n-butyllithium (2.00 mmol). The resulting homogeneous solution was stirred for 30 min at −78 °C, and then *trans*-2-hexenal (0.26 mL, 2.20 mmol) was added. After being stirred for 3 h at −78 °C, the reaction mixture was treated with 5 mL of NH_4Cl-saturated aqueous solution. The organic layer was analyzed by GLC on a 20% Silicone DC 550 on Celite 545 column, using tetralin as an internal standard.

Conjugate Reduction of Cyclohexenone by $LiAlH_4$–Mesitylcopper(I) (1). To a suspension of $LiAlH_4$ (0.0378 g, 0.996 mmol) in 3 mL of THF at −78 °C was added 1 (0.0182 g, 0.0996 mmol) dissolved in a mixed solvent of 1 mL of THF and 1 mL of HMPA. The resulting reaction mixture was stirred for 30 min at −78 °C, and cyclohexenone (0.11 mL, 1.10 mmol) was added. After being stirred for 3 h at −78 °C, the reaction mixture was treated with 3 mL of NH_4Cl-saturated aqueous solution. The organic layer was analyzed by GLC on a 20% Silicone DC 550 on Celite 545 column and on a 20% PEG 20M on Celite 545 column, using tetralin as an internal standard.

Registry No. 1, 75732-01-3; butyllithium, 109-72-8; *sec*-butyllithium, 598-30-1; *tert*-butyllithium, 594-19-4; mesitylmagnesium bromide, 2633-66-1; mesitylene, 108-67-8; copper(I) diethylamide, 71426-07-8; *trans*-2-hexenal, 6728-26-3; 2-cyclohexenone, 930-68-7; 3-propylheptanal, 75732-02-4; 6-decen-5-ol, 75732-03-5; 3-butylcyclohexanone, 39178-69-3; 3-*sec*-butylcyclohexanone, 37172-15-9; 3-*tert*-butylcyclohexanone, 936-99-2; 3-mesitylcyclohexanone, 75732-04-6; cyclohexanone, 108-94-1; cyclohexanol, 108-93-0; 2-cyclohexen-1-ol, 822-67-3; CuCl, 7758-89-6.

The First Spectral Confirmation for the Structures of Anhydro Dimers of *o*-Hydroxybenzaldehydes

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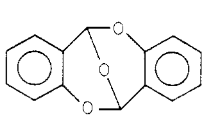
The anhydro dimers of *o*-hydroxybenzaldehydes have been known for over a century. The parent member of the series, "disalicylaldehyde", was first reported by Ettling[1] in 1845 and later by Cahours[2] in 1851 and by Perkin[3] in 1868. By now there are a dozen or more examples[4] of these anhydro dimers, which have been characterized by melting point, elemental analysis, and their tendency to revert to hydroxy aldehyde or a derivative thereof on acidolysis. It is assumed all possess the trioxabicyclo[3.3.1]nonane structure, by analogy with that originally proposed for



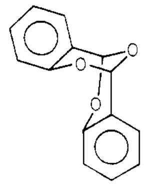
disalicylaldehyde in a publication by Adams, Fogler, and Kreger[5] in 1922. Yet to date there is apparently no information about their spectral properties. We have prepared four of the dimers 1–4 and report herein the results of measurement of their IR, UV, ^1H NMR, ^{13}C NMR, and mass spectra.

Table I. UV Spectral Data of Anhydro Dimers 1-4 ($CHCl_3$)

compd	λ (log ε), nm	UV of *o*-hydroxybenzaldehyde precursor
1	274.3 (3.51), 283.1 (3.44)	211.9 (4.12), 254.7 (3.96), 326.0 (3.49)
2	241.9 (3.86), 292.5 (3.64), 301.2 (3.62)	250 (3.6),[a] 290 (2.5), 342 (3.27)
3	239.6 (4.63), 266.4 (3.97), 277.5 (4.03), 290.2 (3.96), 315.5 (3.56), 330.5 (3.67)	225 (4.8),[b] 330 (3.9), 370 (3.7)
4	295.7 (4.29)	230 (3.92),[c] 258 (3.32), 310 (4.00)

[a] (EtOH) N. A. Valyashko and N. N. Valyashko, *Zh. Obsch. Khim.*, **18**, 1113 (1948). [b] (Isooctane) N. Melchior, *J. Am. Chem. Soc.*, **71**, 3647 (1949). [c] (EtOH) I. A. Kaye, R. S. Matthews, and A. A. Scala, *J. Chem. Soc.*, 2816 (1964).

