Reactions of *N*-(2- and 4-methylsulfonylphenyl)hydroxylamines and 2-methylsulfonylnitrosobenzene in dilute aqueous sodium hydroxide solution[1]

K. B. SHAW, R. M. HEGGIE, AND R. K. MILLER
Defence Research Establishment Ottawa, Defence Research Board, Ottawa 4, Ontario

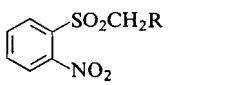
Received November 6, 1969

When *N*-(2-methylsulfonylphenyl)hydroxylamine (**4**) was treated with dilute sodium hydroxide solution the major product was always 2,2′-di(methylsulfonyl)azoxybenzene (**5**). At room temperature other significant products were 2-hydroxy-2′-methylsulfonylazoxybenzene (**6***a*) and 2-methylsulfonylnitrobenzene (**2**), while **6***a* was also formed at reflux together with small amounts of 2-hydroxy-2′-methylsulfonylazobenzene (**8**), 2-methylsulfonylaniline (**7**), 3-methylsulfonyl-3′-nitro-4-amino-4′-hydroxybiphenyl (**3**), and **2**. The compounds **5**, **6***a*, and **7** were also obtained when 2-methylsulfonylnitrosobenzene (**9**) was boiled with alkali. The decomposition of *N*-(4-methylsulfonylphenyl)hydroxylamine (**16**) in dilute alkali at room temperature gave a quantitative yield of 4,4′-di(methylsulfonyl)azoxybenzene (**17**) and at reflux, mixtures of **17** and 4,4′-di(methylsulfonyl)azobenzene (**18**) were obtained. The modes of formation of the various products from the two hydroxylamines are discussed.

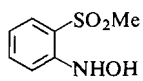
Canadian Journal of Chemistry, 48, 1404 (1970)

Introduction

In an earlier paper (1) the reactions of 2-nitrophenylsulfonylacetic acid (**1**) and 2-methylsulfonylnitrobenzene (**2**) in dilute sodium hydroxide solution were described. In connection with the genesis of the most unusual product of these reactions, i.e. 3-methylsulfonyl-3′-nitro-4-amino-4′-hydroxybiphenyl (**3**), the effect of alkali on *N*-(2-methylsulfonylphenyl)hydroxylamine (**4**) was studied. The biphenyl **3** was one of the products obtained when **4** was treated with alkali and as a result of this observation, and some additional work, a mechanism for the formation of **3** was suggested. However the reactions of **4** were not described in detail earlier (1) and are reported here. Although the experiments with the nitrosulfones were carried out at 100° (**1** was unaffected by dilute alkali, and **2** was insoluble in dilute alkali, at room temperature) **4** was soluble in, and decomposed by, cold alkali, and the reactions occurring under these conditions, as well as those at 100°, were studied.



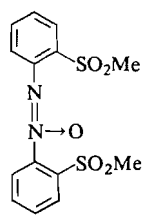
1 R = CO_2H
2 R = H



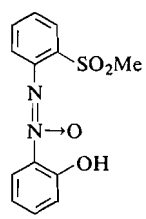
4

Results and Discussion

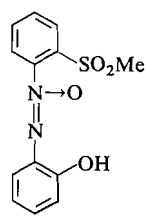
The decomposition of **4** in 0.1 *N* sodium hydroxide yielded a number of products. Those identified were 2-methylsulfonylnitrobenzene (**2**), the biphenyl (**3**), 2-methylsulfonylaniline (**7**), and three other compounds. The first of these other compounds was shown by elemental analysis and by infrared (i.r.) and nuclear magnetic resonance (n.m.r.) spectra to be 2,2′-di(methylsulfonyl)azoxybenzene (**5**) (2). The i.r. spectrum of the second indicated that it was probably a 1,2-disubstituted benzene containing a hydroxyl group and a methylsulfonyl group, and its color suggested an azoxybenzene. The empirical formula $C_{13}H_{12}N_2O_4S$ was shown by mass spectrometry to be the molecular formula (mol. wt. 292) and thus it was probable that the compound was a 2(2′)-hydroxy-2′(2)-methylsulfonylazoxybenzene i.e. **6***a* or **6***b* (other isomers can be neglected since the starting material was ortho-disubstituted). In a recent paper (3) it was concluded that the position of the *N*-oxide link in unsymmetrically substituted azoxybenzenes can always be determined because base peaks in the mass spectra of such compounds are produced by C—*N* cleavage α to the *N*-oxide group. The base peak in the mass spectrum of **6** was at *m/e* 93 (C_6H_5O) and the peak at *m/e* 155 ($C_6H_4SO_2Me$)



5



6*a*



6*b*

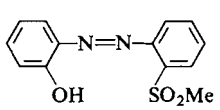
[1]Issued as DREO Report No. 617.

TABLE 1

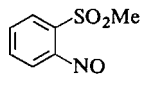
Yields of various products after decomposition of **4** in 0.1 *N* sodium hydroxide

4 (moles)	Reaction time (h)	Reaction temperature	% Yield					
			2	**3**	**5**	**7**	*6a*	**8**
0.0029	6.5	Room	20	<1	41	—	25	—
0.0029	6.5	100°	—	6	35	Trace	ca. 18	ca. 3.5
0.0029	0.25	100°	Trace	6	48	Trace	ca. 18	ca. 3.5
0.005	6.5	100°	—	3	28	Trace	22	

was very weak suggesting that *6a* was the correct structure. The spectral data on the third compound indicated that it was the azo compound corresponding to **6** and this structure (**8**) was confirmed by synthesis from 2-methylsulfonylnitrosobenzene (**9**) and 2-aminophenol. Some evidence (ultraviolet (u.v.) and i.r.) was obtained for the presence of orthanilic acid (**10**) after the decomposition of **4** at 100°. The yields obtained of these various products under different conditions are summarized in Table 1.



