Ozonation of Diarylfurans

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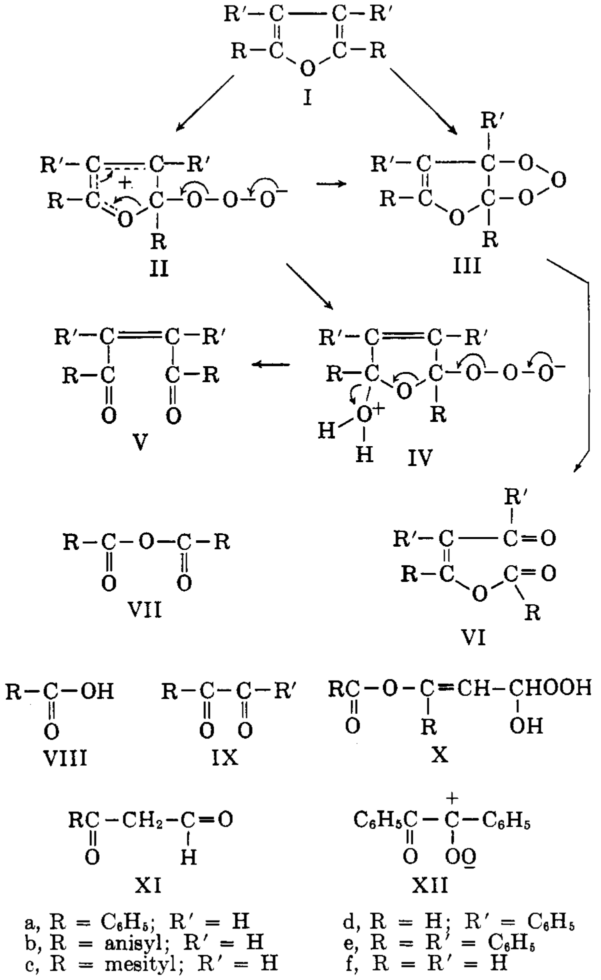
Ozonations of 2,5-dianisylfuran (Ib), 2,5-dimesitylfuran (Ic), and 3,4-diphenylfuran (Id) are reported. The results can be rationalized by the mechanism proposed in the preceding paper for the ozonation of 2,5-diphenylfuran. All three compounds undergo 1,2-bond cleavage to a greater degree than does 2,5-diphenylfuran.

In the preceding paper[1] we (1) reported the ozonation of 2,5-diphenylfuran (Ia) in both nucleophilic and nonnucleophilic solvents, (2) showed that both the type of solvent and the temperature affected the competition between 1,2-bond cleavage and 2,3-bond cleavage, and (3) proposed a mechanism to explain the results. Briefly, the mechanism involved two separate competitions. First is a competition in the initial attack of ozone on I to give a σ-complex (II) or the 2,3-bond adduct (III). The second competition is in regard to the fate of the σ-complex (II), which either loses molecular oxygen and gives the 1,2-bond-cleavage product (V), or cyclizes to III, which cleaves to peroxidic precursors of VI and/or decomposition products thereof. The present paper describes the results of ozonation of 2,5-dianisylfuran (Ib), 2,5-dimesitylfuran (Ic), and 3,4-diphenylfuran (Id) which, although not so clear-cut as were the results with Ia, can be rationalized by the proposed mechanism.



a, R = C_6H_5; R' = H
b, R = anisyl; R' = H
c, R = mesityl; R' = H
d, R = H; R' = C_6H_5
e, R = R' = C_6H_5
f, R = R' = H

Table I shows the results of ozonations of 2,5-dianisylfuran (Ib) and 2,5-dimesitylfuran (Ic) with 1 mole equiv. of ozone in methylene chloride and in 90% acetic acid, the two solvents which best illustrated the solvent effect with 2,5-diphenylfuran (Ia).[1] Ozone absorption by 2,5-dianisylfuran (Ib) was quantitative in both solvents. Since no starting material was recovered from the methylene chloride reaction mixture, the 15% yield of 1,2-dianisoylethylene (Vb) obtained (expt. 1, Table I) represents the extent of the 1,2-bond-cleavage reaction in this solvent. These values for the various furans studied are shown in Table II. From the 90% acetic acid reaction mixture, however, 0.26–0.27 mole equiv. of 2,5-dianisylfuran (Ib) was recovered from the 1 mole equiv. of ozone experiments (expt. 2, Table I) indicating that 0.26–0.27 mole equiv. of Vb and/or peroxidic precursors of VIb reacted further with ozone. Thus, the extent to which the 1,2-bond-cleavage reaction occurred, based on the amount of Ib reacting, must be at least 32% (if only precursors of VIb reacted further) and at most 68% (if only Vb reacted further.) We suggest in Table II a value of 40–45%, since Vb with two carbonyl groups attached to the double bond probably is somewhat less reactive toward ozone than are precursors of VIb. This means that 2,5-dianisylfuran (Ib) undergoes the 1,2-bond-cleavage reaction in both solvents to a greater extent than does 2,5-diphenylfuran (Ia). This is to be expected since the anisyl groups of Ib should increase the stability and ease of formation of the complex (IIb or IVb, in comparison to IIa or IVa). At least the data shows a definite solvent effect with Ib as well as with Ia.

