79. *Diphenylenes. Part IV.*[1] *Bond Structure.*

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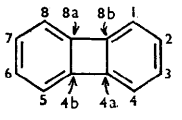
2-Acetamidodiphenylene (V) undergoes monobromination in position 3 to give the compound (VI); this is in accordance with molecular-orbital calculations but contrary to expectations on the simplest resonance theory. Further bromination gives the addition product 3-acetamido-4,6,2′-tribromodiphenyl (VIII), with rupture of the four-membered ring. Bromination of 2,6-diacetamidodiphenylene (XII) yields the 3,7-dibromo-derivative (XIII).

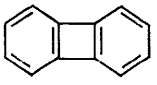
It is concluded that the preferred, reacting Kekulé structure of diphenylene is that shown in formula (I).

The chemical reactivity and bond structure of the diphenylene nucleus are of considerable theoretical interest, and it was shown in Parts I and III of this series [1,2] that many electrophilic and some probably free-radical substitution reactions occur solely in position 2 in accordance with theoretical predictions. It was also shown that diacetylation and dinitration give only the 2,6-disubstituted derivatives corresponding to *meta*-substitution in the benzene ring, so that there must be effective conjugation between the two six-membered rings *via* the four-membered ring (see XI). These facts, however, do not suffice to establish the preferred bond structure of diphenylene which comes into play during reaction.

Of the five Kekulé structures which may be written for diphenylene, formula (I) represents it as a derivative of cyclobutane, (II) and (III) as a cyclobutadiene, and the other two (not shown) as a cyclobutene. On the simplest resonance theory it may be assumed that these five canonical forms contribute equally to the hybrid molecule (any other



(I)



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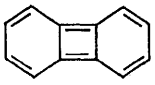
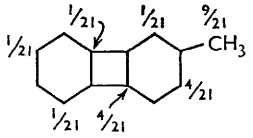


(III)



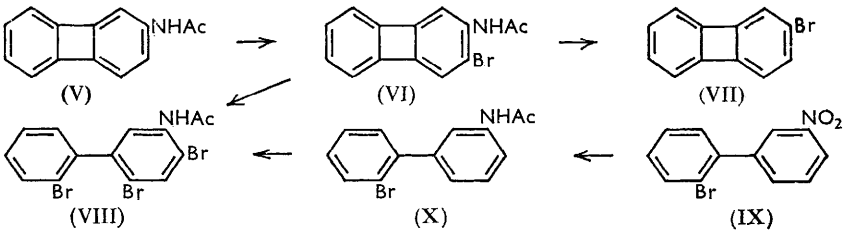
(IV)

supposition must involve some element of speculation), and so the bonds in positions 1,2 and 2,3 would have 3/5 and 2/5 double-bond character respectively, and structure (II) would be preferred, so that an *ortho,para*-activating group in position 2 of diphenylene should direct an entering substituent into position 1 as it does in the case of naphthalene. Longuet-Higgins has pointed out [3] that molecular-orbital calculations lead to the opposite conclusion, namely, that an *ortho,para*-directing group in position 2 should direct the new substituent into position 3, so that the establishment of the experimental facts in such a case would provide evidence to support one or other of the two theoretical predictions. It may be recalled that Waser and Schomaker [4] had earlier noticed a discrepancy between the relative bond orders of the 1,2- and 2,3-bonds calculated by the resonance and the molecular-orbital methods.

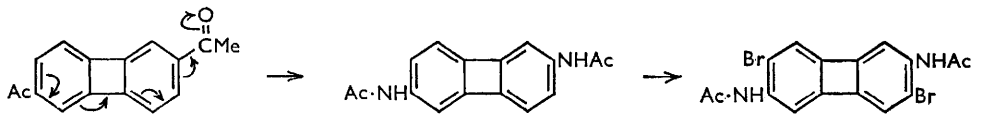
Longuet-Higgins showed that the relative reactivity of the different positions in the nucleus of a diphenylene bearing an *ortho,para*-directing group in position 2 could be calculated by considering the distribution of the extra electron in the carbanion derived from 2-methyldiphenylene. The result is shown in formula (IV), and electrophilic substitution should clearly occur in position 3, and not in position 1 as might be deduced either by the simple resonance theory or by analogy with a similarly substituted naphthalene.