8



9

It is well known that phenylhydroxylamine (and its homologues) is easily oxidized by air in aqueous solution (*4a*, *5a*). The main product is azoxybenzene, formed by condensation of nitrosobenzene, the first oxidation product, with phenylhydroxylamine, and hydrogen peroxide is also formed. In alkaline solution, azoxybenzene and nitrobenzene but no hydrogen peroxide are obtained; the last compound is used up in the oxidation which leads to the nitro compound (*5a*), although peroxide may also oxidize phenylhydroxylamine to azoxybenzene (6). Thus in the reaction of **4** in alkali in air, the initial transformation product must be **9**; reaction of this intermediate with **4** gives **5** and, at room temperature, further oxidation of **9** gives **2**. At 100° any hydrogen peroxide formed presumably decomposes readily and only a small quantity of **2** was detected after a 15 min reaction time. However, another possible source of **9**, which is potentially important in the reaction under reflux when air has less access to the reaction mixture, is the disproportionation reaction of phenylhydroxylamines (*5a*): 2 RNHOH → RNO + RNH_2 + H_2O. It is possible in the case of **4** that this reaction requires an elevated temperature because the amine **7** was not formed from **4** at room temperature, but even at 100° the yield of **7** was small and unless some was lost by reaction with other compounds in the mixture it seems likely that the disproportionation reaction was not a significant source of **9**. Hence the formation of **2** and **5** was unexceptional but the same cannot be said of *6a*. There appear to be four possible modes of formation of *6a*: (*1*) displacement of a methylsulfonyl group in **5** by hydroxide ion; (*2*) from **9** and 2-hydroxyaminophenol (**11**); (*3*) from **4** and 2-nitrosophenol (**12**), and (*4*) loss of a methylsulfonyl group from a 'bimolecular' precursor of **5**.

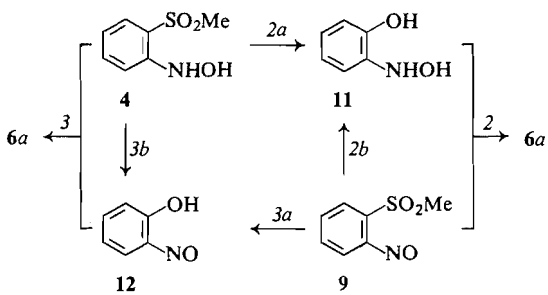
The first and most obvious route to *6a* is untenable. The azoxy compound **5** was unaffected by dilute alkali at room temperature and when the suspension was boiled for several hours **5** was recovered (80%), the u.v. spectrum of the aqueous solution, alkaline or acid, differed from that of *6a* in alkali or acid and *6a* was not isolated (the products of this reaction were not identified). In addition when **5** was boiled for 15 min with dilute alkali containing sufficient ethanol or *n*-propanol to ensure that all solid was in solution at the boiling point, **5** was again recovered (80–90%) and *6a* was not isolated. It should also be noted (Table 1) that the main difference between the reaction mixtures obtained when **4** was boiled in alkali for 15 min and 6 h was that, in the latter reaction, the yield of **5** was only about 75% of that obtained in the former, whereas the yield and composition of the mixture of *6a* and **8** were approximately the same in both cases.

The mechanism of formation of azoxybenzenes from a nitrosobenzene and a phenylhydroxylamine in alkali (7) involves a one electron transfer (eq. [1]) and the formation of free radicals (eq. [2]). If the hydroxylamine and the nitroso

[1] $RNHOH + 2\,OH^- \rightleftharpoons (RNO)^{2-} + 2\,H_2O$

[2] $(RNO)^{2-} + RNO \rightleftharpoons 2\,(RNO\cdot)^-$

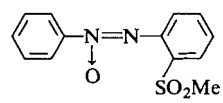
compound are differently substituted (e.g. **11** and **9**), two different anion-radicals are produced (eq. [2]). The same pair is also produced if the substituents in the reactants are transposed (e.g. as in **4** and **12**) and thus it might seem that routes *2* and *3* to **6***a* are indistinguishable. This is of course true in the later stages of the formation of **6***a*, but initially, two different pairs of reactants must be involved and the real problem is whether **11** or **12** is formed. There appeared to be two possible pathways to **11** and **12** from **4** or **9** and these are depicted in Scheme 1. It was realized however that since both **4** and **9** were present in the reaction mixture it would not be possible to differentiate between routes *2* and *3*, or between the various pathways to **11** and **12**, in the absence of additional experimental results.



SCHEME 1

Reaction *2a* (Scheme 1) was thought to be feasible through an intramolecular general base-catalyzed mechanism. However, when nitrogen was passed through a solution of **4** in dilute alkali for several hours and the solution then acidified, **4** was recovered (ca. 85%) and the u.v. spectrum of the aqueous solution was the same as that of **4**. Thus reaction *2a* was improbable.

The formation of **12** directly from **4** (reaction *3b*, Scheme 1) would involve a simultaneous oxidation and hydrolysis, and although a precise mechanism for such a reaction was difficult to formulate it could not be ruled out. Thus it was relevant to know what happened when **4** was treated with alkali at 100° in the absence of oxygen when an alternative means of formation of **9**, i.e. by disproportionation of **4** was available. Unfortunately this reaction was unexpectedly complex. The major product was again **5** (ca. 20%) although this time it did not separate from solution during the reaction and it was more deeply colored than all previous samples. The extract which in earlier experiments had contained only **6***a* and **8** was a mixture of several compounds from which **6***a* and **8** were isolated in small yield by chromatography. Several other colored fractions had u.v. spectra which had not been encountered before in this or earlier (1) work. One fraction was tentatively identified (i.r., u.v., and mass spectra) as 2′-methylsulfonylazoxybenzene (**13**) and there was spectroscopic evidence that azoxybenzene was also formed during the reaction. The mode of formation of



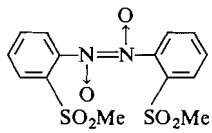
13

these compounds in which a methylsulfonyl group has apparently been replaced by a hydrogen atom posed additional problems (see below). A likely reason for the lower yield of **5** in the present reaction compared with the corresponding one in air is that **9** is formed less readily by disproportionation than by aerial oxidation. As a result, more of **4** would be lost by other modes of decomposition (cf. the many unidentified transformation products). The formation of **6***a* under conditions where oxidation is excluded implies that reaction *3b* is not followed. However the yield of **6***a* was low and thus the result was not conclusive (although **6***a* was difficult to isolate and may have been formed in higher yield) and it was felt that an examination of the behavior of **9** in dilute alkali might be rewarding.

The oxidation of phenylhydroxylamine to nitrosobenzene by chromic acid is carried out at 0° (8) but **4** was too insoluble in dilute sulfuric acid at this temperature and the oxidation to **9** was carried out at about 25°. When **9** was heated under reflux with dilute alkali for several hours the products identified were **5** (34%), **7** (ca. 6%), and **6***a* (ca. 20%) containing only a trace of **8**. No biphenyl (**3**), nitro compound (**2**), or orthanilic acid (**10**) was isolated but there was spectroscopic evidence that **10** was formed (ca. 6%). When the reaction was repeated under nitrogen a similar mixture of products was obtained in comparable yield although **8** was not detected in the fraction containing **6***a*.