A 61% yield of anisic acid (VIIIb) was obtained from ozonation of Ib in 90% acetic acid solvent with 1 mole equiv. of ozone (expt. 2, Table I). This, presumably, resulted both from hydrolysis and further ozonation of peroxidic precursors of VIb. Ozonation of Ib in methylene chloride with 1 mole equiv. ozone also gave a good yield of anisic acid (expt. 1, Table I). When 2 mole equiv. of ozone was employed, both anisic acid (VIIIb) and anisic anhydride (VIIb) were obtained.

From ozonations of 2,5-dimesitylfuran (Ic) with 1 mole equiv. of ozone in both methylene chloride and 90% acetic acid, unchanged starting material was recovered (Table I, expt. 3 and 4, 25% from methylene chloride and 12% from 90% acetic acid), and the molecular oxygen yields were considerably higher than the 1,2-dimesitoylethylene (Vc) yields. It is noteworthy that from the methylene chloride reaction mixture (expt. 3, Table I) mole equivalents of Ic recovered and of molecular oxygen evolved are equal (0.25–0.27), but only a trace of 1,2-dimesitoylethylene (Vc) was found in the reaction mixture. The most likely ex-

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[1] H. M. White, H. O. Colomb, Jr., and P. S. Bailey, *J. Org. Chem.*, **30**, 481 (1965).

TABLE I

OZONATIONS OF 2,5-DIANISYLFURAN (Ib) AND 2,5-DIMESITYLFURAN (Ic) WITH 1 MOLE EQUIV. OF OZONE[a]

Expt.	Furan	Solvent	Temp., °C.	Furan recovered, mole equiv.[c]	O₂ evolved		Yield of V[b]		Yield of VIII, %[d]
					Mole equiv.[c]	%[d]	Mole equiv.[c]	%[d]	
1	Ib	CH_2Cl_2	0	0	0.12	12	0.15	15	64
2	Ib	HOAc–HOH[e] (9:1)	25	0.26–0.27	0.26–0.30	35–41	0.24–0.23	32	61
3	Ic	CH_2Cl_2[e]	0	0.25	0.27	36	Trace		20
4	Ic	HOAc–HOH (9:1)	25	0.12	0.19	22	0.15	17	81

[a] One mole of ozone, from ozone–nitrogen mixtures, was employed per mole of starting furan (Ic or Ib). See Experimental for ozonation and work-up procedures. [b] Isolated as *cis* isomer except in expt. 1. [c] Expressed in mole/mole of starting furan. [d] Expressed in % yield based on an expected 1 mole/mole of furan reacting. [e] Results of two experiments.

TABLE II

COMPARISON OF PERCENTAGES OF 1,2-BOND CLEAVAGE DURING OZONATION OF ARYLFURANS

Furan	CH_2Cl_2 at 0°[a]	HOAc-HOH (9:1) at 25°[a]
2,5-Diphenylfuran (Ia)	10[b]	30–33[b]
2,5-Dianisylfuran (Ib)	15	40–45[c]
2,5-Dimesitylfuran (Ic)	35[c]	31–35[c]
3,4-Diphenylfuran (Id)	18–44[c]	40–68[c,d]
2,3,4,5-Tetraphenylfuran (Ie)	35[e]	

[a] Solvent and temperature employed in ozonations. [b] See ref. 1. [c] Estimated value, see discussion. [d] Temperature was 0° rather than 25°. [e] See ref. 3. Solvent was carbon tetrachloride.

planation of this is that about 0.25 mole equiv. of dimesitoylethylene (Vc) was produced (along with an equivalent amount of molecular oxygen) and reacted with ozone as fast as it was produced. The principal alternative to this (that essentially no Vc was produced and that the 0.25–0.27 mole equiv. of molecular oxygen yield resulted from the reaction of an equivalent amount of precursors of VIc with ozone) appears to be eliminated by the fact that complete ozonations of both Ia[1] and Ic showed that not enough molecular oxygen comes from ozonation of precursors of VI to account for the facts; it was also shown that no molecular oxygen comes from ozonation of Vc. It is not unreasonable that Vc should react with ozone as fast as it is produced, since the double bond of Vc is not so hindered by the mesityl groups as are the double bonds of the starting furan (Ic) and the precursors of VIc. Thus, it appears that the extent of the 1,2-bond-cleavage reaction during ozonation of 2,5-dimesitylfuran in methylene chloride is about 35% based on the amount of Ic reacting, as shown in Table II. This is considerably greater than the amount of 1,2-bond cleavage of Ia during ozonation in methylene chloride,[1] but is reasonable on the basis of the proposed mechanism, since the mesityl groups of Ic, like the anisyl groups of Ib, should activate the furan ring for electrophilic ozone attack. Although the mesityl group should sterically hinder to some extent the formation of the sp^2-transition state leading to IIIc,[2] the formation of σ-complex IIc should not be greatly hindered. In agreement with this reasoning is the report of Lutz and co-workers[3] that ozonation of 2,3,4,5-tetraphenylfuran (Ie) in carbon tetrachloride gave a 35% yield of *cis*-dibenzoylstilbene (Ve), Table II. Here, again, hindrance of the 2,3-bond of Ic is considerably increased over that of Ia, whereas no change has occurred at C-2. Thus, the per cent of IIIe produced from Ie should be less than that of IIIa from Ia, and the yield of Ve should be correspondingly greater than that of Va.

