further 30 min at the same temperature, and the resulting solution was worked up as above. Distillation at 10 mm yielded (i) bp 40-60° (6.6 g), (ii) bp 60-69° (3.7 g), (iii) bp 69-120° (1.7 g), and (iv) bp 120° (1.8 g). Fractions i and ii were 1-phenyl-2-butene contaminated with a few per cent of 3-phenyl-1-butene. Fraction iii also contained 1-phenyl-2-butene (24%). Fractions iii and iv gave rise to several overlapping glpc peaks which were not subjected to further examination. The total yield of 1-phenyl-2-butene was about 10.2 g and that of 3-phenyl-1-butene was 0.3 g (from glpc peak area). 1-Phenyl-1-butene was absent in all of these fractions.

Sulfuric Acid Catalyzed Reaction of Phenylbutenes with Benzene. General Procedures.—To a stirred suspension of 5 g of concentrated sulfuric acid in 150 ml of benzene at 0-5° was added 3 g of the phenylbutene dissolved in 30 ml of benzene in 5 min, and the mixture was stirred for 1.5 hr. The reaction mixture was made alkaline by adding aqueous potassium carbonate and was steam distilled. The product was collected by extraction with benzene, vacuum distilled, and analyzed by glpc. **1-Phenyl-2-butene** (expt 6 and 7) gave a mixture of diphenylbutanes (Table I) in a 40% yield. **1-Phenyl-1-butene** (expt 8) gave only 1,1-diphenylbutane, n^{20}_{D} 1.5568 (lit.[11] n^{20}_{D} 1.5568) in 52% yield. **3-Phenyl-1-butene** was 60% recovered; the residue of distillation contained a trace of materials whose glpc retention times coincide with those of diphenylbutanes.

Acknowledgment.—The author wishes to thank Mr. Michio Kasai for valuable technical assistance.

Fixation of an Enediol by Acetal Formation. Synthesis of a 1,3-Dioxole

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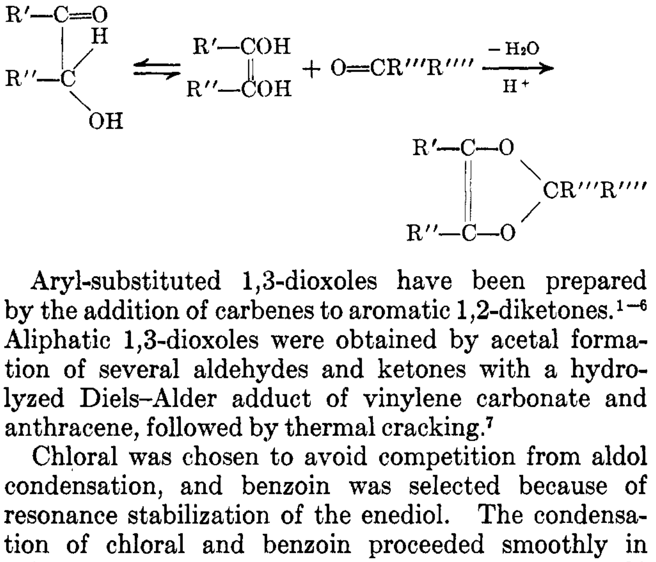
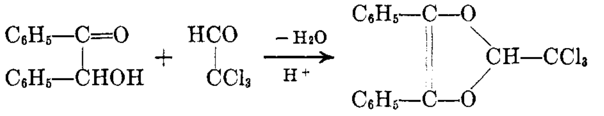
The first case of a fixation of an enediol (benzoin) by an aldehyde (chloral) is reported, yielding the new 2-trichloromethyl-4,5-diphenyl-1,3-dioxole. Acetoin cannot be condensed directly with chloral but requires base-catalyzed addition to give a 5-hydroxydioxolane from which the corresponding dioxole can be prepared. The reactions of chloral with several other hydroxycarbonyls and of other aldehydes with benzoin result in structures other than dioxoles.