Nitroso compounds are dimeric in the solid

state and although reversion to the monomer usually occurs on dissolution, some compounds, particularly those with ortho-substituents, can exist as dimers in solution (*5b*). A chloroform solution of **9** was deep green demonstrating that a considerable part of it was monomeric in this solvent. When **9** was boiled with water the liquid was pale green but in dilute alkali at 100° no green color was detected, indicating either that **9** dissolved as the dimer or that, more probably, the monomer was converted into other compounds as it was formed. The dimeric form of **9** (**14**) is analogous to **5** which, as noted earlier, is rather insoluble in boiling dilute alkali and there is no reason to expect that **14** would be any

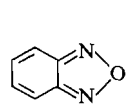


14

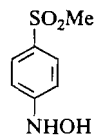
more soluble. In addition, the extent of dissociation to monomer increases with temperature (*9*) and at 100° would be very high. Thus it seems more reasonable to interpret the reactions of 2-methylsulfonylnitrosobenzene on the basis of the monomeric structure **9**.

Clearly, at 100° in dilute alkali, **9** is readily reduced to **4** (cf. the formation of **5**) although the mechanism of this reduction is obscure. Nitrosobenzene is reduced to phenylhydroxylamine, or its anion, by alcohol and a base and the mechanism of this reduction has been established (*10*), but alcohol was absent in the present reactions. When **9** was boiled in water alone **5** was not produced (**9** was recovered (> 90%)), and when **9** was stirred in dilute alkali for 14 days at room temperature, ca. 50% of it was recovered and the only other identifiable product was **2**. There was no evidence that **5** or **6***a* was formed, and thus it appeared that the reduction of **9** to **4** requires alkali and an elevated temperature. The reduction should not be affected by an inert atmosphere, and this was apparently the case, but even more important, in contrast to reaction *3b*, reactions *3a* and *2b*, Scheme 1, should not be affected either, and as noted, the yield of **6***a* was, within experimental error, the same in air or under nitrogen. This is good evidence that **9** is the precursor of **11** or **12**. The formation of **11** from **9** (reaction *2b*) would involve two steps and a mechanism for this reaction is difficult to visualize and thus the formation of **12** from **9** (*3a*) seems most likely. In view of the formation of **6***a* when **4** was treated with dilute alkali at room temperature, the reaction **9** → **12** must be facile and it might be expected in the reaction of **9** with alkali, in which **4** was formed, that the yield of **6***a* would be higher than actually observed. However, the relative ease of the numerous reactions which occur when **9** (or **4**) is treated with alkali is unknown and the insolubility of **9** in dilute alkali at room temperature, together with the apparent ease of the reaction **9** → **4** at 100°, prevented any assessment of the facility of the reaction **9** → **12**.

It has been noted already that **9** is unaffected by boiling water, and when a mixture of **9** and **4** was refluxed in water, **5** was obtained (82%) and **6***a* was not isolated. Thus hydroxide ion has a role in the formation of **6***a* that involves more than the catalysis of the reaction between a nitrosobenzene and a phenylhydroxylamine and clearly such a role could be in the conversion of **9** into **12**. The precise mechanism of this reaction is not known, but methylsulfonyl is a good leaving group (*11*) and it is likely that the reaction involves nucleophilic attack by hydroxide ion on the carbon atom bearing the methylsulfonyl group in **9**. Good evidence that the methylsulfonyl group in **9** can be displaced by a nucleophile was obtained when benzofurazan (**15**), identified by u.v. (*12*) and n.m.r. spectra (*13*) was isolated in small yield after treatment of **9** with sodium azide in water at 100° (cf. (*14*)). This reaction clearly



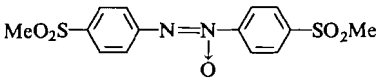
15



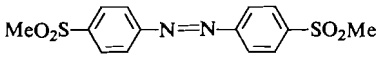
16

involved attack by azide ion on **9** to give 2-azidonitrosobenzene, which then cyclized with loss of nitrogen to give **15**; however the reaction was not investigated in detail and the optimum conditions for the formation of **15** were not established.

In order to determine to what extent ortho effects were important in the reactions of **4** and **9**, the effect of alkali on *N*-(4-methylsulfonylphenyl)hydroxylamine (**16**) was studied. When a solution of **16** in 0.1 *N* sodium hydroxide was stirred at room temperature for several hours,



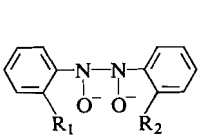
17



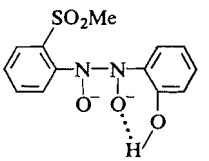
18

the solution became pale yellow and a solid gradually separated. This solid was identified as 4,4′-di(methylsulfonyl)azoxybenzene (**17**) (15) (96%) and no other compound was isolated. When **16** was treated with alkali at 100°, mixtures of **17** and 4,4′-di(methylsulfonyl)azobenzene (**18**) were obtained in high yield (80–90%) together with traces of 4-methylsulfonylaniline (**19**) (16), but, as in the experiment at room temperature, compounds analogous to **6***a* and **8** were not isolated. The constitutions of the mixtures of **17** and **18** depended somewhat on the experimental conditions, and were estimated by u.v. spectroscopy. Thus, when a cold solution of **16** in dilute alkali was heated to 100° and then boiled for 15 min, the solid obtained, after removal of a small amount of ethanol-soluble material, was a mixture of **18** and **17** in the approximate ratio 3:1. On the other hand, when **16** was added to dilute alkali at > 90° and the solution then boiled for 15 min the ratio of **18** to **17** in the solid obtained was about 5:1. In all experiments the ethanol-soluble solid had spectroscopic properties very similar to those of the mixture of **17** and **18**, but it melted considerably lower and was not identified. Similar mixtures to those just described were obtained when the respective experiments were carried out under nitrogen but the combined yield of **17** and **18** was slightly lower (ca. 75%). The formation of **18** is considered below but 4-methylsulfonylnitrosobenzene (**20**) must be an intermediate in the formation of **17**. Since 4-nitrosophenol was apparently not formed from **20** the inference is that an ortho effect was operating in the formation of **12** from **9**. However the evidence is inconclusive because condensation reactions (e.g. azoxybenzene formation) probably proceed so readily in the para series owing to the absence of steric hindrance, that other reactions e.g. displacement of a methylsulfonyl group (or oxidation of **20** to 4-methylsulfonylnitrobenzene (**21**)) cannot occur to any significant extent.