Ozonation of 2,5-dimesitylfuran (Ic) with 1 mole equiv. of ozone in 90% acetic acid gave a 22% yield of molecular oxygen and a 17% yield of 1,2-dimesitoylethylene (Vc) (expt. 4, Table I). A 12% recovery of starting material (Ic) was made. If the 12% of initial ozonation products which reacted further with ozone consisted entirely of 1,2-dimesitoylethylene (Vc), as apparently was the case in methylene chloride solvent (expt. 3), the actual yield of Vc (and the per cent of Ic undergoing 1,2-bond cleavage) would be about 31%. A yield of about 33% can be deduced from the molecular oxygen yield (expt. 4) which, by comparison to the analogous experiment with 2,5-diphenylfuran (Ia),[1] should be approximately two-thirds the yield of Vc. Thus, in Table II, we estimate 31–35% 1,2-bond cleavage with 2,5-dimesitylfuran (Ic) in 90% acetic acid solution, and it appears that, within experimental error, there is no solvent effect with Ic. This, perhaps, indicates that there is some resistance to the formation of structures such as IV when mesityl groups are in α-positions of the furan ring, but not to the formation and decomposition of II. It is interesting and perhaps mechanistically significant that oxidation of Ic to Vc does not occur with the usually characteristic nitric acid–acetic acid reagent,[4,5] but readily occurs with hydrogen peroxide[6] and, apparently, also with ozone. Lutz and Dien[6] report that hydrogen peroxide oxidation of 2,5-dimesitylfuran (Ic) and other dimesitylfurans gave the highest yields of diaroylethylene (67% Vc from Ic) of any of the furans tried. This, by analogy, further supports our interpretation of the data from ozonation of 2,5-dimesitylfuran (Ic).

"Bond-attack" products isolated from 1 mole equiv. ozonations of 2,5-dimesitylfuran (Ic) in 90% acetic acid solution were a small amount of β-mesitoyloxy-2,4,6-trimethylcinnamaldehyde (VIc), which probably came from loss of hydrogen peroxide from Xc, and 81–106% yields of mesitoic acid (VIIIc). Since the combined Vc and mesitoic acid (VIIIc) yields from a 1 mole equiv. ozonation of Id should not exceed 100%, some mesitoic acid must have arisen from further ozonation of VIc (or precursors such as Xc) and/or a peroxide-catalyzed autoxidation of XIc, analogous to that proposed earlier in the case of 2,5-diphenylfuran (Ia).[1]

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(2) P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Am. Chem. Soc.*, **82**, 6136 (1960).

(3) (a) R. E. Lutz, W. J. Welstead, Jr., R. G. Bass, and J. I. Dale, *J. Org. Chem.*, **27**, 1111 (1962). (b) W. J. Welstead, Jr., Ph.D. Dissertation, The University of Virginia, 1962; *Dissertation Abstr.*, **23**, 2709 (1963).

(4) R. E. Lutz and F. N. Wilder, *J. Am. Chem. Soc.*, **56**, 978 (1934).

(5) R. E. Lutz and W. P. Boyer, *ibid.*, **63**, 3189 (1941).

(6) R. E. Lutz and C. K. Dien, *J. Org. Chem.*, **23**, 1861 (1958).

TABLE III

OZONATION OF 3,4-DIPHENYLFURAN(Id) WITH 2 MOLE EQUIV. OF OZONE[a]

Expt.	Solvent	Temp., °C.	Work-up[a]	Benzil (IXe), % yield	Benzoic acid (VIIIa), % yield[b]	Phenylglyoxal (IXa), % yield[b]
5	HOAc-HOH (9:1)	0	Decompn.	25	26	11
6	HOAc-HOH (9:1)	0	Redn.	32	*c*	40
7	CH_2Cl_2	0	Redn.	56	21	18

[a] See Experimental for details. [b] Based on 1 mole of Id reacting to give 2 moles of VIIIa and 2 moles of IXa. [c] Not determined.

