

TABLE IV
RATE OF FORMATION OF SUBSTITUTED ANTHRAQUINONE FROM
2-BENZOYL-5-X-BENZOIC ACIDS AT 60°

X	H ₂ SO ₄ , %	<i>k</i> _{obsd} , sec ⁻¹
H	99.80	4.0 × 10 ⁻⁶ ^a
H	99.10	4.2 × 10 ⁻⁶ ^b
OCH ₃	96.19	3.77 × 10 ⁻⁶
NO ₂	100.1	1.67 × 10 ⁻⁴

^a Interpolated from Table II. ^b Reference 11.

of the lactol carbonium ion is an important feature which must be considered in evaluating the reaction sequence. The lactol carbonium ion formed from 2-benzoyl-5-nitrobenzoic acid is less stable than that formed from 2-benzoylbenzoic acid; it requires substantially higher concentrations of sulfuric acid to cause its formation, as may be seen from the data of Table I in ref 1. Once formed it is more reactive; hence the rate of formation of 2-nitroanthraquinone from 2-benzoyl-5-nitrobenzoic acid is larger. This implies that the formal positive charge is moving away ("re-treating") from the ring bearing the nitro group at the activated complex. This is, of course, completely consistent with the results and interpretation in the previous section.

Finally, the rate data for 2-benzoyl-4-nitrobenzoic acid help to delineate the situations under which the Hayashi rearrangement need be considered. The fact that the rate for the 4-nitro isomer is distinctive from

the 5-nitro isomer shows that the Hayashi rearrangement does not intrude in this case.²¹ It would appear from a consideration of the examples in the literature that the Hayashi rearrangement is largely restricted to 3- or 6-substituted 2-benzoylbenzoic acids or to situations in which the point of attachment of the phthaloyl moiety to the other aromatic system is a strongly activated aromatic site.

Experimental Section

The preparation of all materials used in this study has been previously described.¹³

Kinetic Procedures.—Reaction rates were followed by ultraviolet absorption spectroscopy. For runs at temperatures above 50°, the usual sealed-tube technique was used. At temperatures of 50 and 25°, the reactions were followed directly with a Beckman DU spectrophotometer using 1.0-cm cells and a thermostated cell block. The wavelength chosen was selected to give the largest change in absorbance. The spectrum of the reaction mixture on completion matched that of the appropriate anthraquinone.

Registry No.—1, 85-52-9; 3, 2159-36-6; 4, 3274-20-2; 5-nitro-2-benzoylbenzoic acid, 2159-46-8; 4-nitro-2-benzoylbenzoic acid, 2158-91-0; 5-methoxy-2-benzoylbenzoic acid, 2159-48-0; 2-(4-methylbenzoyl)benzoic acid, 85-55-2; 2-(3-methylbenzoyl)benzoic acid, 2159-37-7; 2-(4'-methoxybenzoyl)benzoic acid, 1151-15-1.

(21) An excellent discussion of the factors involved in the Hayashi rearrangement is given by M. S. Newman and K. G. Ihrman, *J. Am. Chem. Soc.*, **80**, 365 (1958).

Photochemical Reactions of Mesityl Oxide in 2-Propanol

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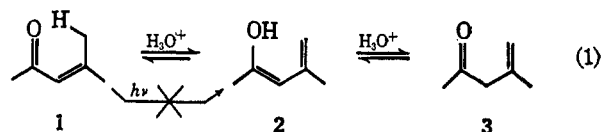
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Irradiation of mesityl oxide in boiling 2-propanol with a low-pressure mercury-argon source yielded 4-methyl-2-pentanone, a furanol (9), and a dihydrofuran (10) among other products. The reaction was apparently initiated by the photodecomposition of 2-propanol by 1849-A emission of the light source. Irradiation of mesityl oxide in methanol yielded similar results.