Two further points which merit comment are that the azoxybenzene (**6***a*) was apparently not contaminated with its isomer **6***b* and that 2,2′-di(hydroxy)azoxybenzene (**22**) was not isolated after treatment of **4** or **9** with alkali. The mechanism of azoxybenzene formation (7) mentioned above readily explains why condensations between a nitrosobenzene and a differently substituted phenylhydroxylamine usually yield mixtures of azoxybenzenes (e.g. (17)), since each anion-radical can react with itself as well as with the other. However the yields of the various possible products probably depend on several factors, particularly the nature of the reactants (cf. (18)) and their relative concentrations. Thus the apparent absence of one possible product, e.g. **22**, is not surprising, and indeed **22** may have been formed when **4** or **9** was treated with alkali, although at room temperature especially, it could only have been formed in very small yield. The combination of the anion-radicals referred to above gives the intermediate (**23**) which then loses hydroxide ion after protonation of one of the oxygen atoms. If $R_1 \neq R_2$, two azoxybenzenes should result. However in the intermediate (**24**) from **9** and **12**, hydrogen-bonding between one oxygen atom and the hydroxyl group favors



23



24

elimination of the other oxygen atom. The presence of hydrogen-bonding in **6***a* was indicated by the appearance of the hydroxyl absorption in its i.r. spectrum and by the fact that it was extracted with chloroform from the alkaline solution in which it was formed.

The fourth possible mode of formation of **6***a* considered at the beginning of the discussion was the loss of a methylsulfonyl group from a bimolecular precursor of **5**; the only such precursors are **23**, $R_1 = R_2 = SO_2Me$ and its protonated form. This possibility is difficult to prove or disprove and is probably not excluded by the experimental results. A mechanism for such a reaction, especially one which was inapplicable in the para case, is difficult to envisage (e.g. a reaction in which **23**, $R_1 = R_2 = SO_2Me$,

functions as a general base is excluded since **6***a* was not formed from **4** and **9** in water) and although this reaction route to **6***a* cannot be rejected, it does seem improbable.

The mode of formation of the azo compounds **8** and **18** will now be considered. The known (5*a*) disproportionation reaction of phenylhydroxylamines to nitrosobenzenes and anilines, with subsequent condensation of these products to azobenzenes would appear to be a feasible route for the formation of **18**. Although unsymmetrical azo compounds are usually prepared from a nitrosobenzene and an aniline in acetic acid (4*b*), the reaction between nitrosobenzene and aniline apparently does proceed in alkali [quote in ref. (7)]. In view of the high yields of **18** obtained when the hydroxylamine (**16**) was boiled in alkali azobenzene formation appears to be a more facile reaction than azoxybenzene formation. However this may be only a reflection of the ease with which **16** disproportionates (cf. the similar mixtures of **17** and **18** obtained in air or under nitrogen). The yield of **17** in the reaction in which **16** was heated from room temperature to reflux was higher than in the reaction carried out from ca. 90° to reflux because **17** was formed from the nitroso compound (**20**), produced by aerial oxidation of **16**, before the temperature was reached at which disproportionation (and hence formation of **18**) became significant.

A similar explanation cannot be accepted a priori for the formation of the hydroxyazobenzene (**8**) which was formed in small yield when the hydroxylamine (**4**) was treated with alkali at 100° but not at room temperature. The reaction between a nitroso compound and an aniline is inhibited by bulky groups in the ortho positions of the reactants, and the amine (**7**) and the nitroso compound (**9**) did not yield 2,2′-di(methylsulfonyl)azobenzene under optimum conditions, i.e. in glacial acetic acid. In addition, when **7** and a molar equivalent of **9** [a precursor of 2-nitrosophenol (12)] were boiled in dilute alkali very little, if any, **8** was formed. These results contraindicated condensation of a nitrosophenol with an aniline as the mechanism of formation of **8** although it should be noted that **8** was formed by condensation of **9** and 2-aminophenol (**25**) in acetic acid. An alternative route for the formation of **8** is the reduction of the azoxybenzene (**6***a*). The possibility was considered that the hydroxylamine acted as the reducing agent and was itself oxidized to the nitroso compound. However, the hydroxylamine (**16**) did not reduce azoxybenzene itself (**26**). When **16** was boiled in alkali in the presence of a molar equivalent of **26**, the mixture of **17** and **18** produced was the same as that in the absence of **26**; **26** was recovered in high yield and no azobenzene was detected. This result does not completely exclude reduction of **6***a* as a source of **8**. The reduction may be facilitated by the presence of the hydroxy function in the ortho position or may be due to a reducing agent formed by unknown decomposition pathways of the hydroxylamine (**4**). It is probably significant that **8** was virtually absent after the treatment of **9** with alkali at 100° when **4** was not present in excess.

2-Methylsulfonylazoxybenzene (**13**) and azoxybenzene (**26**) were the only compounds isolated during the work described in this, or the earlier report (1) in which a methylsulfonyl group had apparently been replaced by a hydrogen atom. However, **26**, azobenzene (**27**), and 2-methylsulfonylazobenzene (**28**) (19) were obtained in small yield after treatment of 3,4-dihydro-4-hydroxy - 3 - oxo - 2*H* - 1,4 - benzothiazine - 1,1-dioxide (**29**) (cf. (1)) with alkali[2] but their modes of formation were not elucidated, although it was concluded that they were products of the action of sodium hydroxide on **29** and, for example, had not been formed from impurities, e.g. nitrobenzene or phenylhydroxylamine, in the hydroxamic acid. It seems inconceivable in experiments carried out in alkaline solution that a substituent, e.g. a methylsulfonyl group, on an aromatic ring, could be displaced, and replaced by a hydrogen atom, and a seemingly more reasonable route to compounds such as **13**, **26**, **27**, and **28** in the above reactions, was that an intermediate sulfinic acid lost sulfur dioxide in a reaction analogous to the decarboxylation of a carboxylic acid. Although the desulfination of sulfinic acids is a known reaction (20) it does not appear to have been carried out in alkaline solution, and indeed 2-aminobenzenesulfinic acid and azobenzene-2-sulfinic acid are stable in refluxing ethanolic sodium hydroxide solution (19, 21). However, the formation of sulfinic acids themselves in the above reactions poses problems, and hence the modes of formation of **13** and **26**,

[2]K. B. Shaw and R. K. Miller. Unpublished work.

and **26**, **27**, and **28** in the respective reactions remain a mystery.

Summary

In dilute sodium hydroxide solution, *N*-(2-methylsulfonylphenyl)hydroxylamine (**4**) is readily oxidized by air to 2-methylsulfonylnitrosobenzene (**9**) and at room temperature the hydrogen peroxide produced in this reaction converts **9** into 2-methylsulfonylnitrobenzene (**2**). In addition, **9** is also produced, together with 2-methylsulfonylaniline (**7**) by the disproportionation of **4** at 100°. The hydroxylamine **4** reacts with **2** to give the biphenyl (**3**)(1), and with **9** to give 2,2′-di(methylsulfonyl)azoxybenzene (**5**). The displacement of the methylsulfonyl group in **9** by hydroxide ion gives 2-nitrosophenol (**12**) which reacts with **4** to give 2-hydroxy-2′-methylsulfonylazoxybenzene (**6***a*). The corresponding hydroxy azo compound (**8**) is also formed, perhaps by reduction of **6***a*, but the reaction of **7** and **9** to give 2,2′-di(methylsulfonyl)azobenzene is not observed (steric hindrance). At 100° in dilute alkali **9** is readily reduced to **4**, and then **5** and **6***a* are formed as before.