[1] Part III, Baker, Barton, and McOmie, *J.*, 1958, 2666.
[2] Baker, Boarland, and McOmie, *J.*, 1954, 1476.
[3] Longuet-Higgins, *Proc. Chem. Soc.*, 1957, 157.
[4] Waser and Schomaker, *J. Amer. Chem. Soc.*, 1943, **65**, 1451.

As already briefly recorded [5] we have shown that bromination of 2-acetamidodiphenylene (V) gives a 65% yield of 2-acetamido-3-bromodiphenylene (VI) as the only isolable product, thus confirming the prediction of the molecular-orbital calculations. The bromine atom was shown to occupy position 3, 6, or 7 by hydrolysing the amide (VI) to the base with ethanolic sulphuric acid and treating this with sodium nitrite, to obtain 2-bromodiphenylene (VII) identical with an authentic specimen.[6] The infrared spectrum of the compound contained a strong band at 750 cm.$^{-1}$ corresponding to 4 adjacent hydrogen atoms and a medium band at 870 cm.$^{-1}$ corresponding to isolated hydrogen atoms. These two results prove that the bromination product is 2-acetamido-3-bromodiphenylene. The 2-acetamidodiphenylene (V) was prepared from 2-acetyldiphenylene by conversion into the oxime followed by Beckmann rearrangement with either polyphosphoric acid [1] or boron trifluoride in acetic acid.



An interesting reaction occurred when 2-acetamido-3-bromodiphenylene (VI) was treated with bromine in acetic acid at 80°: a molecule of bromine was added, with rupture of the four-membered ring to give 3-acetamido-4,6,2′-tribromodiphenyl (VIII). The only previously recorded conversion of a diphenylene into a diphenyl is reduction by means of Raney nickel in ethanol.[1] The structure of the acetamidotribromodiphenyl was established by synthesis as follows. An application of the Gomberg–Bachmann–Hey free-radical coupling reaction [7] to diazotised *m*-nitroaniline and bromobenzene in presence of sodium acetate gave 2-bromo-3′-nitrodiphenyl (IX), identical with that prepared by Case by a crossed Ullmann reaction.[8] Reduction and acetylation then yielded 3-acetamido-2′-bromodiphenyl (X), and dibromination in boiling acetic acid–acetic anhydride in presence



of sodium acetate gave 3-acetamido-4,6,2′-tribromodiphenyl, identical with that prepared by the addition of bromine to 2-acetamido-3-bromodiphenylene (VI). Had rupture of the four-membered ring of (VI) occurred in the alternative manner the product would have been 4-acetamido-2,5,2′-tribromodiphenyl which could not have arisen by the bromination of (X). The addition of bromine to the diphenylene (VI) thus follows the course expected from the molecular-orbital theory, as the electrophilic attack by the bromine would be expected to occur at carbon atom 4a with its high electron availability (see IV), followed by addition of the second bromine atom at position 4b. Initial attack at the more nearly neutral carbon atom 8a is much less likely.

During the investigation of the bromination of 3-acetamido-2′-bromodiphenyl (X) it

[5] Baker, McOmie, and Rogers, *Chem. and Ind.*, 1958, 1236.
[6] Baker, Barton, and McOmie, *J.*, 1958, 2658.
[7] Bachmann and Hoffman, *Organic Reactions*, 1944, **2**, 224.
[8] Case, *J. Amer. Chem. Soc.*, 1938, **60**, 424; 1939, **61**, 3487.

was found that treatment with bromine in acetic acid gave the known 3-acetamido-6,2′-dibromodiphenyl [8] whereas in presence of anhydrous sodium acetate it yielded 3-acetamido-4,2′-dibromodiphenyl, the entering bromine atom taking up the *ortho*- instead of the *para*-position to the acetamido-group.

The partial bond structure of diphenylene revealed by bromination of 2-acetamidodiphenylene in position 3 is shown to extend to both six-membered rings by a study of the bromination of 2,6-diacetamidodiphenylene (XII). 2,6-Diacetyldiphenylene [1,6] (XI) was converted into the dioxime, Beckmann transformation of which with polyphosphoric acid at 100° or boron trifluoride–acetic acid at 120° gave 2,6-diacetamidodiphenylene (XII) in high yield. Bromination of the diamide (XII) in acetic acid in presence of sodium acetate gave 2,6-diacetamido-3,7-dibromodiphenylene (XIII). The similar orientation of both bromine atoms was established by the infrared spectrum of the compound which has a fairly strong band at 864 cm.$^{-1}$ characteristic of isolated aromatic hydrogen atoms. A similar band appears as a doublet at 867, 886 and 870, 880 cm.$^{-1}$ in 2,3,6,7-tetramethoxy- and 2,3,6,7-tetramethyl-diphenylene respectively (to be published later).