α,β -Unsaturated aliphatic ketones undergo *cis-trans* isomerization under the influence of ultraviolet light, but are otherwise considerably less reactive than their saturated analogs.²⁻⁴ Phorone⁵ and some α,β -unsaturated ketones with secondary and tertiary γ hydrogens undergo photodeconjugation and β -*t*-butyl α,β -unsaturated ketones undergo photocyclization to give acetyl-cyclopropanes.⁶

Mesityl oxide (1) possessing two groups of active allylic γ hydrogens may be expected to undergo a photodeconjugation by a mechanism analogous to the type II process. The product would be an enol (2) which may ketonize to its β,γ isomer, isomesityl oxide



(3) (eq 1). The acid-catalyzed isomerization of mesityl oxide to isomesityl oxide occurs readily⁷ and pure mesityl oxide, after extended storing at room temperature, is isomerized to an equilibrium mixture of the two isomers. However, mesityl oxide does not undergo a photochemical isomerization, no isomesityl oxide was found, and no loss of starting material was detected under a variety of conditions.⁸ Only when a low-pressure mercury-argon quartz lamp was used as the light source did the photolysis of mesityl oxide prove to be successful. This lamp effects extensive photolysis of simple alcohols, indicating that a substantial amount of the 1849-A emission of mercury was transmitted.⁸ Under comparable conditions, no photolysis was detected with a similar lamp constructed with Vycor

(1) The authors wish to acknowledge the U. S. Atomic Energy Commission for the support of this work, Contract No. AT(11-1)-1043. The authors also wish to thank the National Science Foundation and the Louis P. Block Fund of the University of Chicago for grants to purchase the mass spectrometer and the nmr spectrometer used in this work.

(2) R. S. Tolberg and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **80**, 1304 (1958).

(3) N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).

(4) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966).

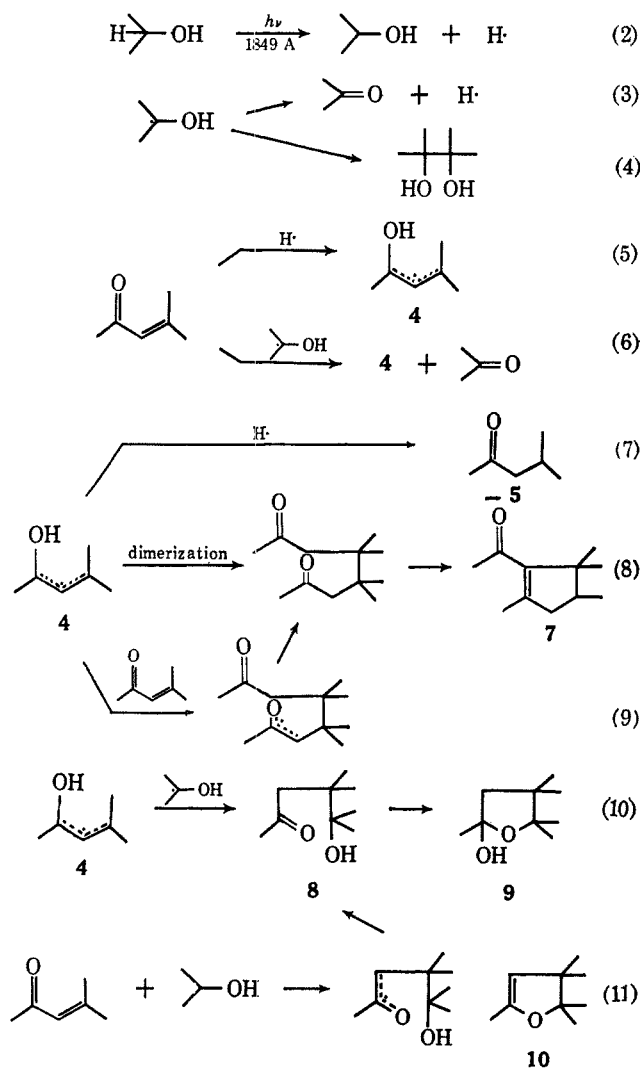
(5) K. J. Crowley, R. A. Schneider, and J. Meinwald, *J. Chem. Soc.*, 571 (1966).