N - (4 - Methylsulfonylphenyl)hydroxylamine (**16**) in dilute alkali is readily oxidized by air to 4-methylsulfonylnitrosobenzene (**20**), which is also formed, together with 4-methylsulfonylaniline (**19**), by the facile disproportionation of **16** at 100°. The nitroso compound **20** reacts with **16** to give 4,4′-di(methylsulfonyl)azoxybenzene (**17**), and with **19** to give 4,4′-di(methylsulfonyl)-azobenzene (**18**); neither the oxidation of **20** to 4-methylsulfonylnitrobenzene (**21**), nor the loss of the methylsulfonyl group from **20**, with the subsequent formation of a compound analogous to **6***a*, is observed.

Experimental

Infrared spectra are for potassium bromide disks. Microanalyses were performed by J. G. Helie and the mass spectra were by Morgan–Schaffer Corporation, Montreal.

Reactions of N-(2-Methylsulfonylphenyl)hydroxylamine (4) in Aqueous Sodium Hydroxide Solution

The preparation of **4** has been described (1). The experiments were carried out as indicated below and the reaction mixtures were worked up as follows. The solid was filtered off (fraction A) and the solution was washed once with ether (fraction B), and then several times with chloroform (fraction C). The aqueous solution was acidified with hydrochloric acid and again washed with ether (fraction D). Each experiment was carried out more than once and after pure **6***a* and **8** had been obtained, the constitutions of some of the mixtures of **6***a* and **8**, and the purity of **6***a* obtained in the reaction at room temperature, were estimated from the intensity of the peak at 330 mμ in the u.v. (**6***a* and **8** had E_1^1 308 and 612 respectively at 330 mμ). Thin-layer chromatography (t.l.c.) of the mixtures of **6***a* and **8** was carried out on activated (220–230° for 3 h) Gelman Type A absorbent (alumina gel and micro glass fibers) with the solvent system chloroform–hexane (2:1). Spots were detected with *N* sodium hydroxide.

(*a*) A solution of **4** (540 mg) in 0.1 *N* sodium hydroxide (60 ml; 2.1 molar equ.) was stirred at room temperature for 6 h. Fraction A (269 mg, m.p. ca. 180–210°) was washed well with ether and the solid was filtered off giving 2,2′-di(methylsulfonyl)azoxybenzene (**5**) (202 mg, 40%), m.p. 229–231°, which crystallized from ethanol containing a little acetone, as very pale yellow prisms, m.p. 232–233° (lit. (2) m.p. 222°); λ_{max} (EtOH) 307 mμ (log ε 4.02); ν_{max} 1310, 1150 and 1120, and 950 cm^{-1} (SO_2Me); n.m.r. (60 MHz) (DMSO-d_6) 500–450 Hz, max at 480 Hz from TMS (intensity 8H), τ 6.73 and 6.57 (each intensity 3H).

Anal. Calcd. for $C_{14}H_{14}N_2O_5S_2$: C, 47.44; H, 3.98; N, 7.91; S, 18.09. Found: C, 47.38; H, 4.10; N, 7.74; S, 17.91.

The ether-soluble portion of fraction A (59 mg, m.p. 101–104°) and fraction B (60 mg, m.p. 99–103°) were slightly impure **2** (ca. 20%). Fraction C (113 mg) was a yellow solid, m.p. 106–109°, estimated to be > 95% **6***a* (26%), but **8** was absent. It was crystallized three times from ethanol giving 2-hydroxy-2′-methylsulfonylazoxybenzene (**6***a*) as yellow needles, m.p. 111–112°; λ_{max} (EtOH) 243, 282, and 330 mμ (broad) (log ε 3.91, 3.85, and 3.95); (EtOH + 1 drop NaOH solution) 234 and 288 mμ (log ε 4.32 and 3.90); ν_{max} ca. 3200–3100 (weak, bonded OH), 1295, 1165, and 970 (SO_2Me), and 750 cm^{-1} (1,2-disubstituted benzene).

Anal. Calcd. for $C_{13}H_{12}N_2O_4S$ (mol. wt. 292): C, 53.42; H, 4.14; N, 9.59; S, 10.97. Found (292 (mass spectrum)): C, 53.64; H, 4.36; N, 9.79; S, 11.23.

Fraction D (35 mg) was treated with a few drops of methanol and filtered giving the biphenyl **3** (3.5 mg, 0.8%), m.p. 209–211°, i.r. spectrum identical with that of an earlier sample (1).

(*b*) A stirred solution of **4** (540 mg) in 0.1 *N* sodium hydroxide was heated under reflux 6 h. Fraction A was **5** (180 mg, 35%), m.p. 230–232° and was not contaminated with **2**. Fraction B was a pale yellow oil (15 mg) containing some 7. Fraction C was an orange solid (94 mg), m.p. ca. 106–108°, which was a mixture of **6***a* and **8** (ca. 22%) in the approximate ratio 5:1. The solid, after crystallization to constant m.p., 110–112°, was **6***a* containing a trace of **8** (elemental analysis and t.l.c.). Fraction D was a sticky red solid (97 mg), which after treatment with methanol as before gave **3** (26 mg, 6%), m.p. 207–212°, raised to 211–214° after crystallization from ethanol. The methanol-soluble material (70 mg) was a mixture of several compounds, none of which was identified.

(*c*) A stirred solution of **4** (540 mg) in 0.1 *N* sodium hydroxide was heated under reflux 15 min. Fraction A (261 mg, m.p. 227–230° with previous softening) was

washed with ether giving **5** (247 mg, 48%), m.p. 231–233°. Fraction B (27 mg) was an orange oil containing **2** and **7**. Fraction C (84 mg), m.p. 102–107°, was a mixture of **6***a* and **8** similar to that obtained under (*b*). Fraction D (93 mg) after treatment with methanol as before gave **3** (22 mg, 5%), m.p. 209–212°.