In trying to synthesise 3-acetamido-4,6,2′-tribromodiphenyl attempts were made to effect mononitration in position 5 of 2,2′-dibromodiphenyl, but only dinitration occurred. The chief product was 2,2′-dibromo-5,5′-dinitrodiphenyl, whose structure was established by synthesis from the known 2,2′-diamino-5,5′-dinitrodiphenyl, and the minor product was 2,2′-dibromo-3,5′- or -3,3′-dinitrodiphenyl. The desired mononitro-compound was approached by partial reduction of the 5,5′-dinitro-compound by sodium polysulphide, but only a trace of 3-amino-6,2′-dibromo-5′-nitrodiphenyl was formed, the bulk of the product being 3,6-dinitrodibenzothiophen.

Ultraviolet absorption maxima of some of our products are summarised in the annexed Table.

Ultraviolet absorption maxima in ethanol.

Diphenylene derivatives	λ (mμ)	log ε	λ (mμ)	log ε	λ (mμ)	log ε
2-Acetamido-3-bromo-	257	4·78	350	3·82	368	3·89
Dioxime of 2,6-diacetyl-	235	4·29	366	3·89	381·5	3·88
	280·5	4·75				
2,6-Diacetamido-	220	4·25	274·5	4·88	360	4·06
	233·5	4·32	284	4·86	380	4·16
2,6-Diamino-	230	4·02	277	4·33	392·5	3·84
2,6-Diamino- in aqueous N-HCl	239	4·62	330	3·35	357	3·60
	248	4·88	338·5	3·60		
2,6-Diacetamido-3,7-dibromo- *	242·5	—	362	—	379	—
	273	—				

* Too sparingly soluble to allow accurate determination of the concentration; a saturated solution was used.

Experimental

2-Acetamidodiphenylene [1] (V).—2-Acetyldiphenylene oxime (90—95% yield), when treated with polyphosphoric acid, gave a 65% yield of 2-acetamidodiphenylene after purification by passage through an alumina column in benzene solution and elution with benzene–chloroform (10 : 1). The elution is conveniently followed in ultraviolet light, the position of the acetamido-compound on the column being indicated by a yellow-brown colour. Treatment of the oxime (0·3 g.) with a 40% w/w solution of boron trifluoride in acetic acid at 115—120° for 10 min.,[9] followed by addition to excess of aqueous sodium hydroxide and purification as before, gave directly a 53% yield of the pure acetamido-compound.

Bromination of 2-Acetamidodiphenylene.—To a stirred solution of 2-acetamidodiphenylene (0·75 g.) in glacial acetic acid (25 ml.) was slowly added at room temperature a 10% solution of bromine in acetic acid (6·5 ml.; 1·1 equivs.). Crystals began to separate after 5 min.; next day the mixture was poured into water, and the precipitate was collected, washed, and dried (1·00 g.). Recrystallisation from ethanol gave *2-acetamido-3-bromodiphenylene* (VI) as cream-coloured needles (0·65 g., 65%), m. p. 211—212° (decomp.) (Found: C, 58·4; H, 3·5; N, 5·0; Br, 27·5. $C_{14}H_{10}ONBr$ requires C, 58·3; H, 3·5; N, 4·9; Br, 27·8%). The *complex* with

[9] Hauser and Hoffenburg, *J. Org. Chem.*, 1955, **20**, 1482.

2,4,7-trinitrofluorenone separates from ethanol as black needles, m. p. 179—181° (Found: C, 53·4; H, 2·5; N, 9·6. $C_{27}H_{15}O_8N_4Br$ requires C, 53·7; H, 2·6; N, 9·3%).