(6) M. J. Jorgenson and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 1698 (1963).

(7) F. S. Stross, J. M. Monger, and H. de V. Finch, *ibid.*, **69**, 1627 (1947).

(8) N. C. Yang, D. P. C. Tang, D. Thap, and J. S. Sallo, *ibid.*, **88**, 2851 (1966).

which effectively cuts off the 1849-A emission. The reaction occurs at room temperature but proceeds considerably faster at boiling point of the solution (85°). The increased rate of photolysis may be due to the increased lamp output at elevated temperature. The photolysis of a solution of mesityl oxide in 2-propanol at 85° gave rise to the products summarized in Table I. The gas evolution was considerably inhibited as compared to the photolysis of pure 2-propanol.⁸ Over 90% of hydrogen was scavenged; the suppression of methane and carbon monoxide occurred to about the same extent. There was no visible gas evolution at the beginning of irradiation. The usual products—acetone and pinacol—were always present, but the yield of acetone was much increased while that of pinacol was decreased. Although the formation of the rest of the products may be rationalized in terms of the reactions of photoexcited mesityl oxide,⁹ in view of the well-established photostability of this conjugated ketone, it is preferably attributed to the secondary reactions of hydrogen atoms and 2-hydroxy-2-propyl radicals (eq 2-11; Scheme I). Since the quantum yield of photol-



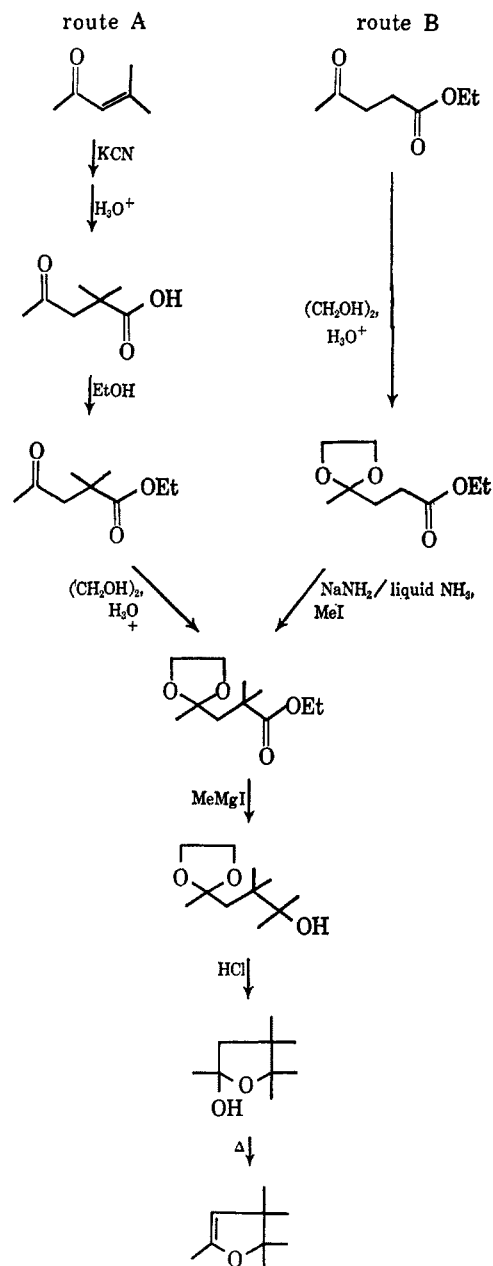
ysis of mesityl oxide at 1849 Å is estimated to be less than unity, the reaction products are likely to be formed *via* interactions between intermediate radicals rather than *via* chain reactions. The detailed mech-

(9) Mesityl oxide may be excited to its n, σ^* excited state with 1849-Å light. A probable mechanism will involve the reaction of mesityl oxide at its n, σ^* state prior to its deactivation to the nonreactive excited states.