(*d*) A stirred solution of **4** (935 mg) in 0.1 *N* sodium hydroxide (105 ml) was heated under reflux 6 h. Fraction A was washed with ethanol giving **5** (253 mg, 28%) m.p. 231–233°. Fraction B (52 mg) was an orange oil containing **6***a*, **7**, and **8**. Fraction C was an orange solid (154 mg) m.p. ca. 125–130°, and was chromatographed on alumina (Neutral 2) in chloroform–hexane (4:1). A fast moving red band which was closely followed by, and not cleanly separated from, a light orange band, was collected giving an orange solid (93 mg) m.p. ca. 142–148°, which was a mixture of **8** and **6***a* in the approximate ratio 4:1. The column was extruded and a broad yellow band was washed off the alumina with 10% acetic acid in methanol. The resulting solid, in chloroform–hexane (1:2), was chromatographed on alumina (acid 3) and the main yellow band was collected, giving a yellow solid (29 mg) m.p. 110–111°, which was a mixture of **6***a* and **8** in the approximate ratio 13:1. The solid was crystallized from methanol but its melting point and constitution were not changed. The main fraction above was rechromatographed on alumina (Neutral 2) but the various fractions were still mixtures of **8** and **6***a*. The solid from the combined fractions was crystallized three times from methanol giving 2-hydroxy-2′-methylsulfonylazobenzene (**8**) as small orange needles, m.p. 149.5–150°; λ_{max} (EtOH) 246, 330, and 388 mμ (log ε 3.99, 4.23, and 3.92); (EtOH + 1 drop NaOH solution) 236 and 335 mμ (log ε 4.17 and 4.03); ν_{max} 1290, 1140, and 950 (SO_2Me), 760 cm^{-1} (1,2-disubstituted benzene).

Anal. Calcd. for $C_{13}H_{12}N_2O_3S$ (mol. wt. 276): C, 56.51; H, 4.38; N, 10.14; S, 11.60. Found (276 (mass spectrum)): C, 56.52; H, 4.50; N, 9.99; S, 11.86.

Fraction D (143 mg) after treatment with methanol as before gave **3** (25 mg, ca. 3%), m.p. 211–213° after crystallization from ethanol–acetone. The remaining aqueous solution was decolorized (charcoal) and evaporated to dryness and the residue (in water) was passed through a column of AG 50W-X8 cation exchange resin (15 ml). The first three fractions collected (30 ml) had similar u.v. spectra and were evaporated giving a sticky solid (108 mg). The u.v. and i.r. spectra of this material were very similar to those of orthanilic acid (cf. (1)).

(*e*) Reaction (*b*) above was repeated under nitrogen. A yellow material (ca. 15 mg) in the condenser was washed out with ethanol and appeared (u.v. and i.r.) to be azoxybenzene. Virtually no solid separated from the aqueous solution hence there was no fraction A. Fraction B (30 mg) contained some **7**. Fraction C was a sticky red solid (367 mg) which was rubbed well with ether and filtered giving a yellow solid (117 mg) m.p. 216–226°, with an i.r. spectrum very similar to that of **5**. The solid was crystallized twice from ethanol containing a little acetone giving golden yellow prisms, m.p. 230–232°, mixed m.p. with **5**, 231–233°, i.r. and u.v. spectra identical with those of **5**. Found: C, 47.37; H, 4.16; N, 7.78. It was not clear why this product did not separate during the reaction or why it was more deeply colored than previous samples. The ether-soluble material (209 mg) was chromatographed on alumina (Neutral 2) in chloroform–hexane (1:1) and the following fractions were collected: (*i*) An orange oil (52 mg) which solidified when rubbed with a little ethanol, m.p. 82.5–83.5, raised to 83.5–84.5° after crystallization from methanol; λ_{max} (EtOH) 239 and 326 (E^1_1 423 and 587 respectively); ν_{max} 1300, 1150, and 955 (SO_2Me), 760 cm^{-1} (1,2-disubstituted benzene); molecular formula (mass spectroscopy) $C_{13}H_{12}N_2O_3S$ (mol. wt. 276). This compound was tentatively identified as 2′-methylsulfonylazoxybenzene (**13**). (*ii*) A yellow oil (68 mg) which was a mixture of at least 3 compounds none of which was identified. (*iii*) A red-brown solid (35 mg), λ_{max} 244 and 319 mμ, ν_{max} 1300, 1150, and 950 cm^{-1}, which was not identified. (*iv*) An orange-red solid (15 mg) which did not melt sharply but which had u.v. and i.r. spectra similar to those of **8**. The column was extruded and treated in the same way as under (*d*) above giving **6***a* (ca. 7 mg) m.p. 108–111°.

*2-Methylsulfonylnitrosobenzene (**9**)*

N-(2-Methylsulfonylphenyl)hydroxylamine (2 g) was dissolved with gentle warming in a mixture of water (300 ml) and concentrated sulfuric acid (27 ml). The vigorously stirred solution was cooled to 25 °C, a solution of sodium dichromate dihydrate (1.07 g) in water (1 ml) was added and then the mixture was cooled (ice bath) for 15 min. The precipitate was filtered off, washed well with cold water (1.63 g, m.p. 162–163°), and crystallized from methanol containing a little chloroform giving **9** as very pale tan prisms (1.2 g, 61%), m.p. 163.5–165° (green liquid), unchanged on recrystallization; λ_{max} ($CHCl_3$) 288, 311, and ca. 775 mμ (log ε 3.82, 3.65, and 1.45); ν_{max} 1320 and 1280, 1155 and 965 cm^{-1} (SO_2Me).

Anal. Calcd. for $C_7H_7NO_3S$: C, 45.39; H, 3.81; N, 7.56; S, 17.31. Found: C, 45.59; H, 3.92; N, 7.52; S, 17.38.

*2-Hydroxy-2′-methylsulfonylazobenzene (**8**)*

A solution of recrystallized 2-aminophenol (44 mg) in glacial acetic acid (15 ml) was added to a solution of 2-methylsulfonylnitrosobenzene (74 mg) in acetic acid (15 ml) and the mixture, which became deep red in ca. 5 min, was stirred at room temperature 48 h. The mixture was poured into water, adjusted to p*H* 8–9 and extracted several times with chloroform, giving a red oil (101 mg) which was chromatographed on alumina (acid 3) in chloroform–hexane (1:1). The main orange band which was not completely separated from faster moving material was collected and the resulting oil was rechromatographed as before, again giving an oil which crystallized from aqueous methanol as orange needles (55 mg, 50%), m.p. 144–146°. Four recrystallizations from the same solvent system raised the m.p. to 148.5–149.5°, mixed m.p. with **8** obtained from **4** 149–150°; λ_{max} (EtOH) 246, 330, and 388 mμ (log ε 4.02, 4.24, and 3.93); (EtOH + 1 drop NaOH solution) 236 and 335 mμ (log ε 4.18 and 4.03); i.r. spectrum identical with that of the earlier sample.

