronowitz, A. R. Katritzky and R. E. Reavill, *J. Chem. Soc.* 3881 (1963).

[19] L. J. Bellamy, *Infra-red Spectra of Complex Molecules* p. 361. Methuen, London (1958).

[20] L. J. Bellamy, *Infra-red Spectra of Complex Molecules* p. 354. Methuen, London (1958).

of a compound possessing both 2- and 3-thienyl rings. The sulphones (IV–VI) show a similar pattern (Fig. 4) to that of the sulphides.

These UV spectra are of some interest since Gronowitz[21] has examined the UV spectra of a number of monosubstituted thiophens, recording those absorptions which occurred at wavelengths greater than 210 mμ. Thus, with 2-substituted thiophens, two bands were recorded in the regions 235–260 mμ and 250–290 mμ whereas 3-substituted thiophens showed only one band in the region 230–250 mμ. Popov *et al.*[22] have recorded similar findings for a number of 2-thienyl sulphides, including I, on examination of the region above 220 mμ. Both these authors have failed to detect the first thiophen absorption which occurs as a sharp, intense band at 200–210 mμ (*vide* Figs. 3 and 4). This also is present in the spectra of the isomeric thienyl n-butyl sulphides which were also examined for comparison purposes. The values for wavelength and molar extinction coefficient (ϵ) of the thiophen compounds examined are summarized in Table 2.

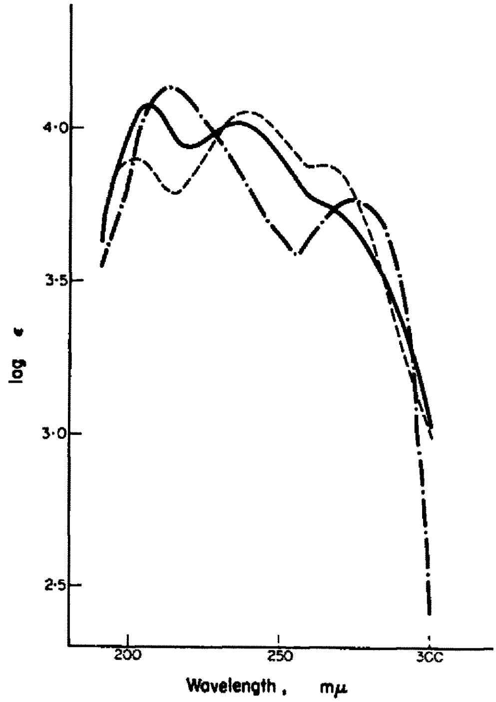

FIG. 3. The UV spectra of the isomeric dithienyl sulphides
- - - - - - 2,2′-dithienyl sulphide (I)
———— 2,3′-dithienyl sulphide (II)
-·-·-·- 3,3′-dithienyl sulphide (III)

From Table 2 it may be seen that the first absorption occurs in the region 200–215 mμ and is common to all the thiophen compounds examined. It is attributed

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[21] S. Gronowitz, *Arkiv Kemi* 13, 239 (1958).

[22] E. M. Popov, F. M. Stoyanovich, B. P. Fedorov and G. M. Andrianova, *Zh. Obsch. Khim.* 33, 2261 (1963).

to the conjugated double bonds of the heterocyclic ring.[23] From Figs. 3 and 4 it is apparent that this band is much more intense in 3-thienyl compounds than in the 2-substituted isomers. The second absorption is encountered in the region 235–245 mμ and has been attributed[24] to the excitation of the π electrons of the thiophen ring.