The usual methods of stabilizing the enolic form of aldehydes or ketones consist in the direct esterification or etherification of the carbonyl group in an enolizing medium. The fixation of an enol by acetal formation with another carbonyl compound has not been discussed in previous literature. It was thought that ring formation from an α-hydroxy carbonyl and an aldehyde or ketone should favor condensation to a 1,3-dioxole.



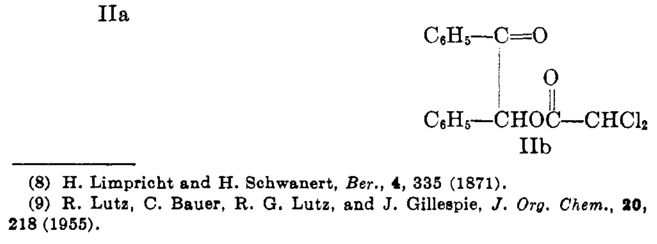
Aryl-substituted 1,3-dioxoles have been prepared by the addition of carbenes to aromatic 1,2-diketones.[1-6] Aliphatic 1,3-dioxoles were obtained by acetal formation of several aldehydes and ketones with a hydrolyzed Diels-Alder adduct of vinylene carbonate and anthracene, followed by thermal cracking.[7]

Chloral was chosen to avoid competition from aldol condensation, and benzoin was selected because of resonance stabilization of the enediol. The condensation of chloral and benzoin proceeded smoothly in refluxing benzene with acidic catalysts to give an 85% yield of crude 2-trichloromethyl-4,5-diphenyl-1,3-dioxole (I).



I

Small amounts of benzil and tetraphenylfuran were isolated from the reaction mixture. These by-products were apparently formed by disproportionation and condensation of benzoin and have been obtained in higher yield from benzoin and sulfuric acid.[8,9] Compound I is hydrolyzed by concentrated hydrochloric acid in ethanol to benzoin and chloral. It is easily oxidized by air to benzil, chloral, and acidic products. Acids catalyze the autoxidation while amines or hydroquinones inhibit it. This was demonstrated by comparing induction periods and rates of oxygen absorption of a neutral solution of I in methanol with an acidic, basic, and neutral hydroquinone-containing solution. It was also observed that thermal degradation during distillation is accelerated by hydrogen chloride gas formed by partial pyrolysis of the chloral acetal. It was therefore necessary to carry out all purification steps including distillation in basic medium. A gradual pyrolysis of I was observed also at room temperature after extended bulk storage in a closed container. An assumed intermediate diene hydrochloride (IIa) was



IIa

IIb

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(1) H. Biltz and R. Paetzold, *Ann.* **433**, 81 (1923).

(2) F. Arndt, J. Amende, and W. Ender, *Monatsh.*, **59**, 208 (1932).

(3) E. Bergmann and J. Hervey, *Ber.*, **62**, 893 (1929).

(4) G. Hahn, *ibid.*, **62**, 2485 (1929).

(5) A. Schoenberg, R. Moubasher, and A. Mostafa, *J. Chem. Soc.*, 348 (1941).