TABLE I

Products	Retention time, min	Yield, % (g)	mmole/hr (g/hr)
Acetone	12.5	(3.6)	(0.83)
Pinacol	43	(5.0)	(0.57)
4-Methyl-2-pentanone (5)	17.5	32	0.52
Furanol 9	24	6.4	0.10
Dihydrofuran 10	21	10	0.16
Ketone 7	29	16	0.13
Residue		(7.0)	(0.093)

SCHEME I



anisms of formation of these products (5, 7, 9, 10) are not clear at this moment, but they may be rationalized by the following steps. Mesityl oxide may react with a hydrogen atom or a 2-hydroxy-2-propyl radical at the carbonyl oxygen, the locus of highest electron density, to give intermediate 4 (reactions 5 and 6). 4-Methyl-2-pentanone (5) may be formed by 1,4-reduction of mesityl oxide through this intermediate (4). The formation of ketone 7 may be rationalized by the

dimerization of intermediate **4** to form diketone **6** followed by cyclization (reaction 8) or the addition of intermediate **4** to another molecule of mesityl oxide followed by termination (reaction 9). The formation of γ -hydroxy ketone **8** may be explained by a coupling of intermediate **4** with a 2-hydroxy-2-propyl radical (reaction 10) or an addition of 2-hydroxy-2-propyl radical to the β position of mesityl oxide¹⁰ followed by termination (reaction 11). The furanol **9** and dihydrofuran **10** are subsequently derived from the γ -hydroxy ketone (**8**).

Furanol **9** and dihydrofuran **10** were characterized by their elemental analyses and spectral properties. Their structures as well as the facile cyclization of the hypothetical parent ketone (**8**) were unequivocally demonstrated by two independent syntheses. The classical routes involved were based on the carbon skeletons of mesityl oxide and ethyl levulinate. Both lead to the synthesis of ethylene ketal of γ -hydroxy ketone **8** which upon hydrolysis cyclizes directly to furanol **9**. In no case was the γ -hydroxy ketone **8** isolated. Dihydrofuran **10** can be obtained by pyrolysis or acid-catalyzed dehydration of **9**.¹¹

The irradiation of mesityl oxide in methanol was somewhat slower. The gas evolution was substantially inhibited. The higher boiling products were ethylene glycol, 4-methyl-2-pentanone (**5**), the reductive cyclic dimer (**7**) of mesityl oxide, two unidentified products, and a polymer. It is again likely that mesityl oxide itself undergoes no photochemical reaction and acts only as a radical scavenger.

Experimental Section

Irradiation of Mesityl Oxide in 2-Propanol with a Low-Pressure Mercury-Argon Lamp.—The lamps were constructed according to the design of Kharasch and Friedlander.¹² The immersion coils were made of Suprasil grade of fused quartz by Engelhard Industries, Newark, N. J. The radiation emitted by the lamp is confined principally to two lines at 1849 and 2537 Å. The lamp was equipped with a nitrogen inlet tube, a magnetic stirrer, and a Friedrich condenser. The outlet of the condenser was connected in series to a Dry Ice trap and then through a three-way stopcock to a gas buret filled with a saturated solution of sodium chloride. The gas was analyzed by vpc on a 15-ft Molecular Sieve 5A column (100° and 80-ml helium flow).