The results of ozonation of 3,4-diphenylfuran (Id) were very difficult to interpret. Yields of identifiable products from 1 mole equiv. ozonations were too low to be of value. The results obtained using approximately 2 mole equiv. of ozone are shown in Table III. The benzoic acid (VIIIa) and phenylglyoxal (IXa) yields are based on a maximum of 2 mole equiv. of each from ozonation of Ie. Since, however, benzoic acid could have arisen from several sources, it is uncertain whether the theoretical yield should be 1 or 2 mole equiv., or something in between. For example, whereas reduction of peroxidic equivalents of zwitterion XII (from ozonolysis of VId) would give rise to benzil (IXe), rearrangement of such a peroxide would result in benzoic anhydride or 2 mole equiv. of benzoic acid,[2,7] and, whereas reduction of peroxidic ozonolysis products of Vd should yield 2 mole equiv. of phenylglyoxal (IXa), rearrangement should lead to 1 mole equiv. each of benzoic acid (VIIIa) and phenylglyoxal (IXa). Thus, the theoretical yield of phenylglyoxal also could be 1 or 2 mole equiv. or something in between. The fact that the benzil (IXe) yields in expt. 5 and 6 (Table III) are very little different whether a decomposition or a reductive work-up was used might indicate that the benzoic acid (VIIIb) came from ozonolysis of Vd and that the benzil yield represents the entire extent of 2,3-bond cleavage. It seems safer, however to call this the minimum extent of 2,3-bond cleavage and to express the extent of 1,2-bond cleavage as a maximum equal to 100% − %IXe and a minimum equal to the per cent yield of phenylglyoxal (IXa) based on an expected 2 mole equiv. from reduction experiments. This is done in Table II, which is shown on p. 488.

As shown in Table II, the minimum yields of 1,2-bond-cleavage products from ozonation of 3,4-diphenylfuran (Id) in both solvents studied are considerably higher than the yields of 1,2-bond-cleavage products from ozonation of 2,5-diphenylfuran (Ia) in the same solvents, and the maximum yields of these products are higher than those from any of the other furans studied. Ozonation of 3,4-diphenylfuran (Id) should result in relatively high 1,2-bond-cleavage product yields on the basis of the proposed theory, since there are no appreciable differences in the steric hindrance of the double bonds of Ia, Ib, and Id, but there is much less hindrance to attack by ozone at the α-position of the furan ring of Id than with any of the other furans. Thus, there should be an increased tendency with Id, in comparison with Ia at least, to give II rather than III.

As a side line in this research the synthesis and certain reactions or 2,5-dianisylfuran (Ib) were briefly studied, since the compound has not been previously reported in the literature.[8] Attempted synthesis by cyclization of 1,2-dianisoylethane with acetic anhydride and sulfuric acid gave, apparently, a sulfonated derivative of Ib, which could be hydrolyzed easily to Ib. Nitration of Ib also occurred under unusually mild conditions. Treatment of Ib with acetic acid–nitric acid at 0°, the conditions which afford 1,2-dibenzoylethylene (Va) from Ia,[4] gave a 51% yield of 3,4-dinitro-2,5-dianisylfuran. Bromination also occurred readily, to give a 72% yield of 3,4-dibromo-2,5-dianisylfuran.

Another side line of this research was the synthesis of substituted mandelic acids in high yield by ozonations of 1,2-diaroylethylenes, followed by reductive work-up.

Experimental

The ozonation setup and procedures are described in earlier publications.[7,9] Solvents were pure and anhydrous, unless otherwise stated. **2,5-Dimesitylfuran** (Ic) was prepared by the previously reported procedure,[10] and melted sharply at 82°.

3,4-Diphenylfuran (Id) was prepared by the method of Backer and Stevens,[11] except that the mixture of 3,4-diphenylfuran-2,5-dicarboxylic acid and 3,4-diphenylfuran-2-carboxylic acid (4 g.) was decarboxylated in quinoline (20 g.) at 160–220° in the presence of 0.5 g. of copper powder. After the evolution of carbon dioxide had ceased, the mixture was cooled and poured into dilute hydrochloric acid; the 3,4-diphenylfuran was filtered from the mixture and recrystallized from ethanol-water (m.p. 110–112°).

2,5-Dianisylfuran (Ib).—About 1 g. of polyphosphoric acid was added to a stirred mixture of 10 g. of 1,2-dianisoylethane[12] in 100 ml. of acetic anhydride, and stirring was continued at room temperature for about 20 min. The resulting solution was poured into ice-water with stirring, and, after at least 2 hr., the crude Ib was removed by filtration and recrystallized from 95% ethanol: m.p. 195–196°; yields, 90–95%. The infrared spectrum (KBr) showed neither hydroxyl nor carbonyl bands.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.8; mol. wt., 280. Found: C, 77.5; H, 5.8; mol. wt. (Rast), 281.

An attempt to cyclize 1,2-dianisoylethane to Ib using concentrated sulfuric acid rather than polyphosphoric acid gave, apparently, a sulfonated derivative of Ib, which was converted to Ib by hydrolysis (boiling 6 *N* hydrochloric acid, 20 min.) in 90% yield, m.p. 193–196°, no depression in mixture melting point with authentic sample.