The dimers, being head-to-tail bis acetals, have been prepared previously under a variety of conditions with dehydrating agents and acid catalysts. **1–3** were obtained by procedures already described; in the case of **4**, we were able to carry out the bimolecular acetalization of 5-nitrosalicylaldehyde under conditions[4b] which had not previously been successful. The anhydro dimer had been prepared earlier by nitration[6] of **1**. The fact that **4** has now been prepared by two independent routes serves to confirm its structure; in particular, it indicates the position of nitration in both rings to be para to the phenolic oxygen.



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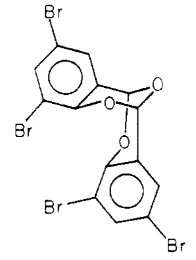

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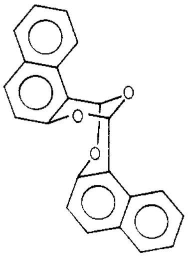

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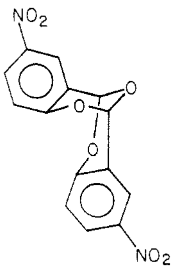

4

All of the spectral properties of **1–4** are consistent with the assigned structures. The IR spectra are devoid of OH and carbonyl stretching bands. The UV spectra of all four, collected in Table I, differ significantly from their precursors, the *o*-hydroxybenzaldehydes. A suitable model compound for **1** would be *o*-methoxybenzaldehyde acetal (**5**), which has apparently not been reported as a pure compound. It was shown by Melchior,[7] however, that the UV spectrum of *o*-methoxybenzaldehyde in acidified

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(1) Ettling, *Justus Liebigs Ann. Chem.*, **53**, 77 (1845).

(2) A. Cahours, *Justus Liebigs Ann. Chem.*, **78**, 225 (1851).

(3) W. H. Perkin, *Justus Liebigs Ann. Chem.*, **145**, 295 (1868).

(4) In addition to those specifically described in this paper, others have been reported in the following: (a) E. Rupp and M. Meyer, *Arch. Pharm.*, **253**, 379–383 (1915); (b) H. Fiedler, *ibid.*, **297**, 226 (1964); (c) E. Profft and W. Krause, *ibid.*, **298**, 148 (1965).

(5) R. Adams, M. F. Fogler, and C. W. Kreger, *J. Am. Chem. Soc.*, **44**, 1126 (1922).

(6) W. P. Bradley and F. B. Dains, *Am. Chem. J.*, **14**, 293 (1892).

(7) N. Melchior, *J. Am. Chem. Soc.*, **71**, 3651 (1949).

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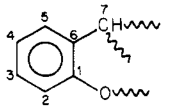
Table II. ^1H and ^{13}C NMR Spectral Data of Anhydro Dimers 1-4 ($CDCl_3$)

compd	^1H, δ	^{13}C (decoupled), δ
1	6.33 (s, 2), 6.73-7.43 (m, 8)	90.149, 116.587, 120.000, 121.463, 127.422, 130.890, 150.556
2	6.53 (s, 2),[a] 7.6 (d, 2), 7.8 (d, 2)	89.661, 111.657, 114.420, 121.951, 129.427, 137.391
3	6.73-8.20 (m)	88.903, 111.495, 117.508, 121.734, 124.864, 127.477, 128.614, 129.210, 130.890, 131.431, 149.201
4	6.5 (s, 2), 6.96-7.26 (m, 2), 8.1-8.26 (m, 4)	89.747, 118.036, 119.272, 124.019, 127.206, 142.489, 155.170

[a] In dioxane.

Table III. ^{13}C NMR Spectral Data (Coupled) of 1



carbon no.	ppm obsd	ppm calcd[a]	$^1J_{CH}$, Hz	$^3J_{CH}$, Hz
1	150.62	161		10.3
2	116.67	115	162.1	7.4
3	127.53	127	158.9	7.3
4	121.54	121	162.5	7.3
5	130.97	131	161.0	8.8
6	120.18[b]	124		
7	90.20		178.8	8.9 (8.9)