A solution of freshly distilled mesityl oxide in spectral grade 2-propanol (12 g, 0.12 mole in 250 ml) was irradiated at reflux temperature of the mixture (85°). 2-Propanol saturated with nitrogen was passed into the mixture throughout this time to keep the solution at a constant volume. Aliquots of the reaction mixture were taken out at several hour intervals and examined both by vpc and infrared spectroscopy. Irradiation was interrupted after 75 hr when practically all mesityl oxide had reacted. The gas evolution followed the usual pattern; it was negligible at the beginning but became appreciable later as mesityl oxide was depleted. The reaction mixture was transferred to a flask and acetone (3.6 g, 0.062 mole) and most of the 2-propanol were separated by fractionation through a 50-plate Heligrad column. The remainder (24.5 g) was then distilled under reduced pressure to yield a volatile fraction, bp 35–72° (0.02–0.05 mm), 17.5 g, and a nonvolatile residue, 7.0 g. Isolation of the products was achieved by analyzing the volatile fraction with a 3/8 in. \times 10 ft.

(10) T. M. Patrick, Jr., *J. Org. Chem.*, **17**, 1269 (1952).

(11) It was reported by Varshavskii and Tomilov that furanol **9** could be prepared in 3% yield by cyclodimerization of acetone and mesityl oxide under electrolytic conditions [*Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva*, **6**, 597 (1960)]. Dehydration to the corresponding dihydrofuran (**10**) was achieved in good yield by refluxing the compound with concentrated hydrobromic acid. However, several attempts to reproduce this dehydration were not successful.

(12) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 245 (1949).

Carbowax column at 175° and 80-ml/min helium flow. 4-Methyl-2-pentanone (**5**) was obtained in 32% yield based on mesityl oxide: 0.52 mmole/hr; bp 115°; retention time 17.5 min. This ketone was identical in all respect with an authentic sample. 2,4,4,5,5-Pentamethyl-2-tetrahydrofuranol (**9**) was obtained in 6.4% yield: 0.10 mmole/hr; bp 220° dec or 28–30° (0.05 mm); retention time 24 min. The compound was identified on the basis of its analysis, its spectral data, and by comparison with an authentic sample synthesized by two independent routes as described later. It exhibits ν_{\max} (cm⁻¹) 3650 w, 3450 m, 1460 s, 1370, 1380 s, d, 1180 vs, 1090 s, weak bands around 800–900; τ_{\max} at 9.25 (singlet, 3 H), 8.92 (singlet, 6 H), 8.80 (singlet, 3 H), 8.55 (singlet, 3 H), 8.08 (quartet, 2 H), 6.50 (singlet, 1 H); phenylurethan, mp 144°. *Anal.* Calcd for C₉H₁₈O₂: C, 68.31; H, 11.47. Found: C, 68.18; H, 11.58. 2,4,4,5,5-Pentamethyl-4,5-dihydrofuran (**10**) was obtained in 10% yield: 0.16 mmole/hr; bp 119°; retention time 21 min. This compound was also similarly identified and its independent synthesis will be described later. It exhibits ν_{\max} (cm⁻¹) 3075 w, 1675 vs, 830 s, 1370, 1380 s, d, 1245 vs, 1180 s, 1115 s, 1125 s; τ_{\max} at 9.15 (singlet, 6 H), 8.85 (quartet, 6 H), 8.40 (doublet, $J = 1$ cps, 3 H), 5.70 (multiplet, 1 H). *Anal.* Calcd for C₉H₁₈O: C, 77.09; H, 11.50. Found: C, 77.06; H, 11.44. 1-Acetyl-2,2,3,3,5-pentamethylcyclopentene (**7**) was obtained in 16% yield: 0.13 mmole/hr; bp 50° (0.025 mm); retention time 29 min. This compound was identified on the basis of its ultraviolet, infrared nmr spectra, and elemental analysis. It exhibits λ_{\max} 254 m μ (ϵ 5560), 310 m μ (ϵ 97); calcd 254 m μ according to a modification by Schubert and Sweeney on Woodward's for endocyclic double bond in a five-member ring system;¹³ ν_{\max} (cm⁻¹) 1670 s, 1630 m, 1460 s, 1360, 1368 s, d, no band at 800–900; τ_{\max} at 9.10 (singlet, 6 H), 9.00 (singlet, 6 H), 8.40 (multiplet, 2 H), 8.10 (multiplet, 3 H), 7.80 (singlet, 3 H); 2,4-dinitrophenylhydrazone, mp 115° (ethanol). *Anal.* Calcd for C₁₂H₂₀O: C, 79.95; H, 11.18. Found: C, 79.96, 79.92; H, 11.17, 11.02. Pinacol, 5 g (0.56 mmole/hr, retention time 43 min) was isolated and identified also in its hexahydrate form.