3,4-Dibromo-2,5-dianisylfuran[8] was obtained by adding about 0.6 g. of bromine in 20 ml. of carbon tetrachloride to a solution of 0.5 g. of Ic in 10 ml. of carbon tetrachloride. A green precipitate formed, but redissolved with evolution of hydrogen bromide. Evaporation of the solution and recrystallization of the residue from 95% ethanol gave a 70% yield of the dibromofuran melting at 138–139°.

Anal. Calcd. for $C_{18}H_{14}Br_2O_3$: C, 49.3; H, 3.2; Br, 36.5. Found: C, 49.8; H, 3.4; Br, 35.9.

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(7) (a) P. S. Bailey and S. S. Bath, *J. Am. Chem. Soc.*, **79**, 3120 (1957); (b) P. S. Bailey and Y. G. Chang, *J. Org. Chem.*, **27**, 1192 (1962).

(8) Both Ib and its 3,4-dibromo derivative have been synthesized in the laboratory of Professor R. E. Lutz, however: J. D. Hutcheson, M.S. Thesis, The University of Virginia, 1935.

(9) (a) P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, *J. Org. Chem.*, **29**, 1400 (1964); (b) P. S. Bailey and A. M. Reader, *Chem. Ind.* (London), 1063 (1961).

(10) R. E. Lutz, E. C. Johnson, and J. L. Wood, *J. Am. Chem., Soc.*, **60**, 716 (1938).

(11) H. J. Backer and W. Stevens, *Rec. trav. chim.*, **59**, 423 (1940).

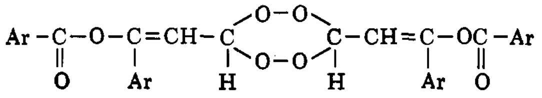
(12) Prepared by method of E. E. Campaigne and W. O. Foye, *J. Org. Chem.*, **17**, 1405 (1952).

3,4-Dinitro-2,5-dianisylfuran.—To a mixture of 1 g. of Ic in 75 ml. of glacial acetic acid, cooled to 0°, was added a solution of 9 ml. of glacial acetic acid and 3 ml. of nitric acid. After 5 min. the solution was poured into water and the resulting mixture was cooled overnight in the freezer. Filtration gave 0.65 g. (50% yield) of the dinitrofuran melting at 172–176°; recrystallized from 95% ethanol, m.p. 175–176°.

Anal. Calcd. for $C_{18}H_{14}N_2O_7$: C, 58.4; H, 3.8; N, 7.6. Found: C, 58.2; H, 3.9; N, 7.7.

Oxidation of the dinitrofuran with alkaline permanganate gave a 41% yield of anisic acid (m.p. and m.m.p., with a known sample, 184–185°) showing that nitration had occurred in the furan ring rather than the benzene ring.

Ozonation of 2,5-Dianisylfuran (Ib) with 1 Mole Equiv. of Ozone. A. In Methylene Chloride.—The ozonation was carried out at 0° with ozone–nitrogen[9b] as described for 2,5-diphenylfuran.[1] Absorption of 1 mole equiv. of ozone was quantitative. The molecular oxygen yield was 0.12 mole equiv. or 12% (since no unchanged Ib was found). Work-up was essentially by procedure A, as described for 2,5-diphenylfuran.[1] After evaporation of the reaction mixture, the residue was dissolved in glacial acetic acid, water was added to turbidity, and the resulting mixture was cooled in the refrigerator for 2 days. Filtration gave a 3% yield (as much as 10% in some cases) of a material which appeared to be crude β-anisoyloxy-*p*-methoxycinnamaldehyde peroxide (XIII), melting at 130–135°; recrystallization of the material several times from 95% ethanol raised its melting point to 136–137° dec. Satisfactory analytical data could not be obtained for this peroxide owing to facile decomposition. However, the infrared spectrum was similar to that of the corresponding compound from 2,5-diphenylfuran (Ia),[1] with a vinyl ester carbonyl band at 5.8, a carbon–carbon double bond band at 6.1, and peroxy bands at 9.3–9.4 μ.



XIII

Ar = *p*-anisyl

The filtrate from which XIII was obtained was reduced and the rest of the work-up procedure was as described for procedure B with 2,5-diphenylfuran.[1] The yield of *trans*-1,2-dianisoylethylene (Vb) was 15% (m.p. 167°) and the yield of anisic acid (VIIIb) was 64% (m.p. 182–184°). Identifications were by comparison of infrared spectra and by mixture melting points with authentic samples. The *trans* isomer of Vb was obtained because the iodide reduction mixture was allowed to stand for several hours.[1]