Hydrolysis and Deamination of 2-Acetamido-3-bromodiphenylene (VI); *Formation of 2-Bromodiphenylene* (VII).—The acetamido-compound (100 mg.) was boiled for 20 min. in ethanol (8 ml.) containing concentrated sulphuric acid (0·5 ml.), and the hot solution was treated in portions with sodium nitrite (200 mg.) in water (1·5 ml.) during ¼ hr. After being boiled for 10 min. the dark solution was extracted with ether, the extracts were washed, dried, and evaporated, and the residue was sublimed at 70—120°/12 mm., giving a 10% yield of crude 2-bromodiphenylene; resublimation gave cream-coloured plates, m. p. and mixed m. p. with an authentic specimen [6,2] 65—67°; the infrared spectra of the specimens were identical. Further sublimation of the residue gave 2-acetamido-3-bromodiphenylene (11 mg.).

Addition of Bromine to 2-Acetamido-3-bromodiphenylene (VI); *Formation of 3-Acetamido-4,6,2′-tribromodiphenyl* (VIII).—A 10% solution of bromine in acetic acid (1·3 ml.; 1·1 equiv.) was added to 2-acetamido-3-bromodiphenylene (200 mg.) in acetic acid (20 ml.), and the mixture was kept at 80° for 2 hr., the colour of the bromine disappearing. The precipitate obtained by pouring the mixture into water was washed, dried, and crystallised from benzene–light petroleum (b. p. 60—80°), giving *3-acetamido-4,6,2′-tribromodiphenyl* (VIII) as colourless needles (180 mg.; 58%), m. p. 156—157° (Found: C, 37·4; H, 2·1; N, 3·1. $C_{14}H_{10}ONBr_3$ requires C, 37·5; H, 2·2; N, 3·1%).

2-Bromo-3′-nitrodiphenyl (IX) *and 3-Acetamido-2′-bromodiphenyl* (X).—*m*-Nitroaniline (35 g.) was diazotised in concentrated hydrochloric acid (80 ml.) with sodium nitrite (20 g.) in water (40 ml.), and after addition of bromobenzene (200 ml.) and then of sodium acetate (44 g.; hydrated) in water (60 ml.), the mixture was stirred for 12 hr. at room temperature and for a further 12 hr. at 60—70°. The bromobenzene layer and a benzene extract were washed, dried, and distilled; the fraction of b. p. 160—175°/0·2 mm. (3·7 g.) solidified on cooling. This was crystallised several times from ether, giving finally 2-bromo-3′-nitrodiphenyl (1·47 g.) as pale yellow plates, m. p. 77—78° (Found: C, 52·1; H, 3·0; N, 5·4. Calc. for $C_{12}H_8O_2NBr$: C, 51·8; H, 2·9; N, 5·0%).

This nitro-compound (2·0 g.), ethanol (40 ml.), concentrated hydrochloric acid (40 ml.), and hydrated stannous chloride (9·0 g.) were heated at 80—90° for 3½ hr., excess of aqueous sodium hydroxide was added, and the free amine isolated by ether-extraction and acetylated by short heating with acetic anhydride in acetic acid and a trace of concentrated sulphuric acid. After addition of water the 3-acetamido-2′-bromodiphenyl (1·7 g.) was crystallised twice from benzene–light petroleum (b. p. 60—80°), giving plates, m. p. 132—133°. Case [8] records m. p.s 78—79° and 135° for compounds (IX) and (X).

3-Acetamido-4,6,2′-tribromodiphenyl (VIII).—3-Acetamido-2′-bromodiphenyl (X) (150 mg.) and anhydrous sodium acetate (325 mg.) were dissolved in boiling glacial acetic acid (5 ml.) and acetic anhydride (0·4 ml.), and to the mixture was added bromine (260 mg.) as a 10% solution in acetic acid; boiling was continued for 1 hr. Addition of the solution to ice-water gave a solid which was collected, washed, and dried and purified by passage in benzene through silica gel and eluted with benzene containing increasing proportions of chloroform. Elution with benzene–chloroform (1 : 1) yielded 3-acetamido-6,2′-dibromodiphenyl, m. p. 140—141° after crystallisation from benzene–light petroleum (b. p. 60—80°). The eluate obtained by using benzene–chloroform (1 : 3) yielded a product (15 mg.) which crystallised from benzene–light petroleum (b. p. 60—80°), giving needles (10 mg.), m. p. 154—155° and 155—156·5° on admixture with the product obtained by the treatment of 2-acetamido-3-bromodiphenylene with bromine. The infrared spectra of these two specimens of 3-acetamido-4,6,2′-tribromodiphenyl were identical.