Hydration of Dihydrofuran 10.—The enol ether (60 mg) was shaken with a few drops of 0.5 N HCl in carbon tetrachloride. The compound rapidly transformed to a product having infrared and nmr spectra identical with those of the tetrahydrofuranol.

Reduction of Mesityl Oxide in Methanol vs. 2-Propanol.—Irradiation of a solution of mesityl oxide in methanol (6 g, 0.06 mole in 150 ml) was carried out to completion under similar conditions. The reaction mixture was maintained at reflux temperature of about 65° during the 100-hr period of irradiation. There were the usual products collected in the gas buret and Dry Ice trap: hydrogen, carbon monoxide, methane, and formaldehyde. Fractionation and vpc trapping experiments on a 10-ft Carbowax column at 170° afforded ethylene glycol (5 g), 4-methyl-2-pentanone (2.4 g, 40% yield), some 1-acetyl-2,2,3,3,5-pentamethylcyclopentene, a polymeric residue (5 g), and at least two unidentified products (2.5 g). The rates of disappearance of mesityl oxide and formation of 4-methyl-2-pentanone in both alcohols at reflux temperature over a period of 50 hr were followed by vpc and by the variations on absorbance of the unreacted mesityl oxide. All rates were found nearly linear with time. The rate of disappearance of mesityl oxide in 2-propanol was always somewhat faster, while the rate of formation of 4-methyl-2-pentanone in 2-propanol was slower.

Irradiation of Mesityl Oxide under Other Conditions.—Additional experiments under various conditions were carried out with no observable change on the part of mesityl oxide or 2-propanol: (1) mesityl oxide in boiling 2-propanol (5 g in 80 ml), 550-w Hanovia medium-pressure mercury arc, quartz well, Pyrex filter and Pyrex vessel, 50 hr; (2) mesityl oxide in pentane (5 g in 80 ml) at 20°, 450-w Hanovia medium-pressure mercury arc, quartz well, 8 hr; (3) mesityl oxide in 2-propanol (10 g in 250 ml) at 40 or 85°, low-pressure mercury Vycor lamp, 30 hr.

Ethyl Mesitonate.—Mesitonic acid was prepared by the addition of cyanide to mesityl oxide followed by hydrolysis¹⁴ and it was esterified with C₂H₅OH-HCl, bp 108–110° (25 mm).¹⁵

(13) W. M. Schubert and W. A. Sweeney, *J. Am. Chem. Soc.*, **77**, 2297 (1955); H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 211.

(14) A. Lapworth, *J. Chem. Soc.*, **85**, 1219 (1904).

(15) M. Quadrati-Khuda and S. K. Gosh, *J. Indian Chem. Soc.*, **16**, 287 (1939).

Ethyl Mesitonate Ethylene Ketal.—A solution of ethyl mesitonate in dry benzene (5.0 g, 0.03 mole in 25 ml) was refluxed with ethylene glycol (2 g, 0.03 mole) and *p*-toluenesulfonic acid (100 mg) for 12 hr. Water was removed in a Dean-Stark trap. The solution was washed with NaHCO₃ and dried over Na₂SO₄; the solvent was removed. The residue was distilled through a 10-cm Vigreux column to give 6 g of the ethylene ketal: yield 95%; bp 91–92° (7 mm). It exhibits ν_{\max} (cm⁻¹) 1730 s, 1375 s, 1160 s; τ_{\max} at 8.90 (singlet, 6 H), 8.82, (triplet, *J* = 6 cps, 6 H), 8.05 (singlet, 2 H), 6.15 (singlet, 4 H), 3.95 (quartet, *J* = 6 cps, 2 H). *Anal.* Calcd for C₁₁H₂₀O₄: C, 61.09; H, 9.32. Found: C, 60.89; H, 9.80.