Anal. Found: C, 56.78; H, 4.12; N, 9.91.

Reactions of 2-Methylsulfonylnitrosobenzene in Aqueous Sodium Hydroxide Solution

The reaction mixtures were worked up as described

above under the reactions of **4** in alkali, except that the solution was adjusted to p*H* 8–8.5 before it was washed with chloroform.

(*a*) A vigorously stirred mixture of 2-methylsulfonylnitrosobenzene (555 mg) and 0.1 *N* sodium hydroxide (60 ml, 2 molar equ.) was heated under reflux 4 h. Fraction A was **5** (181 mg, 34%), m.p. 231–232°. Fraction B (34 mg) was mainly **7** and did not contain any **2**. Fraction C (85 mg), m.p. 99–104°, was mainly **6***a* (ca. 20%) containing only a trace of **8**. Fraction D (24 mg) was not investigated. The remaining aqueous solution was treated 3 times with charcoal, when it showed λ_{max} (NaOH) 236 and 294 mμ, and probably contained orthanilic acid (ca. 6%) (cf. (1)).

(*b*) The foregoing experiment was repeated under nitrogen. Fraction A was **5** (201 mg, 38%), m.p. 228–230°. Fraction B (34 mg) was mainly **7**. Fraction C (82 mg), m.p. 100–106° was mainly **6***a* (ca. 19%). There was a trace of another compound (which did not move on t.l.c.) but **8** was not detected. Fraction D (18 mg) was not investigated. The aqueous solution probably contained orthanilic acid (ca. 3%).

(*c*) A mixture of **9** (555 mg) and 0.1 *N* sodium hydroxide (60 ml) was stirred at room temperature 14 days. Fraction A (366 mg) was clearly a mixture (i.r., wide m.p. range) and was rubbed well with ether. The insoluble portion (238 mg), m.p. 162–165° (green liquid) was **9** (43% recovery). The ether-soluble portion (117 mg), m.p. 101–105° was **2**. Fraction B (60 mg) was **2** (total yield ca. 50% based on recovered **9**) containing a trace of **7**. Fraction C (13 mg) was also a mixture (white solid (**2**) and yellow oil). Fraction D (< 5 mg) was not investigated.

Reaction of N-(2-Methylsulfonylphenyl)hydroxylamine (4) and 2-Methylsulfonylnitrosobenzene (9) in Water

A mixture of **4** (170 mg), **9** (165 mg), and water (20 ml) was heated under reflux 2 h. The solid was filtered off giving slightly impure **5** (265 mg, ca. 82%), m.p. 225–227°. The yellow aqueous solution was washed with chloroform (aqueous now colorless) giving a mixture of white solid and yellow oil (29 mg), λ_{max} 245 and 308 mμ, which was not investigated further.

When **9** (250 mg) was heated under reflux 2 h in water (20 ml) the liquid was pale green at the boiling point, and after the mixture had cooled, **9** was recovered (228 mg, 91%), m.p. 164–166°. The aqueous solution was washed with chloroform giving a mixture of yellow and white solids (9 mg), u.v. spectrum similar to that of **9**. The remaining aqueous solution showed no maximum in the u.v.

The Formation of Benzofurazan from 2-Methylsulfonylnitrosobenzene

(*a*) A stirred mixture of 2-methylsulfonylnitrosobenzene (**9**) (500 mg) and water (50 ml) containing sodium azide (1 g) was distilled for ca. 50 min. The distillate was washed with ether, giving a pale yellow solid (A, 18 mg). The reaction mixture was cooled giving a brown solid (292 mg), m.p. 165–168°, identified as **9**.

(*b*) A mixture of **9** (100 mg) and water (25 ml) containing sodium azide (200 mg) was heated under reflux several minutes. The solid which collected in the condenser was washed out with ether, then the reaction was continued and the solid removed in the same way. The material from four such experiments (18.9 mg) together with solid A above, was identified as benzofurazan (**15**), m.p. 51.5–52° (lit. (22) m.p. 53°; (23) m.p. 51.5–52°); λ_{max} (cf. (12)) (H_2O) 254 sh, 259, 264, 269, 275, 280, 287, and 302 mμ (log ε 3.28, 3.38, 3.51, 3.55, 3.65, 3.59, 3.64, and 3.49); n.m.r. (cf. (13)) (CCl_4) AA′BB′ spectrum, τ 2.20 (2H), 2.65 (2H), $J + J' = 10.0$ Hz. The yield of **15** under (*a*) above, allowing for recovered **9**, was 13%; no attempt to recover starting material was made in experiment (*b*).

N-(4-Methylsulfonylphenyl)hydroxylamine (16)

4-Methylsulfonylnitrobenzene (1) (5 g) was reduced by the method described earlier (1) for the 2-isomer. The crude product (4.1 g) was crystallized from ethyl acetate – hexane giving pale pink crystals (2.53 g, 54%), m.p. 154° (decomp.). Two further crystallizations from the same solvent mixture gave small pale pink needles, m.p. 157.5–158.5° (decomp.); λ_{max} (H_2O) 263 mμ (log ε 4.14); λ_{max} (NaOH) 252 mμ (log ε 3.79); ν_{max} 3360 (OH), 3295 (NH), 1280, 1135, and 970 cm^{-1} (SO_2Me).

Anal. Calcd. for $C_7H_9NO_3S$: C, 44.91; H, 4.85; N, 7.48; S, 17.13. Found: C, 45.10; H, 5.12; N, 7.39; S, 17.11.

Reactions of N-(4-Methylsulfonylphenyl)hydroxylamine (16) in Aqueous Sodium Hydroxide Solution

(*a*) A solution of **16** (540 mg) in 0.1 *N* sodium hydroxide (60 ml; 2.1 molar equ.) was stirred at room temperature for 6 h. The initial pale yellow solution did not change color during the reaction period but a solid gradually separated. The mixture was filtered giving 4,4′-di(methylsulfonyl)azoxybenzene (**17**) (494 mg, 96%), m.p. 295–297° (decomp.). Crystallization from ethanol–dimethylformamide (DMF) gave **17** as pale orange needles, m.p. 295–296° (decomp.), (lit. (15) m.p. 264°); λ_{max} (DMF) 325 mμ (log ε 4.20); ν_{max} 1295, 1140, 960, and 955 cm^{-1} (SO_2Me).

Anal. Calcd. for $C_{14}H_{14}N_2O_5S_2$: C, 47.44; H, 3.98; N, 7.91; S, 18.09. Found: C, 47.63; H, 3.89; N, 7.94; S, 18.21.