3-Acetamido-4,2′-dibromodiphenyl.—To a solution of 3-acetamido-2′-bromodiphenyl (285 mg.) in glacial acetic acid (10 ml.) containing anhydrous sodium acetate (300 mg.) was added bromine in acetic acid (1·7 ml.; 10% w/v). After 3 hr. at room temperature and ¼ hr. on a water-bath the mixture was diluted with water, and the solid was collected and recrystallised from benzene–light petroleum (b. p. 60—80°), giving *3-acetamido-4,2′-dibromodiphenyl* (235 mg., 65%), m. p. 126—127·5° (Found: C, 45·6; H, 3·2; N, 4·2. $C_{14}H_{11}ONBr_2$ requires C, 45·6; H, 3·0; N, 3·8%). The infrared spectrum showed bands at 758vs, 814s, and 894m cm.$^{-1}$, corresponding to 1,2-di- and 1,3,4-tri-substituted rings.

2,6-Diacetyldiphenylene Dioxime.—A mixture of 2,6-diacetyldiphenylene (XI) (0·5 g.), ethanol (250 ml.), 10% aqueous sodium hydroxide (2·5 ml.), and hydroxylamine hydrochloride

(0·6 g.) dissolved in a little water was boiled for 3 hr., cooled, and diluted with water, and the precipitate was collected, washed and dried (0·5 g.). This *dioxime* separated from ethanol as lemon-yellow needles, m. p. 290—291° (decomp.) (Found: C, 72·8; H, 5·4; N, 10·1. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·3; N, 10·5%).

2,6-*Diacetamidodiphenylene* (XII).—(*a*) The powdered dioxime (0·46 g.) was added to polyphosphoric acid (20 g.) at 100° and stirred for 20 min. Water was then added and the solid collected, washed, and crystallised twice from ethanol, giving 2,6-*diacetamidodiphenylene* (0·29 g., 62%) as orange needles, m. p. 328—330° (decomp.) (Found: C, 72·3; H, 5·5. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·3%). (*b*) Treatment of the dioxime (0·15 g.) with a 40% w/w solution of boron trifluoride in acetic acid (5 ml.) at 120° for 10 min., followed by addition of aqueous sodium hydroxide and collection and crystallisation as before, gave a 70% yield of 2,6-diacetamidodiphenylene.

2,6-*Diaminodiphenylene*.—2,6-Diacetamidodiphenylene (0·10 g.) was boiled for 1 hr. with ethanol (5 ml.), concentrated hydrochloric acid (5 ml.), and water (5 ml.). The dihydrochloride of the base separated in part. The alcohol was removed by distillation, aqueous sodium hydroxide added, the precipitated base extracted into methylene dichloride (3 × 30 ml.), dried (K_2CO_3), and distilled, and the residue sublimed at 140—150°/0·01 mm. 2,6-*Diaminodiphenylene* was obtained as a bright yellow powder (50 mg.), m. p. 218—220° after decomp. from 205° (Found: C, 78·8; H, 5·9; N, 15·0. $C_{12}H_{10}N_2$ requires C, 79·1; H, 5·6; N, 15·4%). This base darkens when kept, except *in vacuo*, or in solvents except light petroleum (b. p. 100—120°) from which it may be crystallised with difficulty in deep-yellow plates. The *dihydrochloride* crystallises from a 1 : 1 v/v mixture of concentrated hydrochloric acid and water in maroon-coloured needles which sublime above 215° (Found: C, 56·1; H, 4·9; N, 11·4. $C_{12}H_{12}N_2Cl_2$ requires C, 56·5; H, 4·7; N, 11·0%).

2,6-*Diacetamido*-3,7-*dibromodiphenylene* (XIII).—2,6-Diacetamidodiphenylene (100 mg.) in glacial acetic acid (25 ml.) containing anhydrous sodium acetate (300 mg.) at 80° was treated dropwise with a 10% solution of bromine in acetic acid (1·3 ml.; 2·1 equiv.). A solid was gradually precipitated and was collected after cooling. This product is almost insoluble in organic solvents and was purified by boiling it with dimethylformamide, collecting the remaining solid, washing this with acetic acid, and drying it. The pale yellow 2,6-*diacetamido*-3,7-*dibromodiphenylene* decomposes at *ca.* 260° (Found: C, 45·4; H, 3·2; N, 6·3. $C_{16}H_{12}O_2N_2Br_2$ requires C, 45·3; H, 2·9; N, 6·6%).