4,4,5-Trimethyl-5-hydroxy-2-hexanone Ethylene Ketal.—A solution of the ester in ether (5 g, 0.023 mole in 20 ml) was gradually added to an ether solution of methyl lithium prepared by reacting lithium (0.84 g, 0.12 mole) with methyl iodide (8.5 g, 0.06 mole) in dry ether (65 ml). The reaction mixture was stirred at 10° overnight. It was decomposed with a saturated aqueous solution of NH₄Cl and dried over Na₂SO₄, the solvent evaporated, and the residue distilled under reduced pressure to give the alcohol (4.45 g): bp 60–61° (0.05 mm); yield 95%. It exhibits ν_{\max} (cm⁻¹) 3500 w, 1375 s, 1150 s, 1040 s; τ_{\max} at 9.00 (singlet, 6 H), 8.92 (singlet, 6 H), 8.70 (singlet, 3 H), 9.25 (singlet, 2 H), 6.60 (singlet, 1 H), 6.15 (singlet, 4 H). *Anal.* Calcd for C₁₁H₂₂O₂: C, 65.31; H, 10.96. Found: C, 65.01; H, 10.56.

2,4,4,5,5-Pentamethyltetrahydro-2-furanol.—A solution of the ketal alcohol in pentane (2.9 g, 0.014 mole in 30 ml) was vigorously stirred with HCl (20 ml, 0.5 *N*) for 5 hr in an ice water bath. The pentane layer was separated, washed three times with a dilute aqueous solution of NaHCO₃, and dried over Na₂SO₄. After removal of the solvent, the colorless oil was distilled under reduced pressure to give the furanol product (2.3 g) yield 83%, bp 28–30° (0.05 mm). A redistilled or sublimed sample solidified at 5° (mp 23°). Attempts to recrystallize the compound failed with petroleum ether, pentane, carbon tetrachloride, or alcohol. In preparations of the solid derivatives with benzoyl chloride, 3,5-dinitrobenzoyl chloride reagents were equally unsuccessful. The infrared and nmr of the compound were identical with those obtained from the photoproduct. The mass spectrum showed the P - 18 peak at *m/e* 140; the true parent peak at 158 was not found. *Anal.* Calcd for C₉H₁₈O₂: C, 68.31; H, 11.47. Found: C, 68.14; H, 11.26.

2,4,4,5,5-Pentamethyl-4,5-dihydrofuran.—The furanol (1.3 g) was heated under atmospheric pressure with an oil bath. Decomposition started at 125°; vigorous reaction occurred at 140–

160°. The dehydrated product (0.5 g) was obtained with some water: yield 45%; bp 123°; *n*_D²⁰ 1.4357. It showed identical infrared and nmr spectra with those of the photoproduct.

Ethyl Levulinate Ethylene Ketal.—Ethyl levulinate in benzene (100 g, 0.70 mole in 250 ml) was treated with ethylene glycol (43 g) using *p*-toluenesulfonic acid (150 mg) as catalyst. Water was removed in a Dean-Stark trap. Suitable work-up afforded a quantitative yield of the ketal ester (130 g), bp 110° (0.25 mm). It exhibits ν_{\max} (cm⁻¹) 1745 s, 1150 s; τ_{\max} at 8.98 (triplet, *J* = 7 cps, 3 H), 8.94 (singlet, 3 H), multiplet from 7.75–8.45, 4 H), 4.30 (singlet, 4 H), 4.15 (quartet, *J* = 7 cps, 2 H). *Anal.* Calcd for C₉H₁₆O₄: C, 57.43; H, 8.57; Found: C, 57.27; H, 8.78.