(*b*) Compound **16** (270 mg) was added to 0.1 *N* sodium hydroxide (30 ml) at 95° and the mixture was heated under reflux 15 min and then cooled. The pale orange solid which separated (216 mg, m.p. ca. 280–290°) was crystallized four times from DMF giving 4,4′-di(methylsulfonyl)azobenzene (**18**) as orange prisms (75 mg), m.p. 305–306° (decomp.). λ_{max} (DMF) 323 mμ (log ε 4.37); ν_{max} 1295, 1140, 960, and 955 cm^{-1} (SO_2Me). The i.r. spectrum of **18** differed slightly from that of **17**. In particular the intensities of the bands near 960 cm^{-1} in **18** (955 > 960) were reversed in **17** (955 < 960), and although both compounds showed a band at 1455 cm^{-1}, it was much more intense in **17**.

Anal. Calcd. for $C_{14}H_{14}N_2O_4S_2$: C, 49.68; H, 4.17; N, 8.28; S, 18.95. Found: C, 49.52; H, 4.10; N, 8.18; S, 19.22.

When (*b*) was repeated on twice the scale the crude product (442 mg) was washed with ethanol leaving an orange solid (404 mg), m.p. ca. 295–299°, E_1^1 654, which was a mixture of **18** and **17** in the estimated ratio 5:1. The ethanol solution, which showed λ_{max} 322 mμ, unchanged when the solution was made alkaline, gave a

pale orange solid (31 mg), m.p. ca. 135–140° (decomp.). Its i.r. spectrum was rather similar to that of the mixture of **17** and **18** but it was not identified. The same reaction under nitrogen gave a similar mixture of **17** and **18** (E_1^1 651) in somewhat lower yield (369 mg after removal of the ethanol-soluble portion, 50 mg). The mixture was crystallized from aqueous DMF giving an orange solid (326 mg), m.p. 304–306°, E_1^1 680, which was mainly **18**.

(*c*) A solution of **16** (540 mg) in 0.1 *N* sodium hydroxide (60 ml) was heated under reflux 15 min and then cooled and filtered. The crude product was washed with ethanol leaving an orange solid (444 mg), m.p. 298–299° (decomp.), E_1^1 625, which was a mixture of **18** and **17** in the estimated ratio 3:1. The ethanol-soluble material (28 mg) was similar to that obtained earlier. The original aqueous solution was washed with chloroform giving a yellow oil (12 mg) whose u.v. and i.r. spectra were the same as those of 4-methylsulfonylaniline (16). The aqueous solution was acidified and washed with chloroform giving an oil (6 mg), λ_{max} 268 and 360 mμ, which was not identified.

(*d*) **16** (540 mg) was added to a vigorously stirred mixture of azoxybenzene (580 mg) and 0.1 *N* sodium hydroxide (60 ml) at > 80° and the whole was heated under reflux, under nitrogen, 2 h. The mixture was cooled, shaken well with ether (which had also been used to wash out the condenser), and the contents of the separatory funnel were filtered giving an orange solid (369 mg), m.p. 302–305°, E_1^1 654, which was crystallized from aqueous DMF giving **18** (331 mg, 68%) m.p. 305–306°, raised to 306–307° after recrystallization. Anal. Found: C, 49.68; H, 4.13; N, 8.20; S, 19.19. The ether solution gave an orange oil (580 mg) which was chromatographed on alumina (Basic 3) in benzene–hexane (2:1). A yellow band passed rapidly through the column and was collected giving azoxybenzene (517 mg, 90% recovery). An orange band was eluted with benzene giving a pale orange solid (33 mg) m.p. ca. 137–145°, which was similar to the ethanol-soluble material obtained in the earlier experiments.

Thanks are offered to Dr. M. A. Weinberger for the nuclear magnetic resonance spectra and to Professor R. T. Coutts for useful discussions.

1. K. B. Shaw and R. K. Miller. Can. J. Chem. This issue.
2. M. Claasz. Ber. **45**, 1015 (1912).
3. J. H. Bowie, R. G. Cooks, and G. E. Lewis. Aust. J. Chem. **20**, 1601 (1967).
4. Chemistry of carbon compounds. Vol. 3A. *Edited by* E. H. Rodd. Elsevier Publishing Co., New York. 1954. (*a*) p. 153; (*b*) p. 320.
5. N. V. Sidgwick. The organic chemistry of nitrogen. *Revised and rewritten by* T. W. J. Taylor and W. Baker. Clarendon Press, Oxford. 1942. (*a*) p. 163; (*b*) p. 206 ff.
6. E. Bamberger. Ber. **33**, 119 (1900).
7. G. A. Russell and E. J. Geels. J. Amer. Chem. Soc. **87**, 122 (1965).
8. G. H. Coleman, C. M. McCloskey, and F. A. Stuart. Organic syntheses. Coll. Vol. 3. *Edited by* E. C. Horning, John Wiley and Sons, Inc., New York. 1955. p. 668.
9. C. K. Ingold and H. A. Piggott. J. Chem. Soc. 168 (1924).
10. J. Hutton and W. Waters. J. Chem. Soc. *B*, 191 (1968).
11. G. B. Barlin and W. V. Brown. J. Chem. Soc. *C*, 2473 (1967) and references therein.
12. A. J. Boulton, P. B. Ghosh, and A. R. Katritzky. J. Chem. Soc. *C*, 971 (1966).
13. R. K. Harris, A. R. Katritzky, S. Øksne, A. S. Bailey, and W. G. Paterson. J. Chem. Soc. 197 (1963).
14. A. J. Boulton, P. B. Ghosh, and A. R. Katritzky. J. Chem. Soc. *B*, 1004 (1966); Tetrahedron Lett. **25**, 2887 (1966).
15. Th. Zincke and P. Jörg. Ber. **44**, 614 (1911).
16. E. A. Fehnel and M. Carmack. J. Amer. Chem. Soc. **72**, 1292 (1950).
17. Y. Ogata, M. Tsuchida, and Y. Takagi. J. Amer. Chem. Soc. **79**, 3397 (1957) and references therein.
18. W. Anderson. J. Chem. Soc. 1722 (1952).
19. M. P. Cava and C. E. Blake. J. Amer. Chem. Soc. **78**, 5444 (1956).
20. N. Kharasch, W. King, and T. C. Bruice. J. Amer. Chem. Soc. **77**, 931 (1955).
21. G. Bulmer and F. G. Mann. J. Chem. Soc. 680 (1945).
22. R. J. Gaughran, J. P. Picard, and J. V. R. Kaufman. J. Amer. Chem. Soc. **76**, 2233 (1954).
23. J. M. Prokipcak, P. A. Forte, and D. D. Lennox. Can. J. Chem. **47**, 2482 (1969).