B. In 90% Acetic Acid.—The ozonation was carried out with 10 mmoles of Ib (suspended in 100 ml. of 90% acetic acid) and 10 mmoles of ozone from ozone–nitrogen[9b] at 25°, as described for 2,5-diphenylfuran (Ia).[1] Absorption was quantitative and 2.6 mmoles of molecular oxygen was evolved (in another experiment 3.0 mmoles of oxygen was evolved). Not all of the starting material went into solution during the ozonation. The reaction mixture was diluted with 25 ml. of water, cooled for 1 hr., and filtered, giving 2.6 mmoles of unchanged starting material (2.7 mmoles from another experiment). The filtrate was further diluted with water (50 ml.) and cooled in the refrigerator for 2 days. Filtration gave 3.1 mmoles of crude *cis*-1,2-dianisoylethylene (Vb) melting at 109–112°. Recrystallization from 95% ethanol (by addition of water to turbidity and cooling) gave 2.4 mmoles (2.3 mmoles from another experiment) of Vb melting at 118–119°. The infrared spectrum was identical with that of an authentic sample prepared by the method of Buchta and Schaeffer.[13] The rest of the work-up was as described in procedure B for 2,5-diphenylfuran.[1] The anisic acid yield, based on the amount of Ib reacting, was 61% (m.p. 182–184°, identification by the mixture melting point method and comparison of infrared spectra).

Ozonation of 2,5-Dianisylfuran (Ib) with 2 Mole Equiv. of Ozone.—The ozonation was carried out as usual in methylene chloride solution at 0°. Two mole equivalents of ozone were absorbed. The work-up was by procedure D, as described for 2,5-diphenylfuran.[1] The sodium bicarbonate extract gave a 59% yield of anisic acid (VIIIb), m.p. 184–186°, and the neutral ether layer gave a 42% yield of anisic anhydride (VIIb), m.p. 94–97°,[14] identified by a 98% conversion to anisic acid, m.p. 184–185°. Anisic acid identifications were by the mixture melting point method.

Ozonation of 2,5-Dimesitylfuran (Ic) with 1 Mole Equiv. of Ozone. A. In 90% Acetic Acid Solution.—The ozonation was carried out with ozone–nitrogen at 25°, using 10 mmoles of Ic in 160 ml. of solvent. Absorption of 10 mmoles of ozone was quantitative. The molecular oxygen yield was 1.9 mmoles. The work-up procedure was essentially the same as procedure B as described for 2,5-diphenylfuran.[1] First was obtained 0.71 g. of material melting at 55–70°. Recrystallization from ethanol–water gave 1.2 mmoles of essentially pure starting material Ic (infrared spectrum). The remainder of the 0.71 g. of material was shown to be largely **β-mesitoyloxy-2,4,6-trimethylcinnamaldehyde (VIc)**. Evaporation of the filtrate from which Ic was obtained and recrystallization of the residue from ether–benzene gave VIc melting at 92–94° (*ca.* 1 mmole, or 11% yield based on amount of Ic reacting). Further recrystallization raised the melting point to 98–99°. The infrared spectrum was consistent with the assigned structure (VIc): a band at 5.7 typical of an enol ester carbonyl group, a band at 6.03 typical of an α,β-unsaturated aldehyde carbonyl group, and a band for aldehydic hydrogen at 3.66 μ.

Anal. Calcd. for $C_{22}H_{24}O_3$: C, 78.5; H, 7.2. Found: C, 78.4; H, 7.4.

The n.m.r. spectrum contains single peaks at τ 7.82 (p-CH_3) and 7.73 (o-CH_3), a doublet centered on 3.53 with J = 12 c.p.s. (vinyl proton), a doublet centered on 2.02 with J = 12 c.p.s. (aldehydic proton), and a single peak at 3.2 (aromatic proton). The relative areas are 6, 12, 1, 1, and 4, respectively.

Further dilution with water and cooling of the filtrate from which the 0.71 g. mixture of Ic and VIc was obtained gave, in three fractions, 0.5 g. of crude *cis*-1,2-dimesitoylethylene (Vc) melting at 105–112°; recrystallization from 95% ethanol gave 1.5 mmoles (or 17% yield based on amount of Ic reacting) of Vc melting at 117–119°.[15] The identity of Vc was further verified by zinc–acetic acid reduction to 1,2-dimesitoylethane, the infrared spectrum of which was identical with that of an authentic sample.[15]

After sodium iodide reduction, an 81% yield (based on amount of Ic reacting) of mesitoic acid (VIIIc) was obtained (m.p. 146–148°, infrared spectrum identical with that of authentic sample). In another experiment, where some heating of the reaction mixture occurred, the yield of VIIIc was 106%, based on an expected 1 mole equiv.

B. In Methylene Chloride.—The ozonation was carried out at 0° with 10 mmoles of Id and 10 mmoles of ozone (nitrogen carrier[9b]) as usual; ozone absorption was quantitative. The molecular oxygen yield[9] was 2.7 mmoles. The reaction mixture was evaporated and the residue was dissolved in about 120 ml. of acetic acid. The solution was diluted with water to turbidity and worked up as described in the preceding experiment. The recovery of Ic was 2.5 mmoles, m.p. 78–80°; the infrared spectrum showed it to be nearly pure Ic containing a trace of Vc. No further Ic or Vc was obtained.