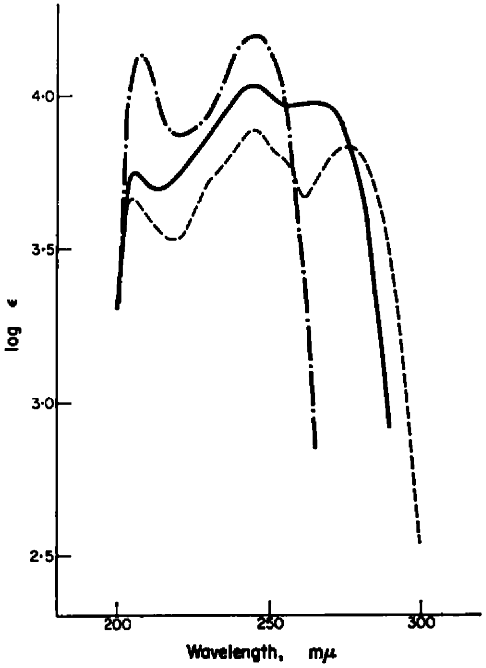
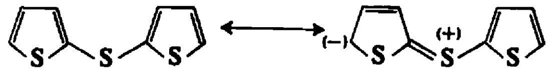


FIG. 4. The UV spectra of the isomeric dithienyl sulphones.
– – – – – – 2,2′-dithienyl sulphone (IV)
———— 2,3′-dithienyl sulphone (V)
– · – · – · – 3,3′-dithienyl sulphone (VI)

This absorption is experienced by the 2-substituted thiophens but is absent in the 3-thienyl isomers. The third absorption in the region 260–275 mμ is common to both the sulphides and sulphones and is probably due to interaction of the substituent with the thiophen ring. For example, with the sulphides conjugation may arise from interaction of the 3pπ electrons of the sulphur with one of the thiophen rings.

Thus,



The existence of a similar conjugated transition state has been postulated[25] to explain the presence of a band at 274 mμ in the spectrum of diphenyl sulphide. Likewise there

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[23] A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry* p. 151. E. Arnold, London (1962).

[24] A. Mangini and A. Tundo, *Z. Electrochem.* **64**, 694 (1960).

[25] N. Kharasch, *Organic Sulphur Compounds* Vol. 1, p. 63. Pergamon Press, London (1961).

TABLE 2

Compound	Absorption maximum	
	λ_{max}	ϵ_{max}
Thiophen	215	2,600
	235	7,080
2,2′-Dithienyl sulphide (I)	200	7,950
	238	11,500
	264	7,600
2,3′-Dithienyl sulphide (II)	204	12,000
	235	10,500
	268*	8,600
3,3′-Dithienyl sulphide (III)	212	13,500
	272	5,900
2,2′-Dithienyl sulphone (IV)	204	4,700
	244	7,800
	276	6,800
2,3′-Dithienyl sulphone (V)	206	5,800
	245	11,000
	264	9,600
3,3′-Dithienyl sulphone (VI)	208	14,000
	245	16,200
2-Thienyl n-butyl sulphide	204	3,900
	238	5,900
	272	3,300
3-Thienyl n-butyl sulphide	212	8,300
	268	2,800

* inflection

is evidence to suggest that the sulphone group can also conjugate with aromatic systems causing bathochromic shifts.[26]

EXPERIMENTAL

M.ps are uncorrected. The IR spectra were recorded on a Perkin-Elmer Infracord (137) with NaCl prisms. The UV spectra of the sulphides were measured in hexane and those of the sulphones in ethanol using a Hilger and Watts Uvispek spectrophotometer.

Preparation of 2,2′-*dithienyl sulphide* (I)

(a) *Using quinoline–pyridine mixture.* 2-Bromothiophen (4·36 g; 0·027 g mole) and 2-thiophen thiol[4] (3·09 g; 0·027 g mole) were added separately to a stirred mixture of Cu_2O (4·5 g; 0·031 g mole), pyridine (3 ml) and quinoline (33 ml) under N_2. The reactants were heated to 110–120° and maintained at this temp. for 19 hr. After cooling, the mixture was poured into excess conc. HCl aq. in crushed ice. The resultant precipitate was extracted with benzene and the extract dried over anhydrous $CaCl_2$. Distillation gave I as a pale yellow oil, b.p. 71–3°/0·05 mm, n_D^{25} 1·6643 (1·8 g; 34% yield).