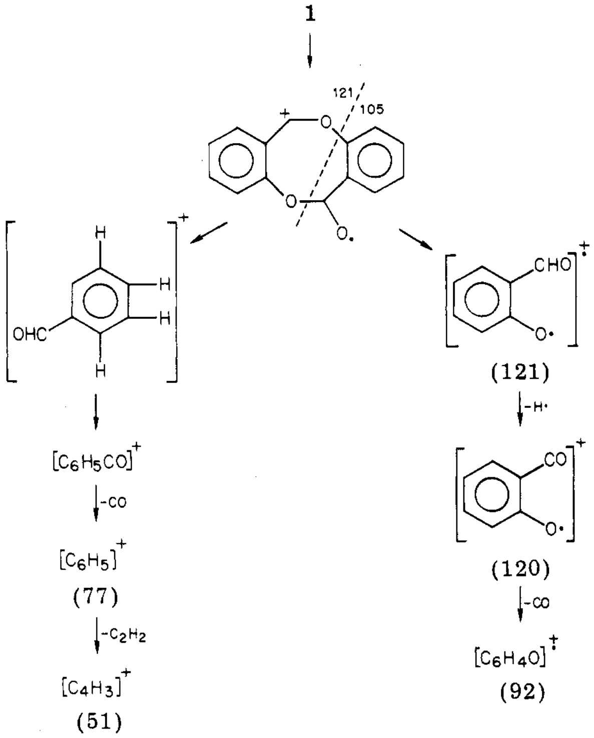
[a] F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra", Heyden, London, 1978, p 47. [b] Estimated.

methanol underwent a change, such that the 321-nm band disappeared and a new stronger band developed at 280–290 nm. (Measurements were conducted only down to 295 nm.) Presumably the aldehyde is being converted to **5**,[8] and the changes in UV absorption parallel the changes in going from salicylaldehyde to **1**.

Because the anhydro dimers have C_2 symmetry, their NMR spectra are expected to be relatively simple. ^1H and ^{13}C NMR data are collected in Table II. The proton spectra show the methinyl singlet and an aromatic multiplet, and all are devoid of a downfield aldehyde or exchangeable OH proton. The ^{13}C spectra are made up of the expected lines, except for the case of the dibromo dimer **2**, which shows only six of the seven resonances. Apparently, either two of the carbon resonances are virtually identical or else the relaxation for one is inordinately slow. Analysis of the coupled ^{13}C NMR spectrum for **1** is presented in Table III.

Finally, the mass spectra of all four compounds show parent ions at the masses calculated for dimeric structures (**1**, 226; **2**, 542; **3**, 326; **4**, 316). The clusters of Br isotopes show clearly in the mass spectrum of **2**. Unlike simple acetals, these compounds show strong parent ions because a single bond rupture does not constitute a fragmentation. A proposed fragmentation route for disalicylaldehyde **1** is outlined in Scheme I. It is clear that the mode of fragmentation is strongly dictated by the ring substituents, for the patterns in **2**–**4** are considerably more complex.

Scheme I



Experimental Section

Unless otherwise noted, spectral data were obtained as follows. IR spectra were recorded as KBr pellets with a Perkin-Elmer Model 337 grating instrument. UV spectra, as $CHCl_3$ solutions, were recorded on a Bausch and Lomb Spectronic 200. ^1H NMR spectra, determined as $CDCl_3$ solutions on a Varian EM-360A instrument, are reported in parts per million downfield from Me_4Si as internal standard. ^{13}C NMR spectra, determined in $CDCl_3$ and reported downfield from Me_4Si, were measured on a JEOL FX-90 Q spectrometer. Mass spectra were obtained with an Hitachi Perkin-Elmer Model RMU-6E instrument. C, H, and N analyses were determined on a Perkin-Elmer 240 B Analyzer. Melting points are uncorrected.

Preparation of Anhydro Dimers 1–3. Freshly distilled salicylaldehyde was dimerized according to the method described by Adams and co-workers[5] in 85% yield, mp 129–130 °C (ethanol) (lit.[5] mp 130 °C). 3,5-Dibromosalicylaldehyde[9] and 2-hydroxy-1-naphthaldehyde[10] were dimerized with $SOCl_2$[11] to give, respectively, **2** [73%; mp 242–243 °C (toluene) (lit.[11] mp 243 °C)] and **3** [50%; mp 242–244 °C (HOAc) (lit.[6] mp 241 °C)].

Preparation of Anhydro Dimer 4. To a solution of 1.7 g (0.01 mol) of 5-nitrosalicylaldehyde, 1.5 g (0.015 mol) of acetic anhydride, and 10 mL of toluene, cooled to 0 °C, was added 4 drops of 20% H_2SO_4. After stirring had been maintained for 24 h, 2 drops of 20% H_2SO_4 was added, whereupon a precipitate formed. This was collected and recrystallized twice from acetic acid, the crystals being washed with toluene: yield 0.3 g (19%); mp 238.5–239.5 °C (lit.[6] mp 220 °C).

Anal. Calcd for $C_{14}H_8N_2O_7$: C, 53.18; H, 2.55; N, 8.86. Found: C, 53.02; H, 2.52; N, 8.81.