After sodium iodide reduction, a 20% yield of mesitoic acid (VIIIc) was obtained; identification was by infrared spectrum.

Ozonation of 2,5-Dimesitylfuran (Ic) with 2 Mole Equiv. of Ozone.—The ozonation was carried out in methylene chloride at 0° with ozone–nitrogen.[9b] Excess ozone was passed through the reaction mixture and 2.5 mole equiv. reacted. The molecular oxygen yield was 7.1 mmoles from 10 mmoles of Ic reacting. The reaction mixture was worked up as in procedure A for 2,5-diphenylfuran.[1] The sodium bicarbonate extract yielded mesitoic acid melting at 147–150° (identification by infrared spectrum, about 28% yield based on an expected 2 mole equiv.). The neutral layer appeared to be mesitoic anhydride (about 70% yield); the infrared spectrum showed characteristic anhydride carbonyl bands at 5.60 and 5.72 and a carbon–oxygen–carbon band at 9.5 μ.

Ozonation of 3,4-Diphenylfuran (Id) with 2 Mole Equiv. of Ozone. A. In 90% Acetic Acid. Alkaline Decomposition.—The ozonation was carried out at 0° with ozone–oxygen as described for 2,5-diphenylfuran.[1] Two mole equivalents of ozone reacted. The reaction mixture was made alkaline with potassium

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(13) E. Buchta and G. Schaeffer, *Ann.*, **597**, 129 (1955).

(14) E. Berliner and L. H. Altschul [*J. Am. Chem. Soc.*, **74**, 4110 (1952)] reported 98–99°.

(15) J. B. Conant and R. E. Lutz [*ibid.*, **45**, 1303 (1923)] reported 120°.

carbonate, during which time it lost its active oxygen content. The alkaline solution was continuously extracted with ether for 36 hr. (extract A). The alkaline layer was acidified with hydrochloric acid and extracted with three 50-ml. portions of ether (extract B). From dried extract B was obtained a 26% yield (based on an expected 2 mole equiv.) of benzoic acid (VIIIa) melting at 120–121°. Ether extract A was dried and evaporated, giving 1.53 g. of an oil (from 10 mmoles of Id), which was dissolved in 20 ml. of benzene and chromatographed over an alumina column (25 × 75 mm.). Elution with petroleum ether gave nothing. Elution with nine 100-ml. portions of a 1:1 petroleum ether-benzene solution, two 100-ml. portions of benzene, and two 100-ml. portions of a 1:1 benzene–chloroform solution gave 0.42 g. of benzil melting at 88–91°. Elution with two 100-ml. portions of 1:1 benzene–chloroform gave a mixture of benzil and phenylglyoxal from which was extracted the phenylglyoxal with strong base, in the form of mandelic acid[2] (0.07 g.), leaving 0.11 g. of benzil melting at 88–91°. Elution with 400 ml. of chloroform gave 0.23 g. of phenylglyoxal, identified as its dinitrophenylhydrazone, m.p. 295–298°. All identifications were by mixture melting points with authentic samples. The yield of benzil (IXe) was 25% and the yield of phenylglyoxal (IXa) was 11%.

B. **In 90% Acetic Acid. Sodium Iodide Reduction.**—The ozonation was carried out as in the preceding experiment, after which the reaction mixture was poured into the sodium iodide solution. The released iodine was reduced with thiosulfate. Filtration of the resulting mixture gave a 32% yield of benzil (IXe) melting at 95–96°. Treatment of the filtrate with 2,4-dinitrophenylhydrazine gave the crude dinitrophenylhydrazone of phenylglyoxal (IXa) which, after recrystallization from ethyl acetate, melted at 293–297° (40% yield, based on an expected 2 mole equiv.) Identifications were by the mixture melting point method. In a similar experiment a 44% yield of phenylglyoxal (IXa) was obtained by pouring the entire ozonation mixture into 2,4-dinitrophenylhydrazine reagent.

C. **In Methylene Chloride Solution.**—The ozonation was carried out at 0° in methylene chloride with 2 mole equiv. of ozone from ozone–oxygen in the usual manner. Work-up started out as in procedure D for 2,5-diphenylfuran.[1] After the sodium carbonate extraction a sodium hydroxide extraction was made. From the ether solution after the carbonate and hydroxide extractions was obtained benzil (IXe) in 56% crude yield, m.p. 75–86°; recrystallized from ethanol, m.p. 95–96°, 70% recovery. From the carbonate extract, after acidification, extraction with ether, and evaporation of the ether extract, was obtained a 21% yield of benzoic acid (VIIIa), m.p. 119–121°. Similarly, the hydroxide extract gave a 14% yield of *dl*-mandelic acid (from phenylglyoxal, IXa[2]) melting at 116–118°. Another 4% yield of phenylglyoxal (IXa) was obtained in the form of the dinitrophenylhydrazone after treating the extracted reaction mixture with 2,4-dinitrophenylhydrazine; it had m.p. 297–298°. All identifications were by mixture melting points with authentic samples.