(b) *Using dimethyl formamide.* 2-Thiophen thiol[4] (11·6 g; 0·1 g mole) was added slowly to 2-bromothiophen (16·4 g; 0·1 g mole), freshly precipitated Cu_2O[27] (7·15 g; 0·05 g mole), KOH (5·6 g; 0·1 g mole) and 100 ml dimethyl formamide. The stirred mixture, under N_2, was heated for 24 hr at 130°, cooled and poured into 6N HCl (100 ml) in ice. After filtration, the residue was extracted with benzene until a colourless extract was obtained. The filtrate was also extracted with benzene and the organic phase washed with water until neutral. These extracts were combined and dried over anhydrous Na_2SO_4. Distillation gave I, b.p. 75–8°/0·06 mm (12·2 g; 62·0% yield).

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[26] E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.* **71**, 231 (1949).

[27] A. King, *Inorganic Preparations* (Revised Edition), p. 40. Allen and Unwin, London (1950).

Oxidation to 2,2′-dithienyl sulphone (IV)

I was dissolved in glacial acetic acid and excess H_2O_2 (100 Vols) added. The mixture was refluxed for 2 hr. The sulphone (IV) was obtained as a crystalline solid on addition of a large excess of water. Recrystallization from MeOH gave white plates m.p. 130·5–131·5° (Found: C, 41·7; H, 2·7; S, 40·8. $C_8H_6O_2S_3$ requires: C, 41·7; H, 2·6; S, 41·8%).

Preparation of 2,3′-dithienyl sulphide (II)

Using method (b), II was obtained by condensation of either 2-thiophen thiol with 3-bromothiophen[28] (in 73·5% yield) or 3-thiophen thiol[29] with 2-bromothiophen (in 63·0% yield). II was a pale yellow oil, b.p. 118°/1·5 mm, 100°/0·6 mm n_D^{25} 1·6633.

Oxidation to 2,3′-dithienyl sulphone (V)

II was oxidized using H_2O_2 in glacial acetic acid, yielding the desired sulphone (V) which was recrystallized from MeOH, m.p. 133–134° (Found: C, 41·9; H, 2·7; S, 41·6. $C_8H_6O_2S_3$ requires: C, 41·7; H, 2·6; S, 41·8%).

Preparation of 3,3′-dithienyl sulphide (III)

III was prepared by method (b) from 3-thiophen thiol[29] and 3-bromothiophen[28] as a pale yellow oil, b.p. 115°/0·4 mm, n_D^{25} 1·6671 (48% yield).

Oxidation to 3,3′-dithienyl sulphone (VI)

Peroxide oxidation of III gave the sulphone (VI) as white plates from MeOH, m.p. 165° (Found: C, 41·6; H, 2·6; S, 41·8. $C_8H_6O_2S_3$ requires: C, 41·7; H, 2·6; S, 41·8%).

Preparation of 2-thienyl n-butyl sulphide

Reaction of 2-thienyl magnesium bromide with n-butyl bromide gave 2-thienyl n-butyl sulphide as a colourless oil, b.p. 74–9°/1·8 mm (lit.[18] b.p. 115–116°/5 mm), yield 23%. The method used was based on the synthesis of 2-thienyl methyl sulphide.[30]

Preparation of 3-thienyl n-butyl sulphide

Condensation of the lithium salt of 3-thiophen thiol with n-butyl bromide gave the desired 3-thienyl n-butyl sulphide as a colourless oil, b.p. 57–60°/0·5 mm (lit.[31] b.p. 137–150°/30 mm), yield 28%.

Acknowledgement—The work described in this paper forms part of a programme sponsored by the the Ministry of Aviation.

[28] S. Gronowitz, *Acta Chem. Scand.* **13**, 1045 (1959).

[29] S. Gronowitz and R. Håkansson, *Arkiv Kemi* **16**, 309 (1960).

[30] J. Cymerman-Craig and J. W. Loder, *Organic Syntheses* **35**, 85 (1955).

[31] S. Gronowitz, *Arkiv Kemi* **13**, 269 (1958).