Methylation.—Ethyl levulinate ethylene ketal (28 g, 0.14 mole) was added to a solution of sodamide (0.30 mole) in liquid ammonia prepared according to the procedure of Khan¹⁶ and co-workers (7 g of sodium, 0.14 mole and 0.2 g of ferric nitrate in 600 ml of liquid ammonia). After stirring for 2 hr, methyl iodide (60 g, 0.42 mole) was gradually added. The reaction mixture was vigorously stirred for 5 hr in a Dry Ice-acetone bath and was left overnight. It was decomposed with water (50 ml), extracted with ether, and dried over Na₂SO₄. After removal of the solvent by a water aspirator, the residue was distilled under reduced pressure to give 65% yield of a product (19 g), bp 60–64° (0.25 mm). The infrared and nmr spectra indicated that it was a mixture of largely monomethyl and a small amount of the dimethyl product. Consequently similar steps were taken to introduce a second methyl group (5 g of sodium, 40 g of methyl iodide, and 700 ml of liquid ammonia). The reaction afforded 35% yield of a product with boiling point considerably lower, 54–56° (0.050 mm). On comparison with ethyl mesitonate ethylene ketal, the two compounds proved to be identical in all respects.

Registry No.—1, 141-79-7; 5, 108-10-1; 7, 13144-88-2; 7 2,4-dinitrophenylhydrazones, 13144-89-3; 9, 13144-90-6; 10, 13144-91-7; 2-propanol, 67-63-0; ethyl mesitonate ethylene ketal, 13144-92-8; 4,4,5-trimethyl-5-hydroxy-2-hexanone ethylene ketal, 13144-93-9; ethyl levulinate ethylene ketal, 941-43-5; 9-phenylurethan, 13144-87-1.

(16) N. A. Khan, *et al.*, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 970.

Stereoisomeric Thioxanthene-9-ol 10-Oxides

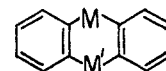
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The X-ray analysis of β -thioxanthene-9-ol 10-oxide (mp 206°) has revealed this to have the *trans* configuration. In the solid state the sulfur-oxygen bond occupies a pseudo-equatorial position while the HOCH dihedral angle is 34°. Configurations have also been assigned to the stereoisomeric 2-chlorothioxanthene-9-ol 10-oxides. Stereoselective oxidations of thioxanthene-9-ol and 2-chlorothioxanthene-9-ol are described.

Heterocyclic analogs of 9,10-dihydroanthracene (**1a**) possessing heteroatoms at either one or both of the *meso* positions (C-9 and C-10 in dihydroanthracene) generally exist in a conformation that is folded about an axis connecting the *meso* positions.⁴ For atoms (M and/or M') which are configurationally stable under the conditions of investigation (*e.g.*, the sulfoxide-



1a, M = CH₂; M' = CH₂
b, M = S(O); M' = S(O)
c, M = CHR; M' = CHR

sulfur atom at room temperature), appropriately substituted compounds may exhibit both configurational and conformational isomerism. These phenomena have been discussed for a number of molecular systems including 9,10-dihydroanthracenes (**1a**),^{5a} thianthrene

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(2) Recipient of a National Science Foundation Teaching Assistant Summer Fellowship, 1965.

(3) The X-ray crystallographic study was performed in the Crystallography Laboratory of the University of Pittsburgh, Pittsburgh, Pa.

(4) E. E. Turner in "Chemistry of Carbon Compounds," Vol. I, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1951, Chapter 9.

(5) (a) A. H. Beckett and B. A. Mulley, *Chem. Ind.* (London), 146 (1955); (b) S. Hosoya and R. G. Wood, *ibid.*, 1042 (1957); (c) W. Michaels, O. Schindler, and R. Signer, *Helv. Chim. Acta*, **49**, 42 (1966).