Ozonation of 1,2-Diaroylethylenes. A. To Give the Respective Mandelic Acids.—The diaroylethylenes ozonized were *trans*-1,2-di(*p*-bromobenzoyl)ethylene,[16] *trans*-1,2-dianisoylethylene,[12] and *trans*-1,2-dimesitoylethylene.[15] A solution of 10 mmole of the diaroylethylene in 100 ml. of either 1:1 methylene chloride–methanol or 5:1 methylene chloride–90% acetic acid was treated with 10 mmoles of ozone at 0°. Ozone absorption was quantitative, except with the bromobenzoylethylene. The reaction mixture was worked up according to procedure D for 2,5-diphenylfuran.[1] Both a sodium carbonate and a sodium hydroxide extraction were made. From the carbonate layer by the usual procedure was obtained the corresponding substituted benzoic acid, and, from the sodium hydroxide layer, the corresponding substituted mandelic acid.[2] From the *trans*-di(bromobenzoyl)ethylene was obtained a 53% recovery of starting material and 8.2 mmoles of *p*-bromomandelic acid (m.p. 118–120)[17]; *p*-bromobenzoic acid was not determined. From the *trans*-dianisoylethylene was obtained 3.5 mmoles of anisic acid (m.p. 177–182°) and 1.39 mmoles of *p*-methoxymandelic acid (m.p. 107–108°).[18] From the *trans*-dimesitoylethylene was obtained 6.3 mmoles of mesitoic acid (m.p. 148–154°) and 1.35 mmoles of 2,4,6-trimethylmandelic acid (m.p. 155–157°[19]; m.m.p., with mesitoic acid, 122–127°).

B. ***cis*-1,2-Dimesitoylethylene (VIId)**[15] (1 mmole) in 25 ml. of methylene chloride was ozonized at 0° with 1 mmole of ozone from ozone–nitrogen.[9b] Ozone absorption was quantitative, and only a trace of molecular oxygen was evolved.

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(16) Prepared by the method of J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, **47**, 881 (1925)] with m.p. 193–194°.

(17) J. L. Riebsomer, R. Baldwin, J. Buchanan, and H. Burkett, *ibid.*, **60**, 2974 (1938).

(18) K. Kindler, W. Metzendorf, and D-y-Kwok, *Ber.*, **76**, 308 (1943).

(19) R. C. Fuson, W. S. Emerson, and H. W. Gray, *J. Am. Chem. Soc.*, **61**, 480 (1939).

The Reactions of -Aminoalkyl Hydrogen Sulfates. I. The Preparation of Some Substituted Thiazolidine-2-thiones[1]

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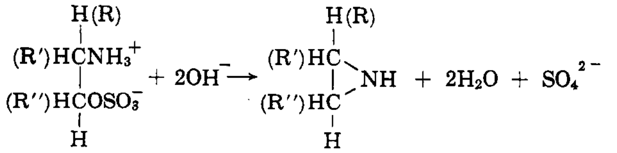
Sodium 2-aminoethyl sulfate reacts with potassium ethyl xanthate to give thiazolidine-2-thione in good yield. This reaction has been used to prepare aryl- and alkyl-substituted thiazolidinethiones from suitably substituted derivatives of 2-aminoethyl hydrogen sulfate. The preparation of the aminoalkyl hydrogen sulfates is described.

The reaction of β-aminoalkyl hydrogen sulfates (I) with strong bases is a convenient method for the preparation of aziridines (II). However, little study has been made of other reactions of these bifunctional compounds. Unlike the β-aminoalkyl halides, the aminoalkylsulfate salts are fairly stable in aqueous alkaline solution at room temperature. They are slowly converted to aziridines only at elevated temperatures.



$$\begin{array}{c} \mathrm{H(R)} \\ | \\ \mathrm{(R')HCNH_3^+} \\ | \\ \mathrm{(R'')HCOSO_3^-} \\ | \\ \mathrm{H} \\ \mathrm{I} \end{array} + 2OH^- \longrightarrow \begin{array}{c} \mathrm{H(R)} \\ | \\ \mathrm{(R')HC} \\ | \\ \mathrm{(R'')HC} \\ | \\ \mathrm{H} \\ \mathrm{II} \end{array}\!\!\!\!\!>\mathrm{NH} + 2H_2O + SO_4^{2-}$$

For example, the half-life of sodium 2-aminoethyl sulfate in alkaline solution at 75° is about 24 hr.,[1] while under the same conditions the half-life of 2-aminoethyl bromide is about 5 sec.[3] In acidic solution,

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(1) From The Ph.D. Thesis of R. A. Bafford, University of Maryland, June 1960.

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(3) Estimated from the data of H. Freundlich and Kroepelin [*Z. Physik Chem.* (Leipzig), **122**, 139 (1926)].