Repetition of this procedure on twice the scale afforded a mixture of **4** and the triacetate, which was separated by preparative TLC on silica gel GF-254, with CH_2Cl_2 as eluent, **4** being the faster moving component, R_f 0.42. When the dimerization was attempted in acetic anhydride/concentrated H_2SO_4,[5] the

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(8) J. M. Bell, D. G. Kubler, P. Sartwell, and R. G. Zepp, *J. Org. Chem.* **30**, 4284–4292 (1965).

(9) C. M. Brewster, *J. Am. Chem. Soc.*, **46**, 2463 (1924).

(10) A. Russell and L. B. Lockhart, "Organic Syntheses", Collect. Vol. III, 1955, p 463.

(11) H. Lindemann and H. Forth, *Justus Liebigs Ann. Chem.*, **435**, 219 (1924).

triacetate was obtained in 87% yield, mp 116–117.5 °C (lit.[12] mp 110 °C).

Mass spectral data [m/z (relative intensity)] of 1–4 are as follows.

1: 227 (15), 226 (96), 225 (11), 196 (30), 181 (26), 121 (26), 120 (100), 92 (44), 77 (41), 51 (93), 42 (37).

2: 546 (12), 544 (42), 542 (64), 540 (36), 538 (11), 499 (6), 497 (10), 495 (7), 464 (9), 462 (24), 460 (25), 458 (11), 431 (5), 433 (15), 435 (14), 437 (7), 393 (4), 280 (82), 278 (100), 276 (88), 252 (6), 250 (10), 248 (6), 198 (8), 196 (9), 185 (18), 183 (19), 157 (9), 156 (19), 155 (17), 154 (19), 153 (11), 143 (11), 141 (11), 76 (11), 75 (64), 74 (34), 63 (21), 62 (14), 53 (10), 50 (8), 28 (9).

3: 327 (16), 326 (63), 298 (13), 297 (45), 280 (23), 279 (100), 243 (3), 170 (20), 169 (84), 153 (10), 152 (11), 151 (18), 146 (15), 141 (19), 128 (29), 127 (36), 126 (29), 115 (26), 114 (31), 78 (23), 76 (13).

4: 318 (5), 317 (11), 316 (57), 300 (8), 299 (27), 283 (5), 273 (19), 272 (5), 274 (24), 244 (11), 243 (24), 228 (8), 199 (14), 198 (8), 171 (19), 170 (100), 144 (19), 140 (30), 124 (14), 123 (11), 110 (32), 108 (14), 106 (12), 96 (16), 95 (19), 85 (30), 83 (34), 82 (65), 81 (49), 80 (16), 69 (27), 68 (22), 67 (43), 58 (19), 57 (14), 56 (38), 55 (65).

Acknowledgment. We are grateful to the National Science Foundation for a major instrument grant used to purchase the FX-90 spectrometer.

Registry No. 1, 252-72-2; 2, 75625-88-6; 3, 52243-98-8; 4, 75625-89-7.

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[12] C. Taege, *Chem. Ber.*, **20**, 2109 (1887).

An Improved Synthesis of Ketene Dimethyl Thioacetal Monoxide

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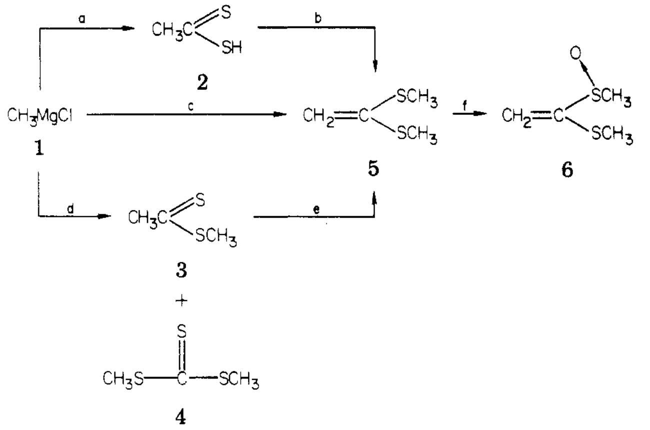
Ketene dimethyl thioacetal monoxide (**6**) has found varied use as a formylmethyl synthon[1] since it reacts as a Michael acceptor with a variety of enolate anions to yield, after hydrolysis of the intermediate adduct, 1,4-dicarbonyl compounds in which the carbonyl group derived from **6** is an aldehyde.

Our research required substantial quantities of **6** and we found the reported six-step route[1a] unsatisfactory because of cost in time and reagents. In view of Ziegler and Chan's recent synthesis of ketene thioacetals from dithioic acid dianions[2] we undertook an investigation of the synthesis of **6** by the related routes outlined in Scheme I.