2,2′-*Dibromo*-5,5′-*dinitrodiphenyl* (with Dr. J. W. Barton).—(*a*) Powdered 2,2′-dibromodiphenyl (5 g.) was added in portions to a stirred mixture of concentrated nitric acid (5 ml.) and concentrated sulphuric acid (6 ml.), and the mixture was warmed on the water-bath for 1 hr., then poured on ice. The washed, dried solid was stirred with ether (200 ml.) for 10 min., collected, and crystallised from acetone–methanol, giving 2,2′-*dibromo*-5,5′-*dinitrodiphenyl* as pale yellow prisms (3·8 g.), m. p. 220—221° (Found: C, 36·4; H, 1·5; N, 7·1. $C_{12}H_6O_4N_2Br_2$ requires C, 35·8; H, 1·5; N, 7·0%).

Evaporation of the ethereal washings (above) and crystallisation from methanol gave 2,2′-dibromo-*x*,*x*′-dinitrodiphenyl as yellow prisms (0·6 g.), m. p. 120—123°, raised after two further crystallisations to 124—125° (Found: C, 36·1; H, 1·3; N, 7·0%). This compound is probably 2,2′-dibromo-3,5′-dinitrodiphenyl or 2,2′-dibromo-3,3′-dinitrodiphenyl.

(*b*) 2,2′-Diamino-5,5′-dinitrodiphenyl [10] (2·5 g.) was added to a solution of cuprous bromide (20 g.) in hydrobromic acid (60 ml.; *d* 1·49) which had been previously boiled with copper turnings till colourless. A solution of sodium nitrite (3 g.) in water (25 ml.) was then added dropwise at 40—50° with rapid stirring which was continued for ½ hr. After the mixture had been heated on the water-bath, concentrated hydrochloric acid (50 ml.) was added, and the whole extracted with benzene (3 × 50 ml.). The extracts were shaken with hydrochloric acid and then with dilute ammonia, then concentrated and chromatographed on alumina, with benzene as the eluant which yielded 2,2′-dibromo-5,5′-dinitrodiphenyl, m. p. and mixed m. p. with the specimen previously prepared, 220—221° (1·6 g.) (from acetone–methanol).

Reaction of 2,2′-*Dibromo*-5,5′-*dinitrodiphenyl with Sodium Polysulphide*.—An aqueous solution of sodium polysulphide (1·0 ml.; prepared according to Purdie [11]) was added to a stirred, boiling mixture of 2,2′-dibromo-5,5′-dinitrodiphenyl (0·5 g.) in ethanol (40 ml.). After 15 min. a further amount (0·5 ml.) of the polysulphide solution was added, heating continued

[10] Sako, *Mem. Coll. Eng. Kyushu*, 1932, **6**, 327; *Brit. Chem. Abs.*, *A*, 1932, 508.
[11] Purdie, *J. Amer. Chem. Soc.*, 1941, **63**, 2276.

for 1½ hr., and the alcohol removed by distillation. The residue was digested with hot 10% aqueous hydrochloric acid, and the filtrate basified, giving 3-*amino*-6,2′-*dibromo*-5′-*nitrodiphenyl* as a yellow powder which after purification by further precipitation from acid (yield, 17 mg.) had m. p. 219—221° (Found: C, 38·3; H, 2·5; N, 7·5. $C_{12}H_8O_2N_2Br_2$ requires C, 38·7; H, 2·7; N, 7·5%). The acid-insoluble material was recrystallised from acetone, giving 3,6-dinitrodibenzothiophen (0·24 g.) as pale yellow needles, m. p. 350—352° (decomp.) (Found: C, 52·9; H, 2·1; N, 10·6; S, 11·8. Calc. for $C_{12}H_6O_4N_2S$: C, 52·6; H, 2·2; N, 10·2; S, 11·7%) (Gilman and Nobis [12] give m. p. 339—340°).

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[12] Gilman and Nobis, *J. Amer. Chem. Soc.*, 1949, **71**, 274.