We have found the most efficient preparation of the intermediate, ketene dimethyl thioacetal (**5**), to be a "one-pot" synthesis from methylmagnesium chloride. Thus, reaction of **1** with carbon disulfide, followed by reaction of the adduct with lithium diisopropylamide (LDA) at -78 °C and then with dimethyl sulfate afforded **5** in 60% yield. In this synthesis, if the temperature of the reaction mixture was allowed to increase above 0 °C then tar formation occurred with a lowering of the yield of **5**. Further, small amounts of dimethyl trithiocarbonate (**4**)[3] were formed in the reaction, requiring purification of the ketene before its conversion to the monoxide. In a similar procedure, with n-butyllithium substituted for LDA, **5** was obtained in lower yield along with other unidentified products.

Scheme I[a]



[a] a, CS_2/THF, 40-45 °C, 2 h, H^+, room temp; b, 2 n-BuLi/THF, -78 °C, 2 $(CH_3O)_2SO_2$, -78 °C; c, CS_2/THF, 1 LDA, 2 $(CH_3O)SO_2$; d, CS_2/THF, 40-45 °C, 2 h, 1 $(CH_3O)_2SO_2$, room temp; e, LDA/THF, -78 °C, 2 h, 1 $(CH_3O)_2SO_2$, -78 °C; f, m-CPBA, CH_2Cl_2, -5 °C.

Oxidation of **5** with m-chloroperbenzoic acid gave virtually pure ketene monoxide **6** uncontaminated with starting **5** or the other possible oxidation products (sulfone, bis sulfoxide or epoxide derived from **5**) as determined by NMR analysis. Similarly, oxidation of **5** with sodium metaperiodate by a slight modification of Johnson's method[4] gave monoxide **6** as the major product along with some unidentified compounds, necessitating purification of the crude material. Attempts to oxidize **5** to **6** with N-chlorosuccinimide and pyridinium chlorochromate failed to give the expected monoxide.

The intermediate ketene thioacetal **5** was also prepared by two other routes related to the "one-pot" procedure. In one route, dithioacetic acid (**2**), prepared in 56% yield[5] from Grignard **1**, was allowed to react with 2 equiv of n-butyllithium in THF/hexane at -78 °C followed by treatment of the intermediate dianion with dimethyl sulfate to give **5** in 70% yield. In the other route, methyl dithioacetate (**3**), prepared in 55% yield from Grignard **1**, was allowed to react with 1 equiv of LDA in THF at -78 °C followed by treatment of the intermediate anion with dimethyl sulfate to give **5** in 94% yield.

We have found both dithioacetic acid and ketene dimethyl thioacetal to be unstable under normal conditions. The acid polymerizes over a period of several months even when stored at 0 °C [6] and the thioacetal reacts slowly with air and will darken noticably within a few hours when exposed to a stream of oxygen. The oxidation products of this last reaction are currently under investigation.

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[1] (a) J. L. Herrmann, G. R. Kieczykowski, R. F. Romanet, J. P. Wepplo, and R. H. Schlessinger, *Tetrahedron Lett.*, 4711 (1973); (b) J. L. Herrmann, G. R. Kieczykowski, R. F. Romanet, and R. H. Schlessinger, *ibid.*, 4715 (1973); (c) Y. Ban, T. Ohnuma, K. Seki, and T. Oishi, *ibid.*, 727 (1975); (d) G. R. Kieczykowski, C. S. Pogonowski, J. E. Richman, and R. H. Schlessinger, *J. Org. Chem.*, **42**, 176 (1977); (e) R. Davis and K. G. Untch, *ibid.*, **44**, 3755 (1979).

[2] F. E. Ziegler and C. M. Chan, *J. Org. Chem.*, **43**, 3065 (1978).

[3] Dimethyl trithiocarbonate was purified by fractional distillation, bp 106–110 °C (27 mm) [lit.[3a] bp 86–88 °C (5.4 mm)], and identified by comparison of its IR and NMR spectra with those of an authentic sample. (a) H. C. Godt, Jr., and R. E. Wann, *J. Org. Chem.* **26**, 4047 (1961).

[4] N. J. Leonard and C. R. Johnson, *J. Org Chem.* **27**, 282 (1962).

[5] This yield of **2** represents a substantial increase over the lower yields of about 20% which have been reported.[2,5a] (a) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall, Englewood Cliffs, NJ, 1954, p 1287.

[6] A. Ohno and S. Oae in "Organic Chemistry of Sulfur", S. Oae, Ed., Plenum, New York, 1977, p 173, report that "dithioacetic acid kept standing for a prolonged period affords tetramethylhexathioadamantane".

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