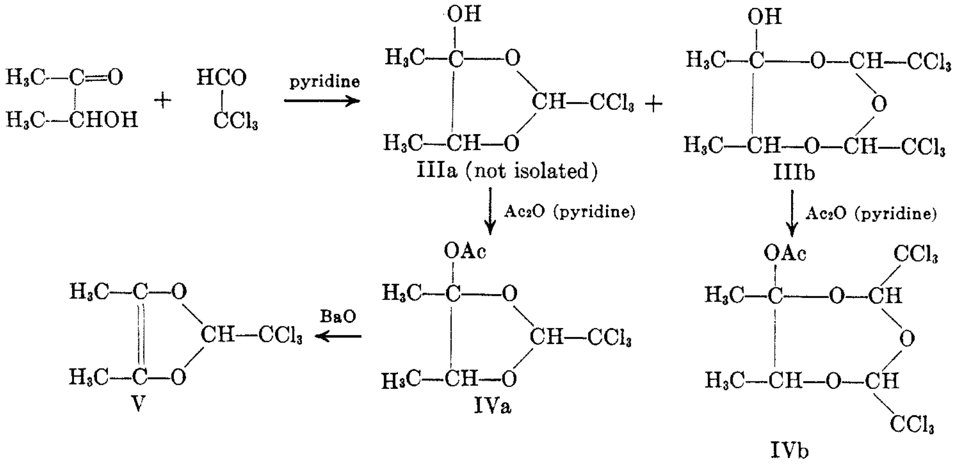
(6) W. Ried and J. Omran, *Ann.*, **673**, 120 (1964).

(7) N. Field, *J. Am. Chem. Soc.*, **83**, 3504 (1961).

(8) H. Limpricht and H. Schwanert, *Ber.*, **4**, 335 (1871).

(9) R. Lutz, C. Bauer, R. G. Lutz, and J. Gillespie, *J. Org. Chem.*, **20**, 218 (1955).

SCHEME I



a light pink solid, stable at room temperature, but had a noticeable vapor pressure of hydrochloric acid gas. It was not further investigated. Neutralization of a benzene solution of IIa with excess aqueous sodium bicarbonate resulted in hydration and ketonization to benzoin dichloroacetate (IIb).

Since IIb could not be obtained independently by esterification, it was characterized by transesterification to benzoin and methyl dichloroacetate and by its infrared spectrum, which showed absorptions characteristic for one dichloromethyl and two carbonyl groups. Resonances in its nmr spectrum were assigned to the aromatic ring at 7.18–7.70, aromatic, *ortho* to carbonyl at 7.93, benzylic at 6.92, and dichloromethyl aliphatic protons at 6.10 ppm, the latter falling within 0.07 ppm of the resonance of dichloroacetic acid. The area ratios were 8:2:1:1, respectively, in agreement with structure IIb. A few attempts of controlled pyrolysis of I at temperatures up to 120° and varying conditions or of dehydrochlorination with sodium bicarbonate solutions or alcoholic caustic did not yield identifiable products.

The structural proof of I was based on the results of the hydrolysis, as well as of the oxidation, and on its infrared and nmr spectra. The infrared spectrum showed a weak band at around 6 μ, believed to be due to the carbon–carbon double bond. Intense and narrow bands at 8.0 and 8.9 μ can be attributed to the acetal grouping and bands around 11.8 and 12.4 μ to the trichloromethyl group by comparison with 2-trichloromethyl-1,3-dioxolanes. The nmr analysis revealed two peaks in an area ratio of 10 aromatic, at from 7.07 to 7.72 ppm, to 1.02 aliphatic protons, at 6.22 ppm, the latter being shifted to lower field as expected for chloral derivatives.

Attempted hydrogenation of I to the dioxolane with palladium on charcoal catalyst was unsuccessful. Attempted independent synthesis of the dioxolane from chloral and hydrobenzoin resulted in partial rearrangement of the latter to diphenylacetaldehyde which condensed with hydrobenzoin to the previously described 2-diphenylmethyl-4,5-diphenyl-1,3-dioxolane.[10]

Various attempts to condense chloral directly with acetoin, α-hydroxyacetophenone, 1-hydroxybutanone, and acetaldol resulted in the formation of resins. It was demonstrated, however, that aliphatic 1,3-dioxoles are accessible by base-catalyzed condensation to 4-hydroxy-1,3-dioxolane (IIIa) which upon esterification and splitting out acid yields dioxole (V). The liquid 2-trichloromethyl-4,5-dimethyl-5-acetoxy-1,3-dioxolane (IVa) was obtained in over 60% yield. Part of IVa was separated by vapor phase chromatography into two isomers which showed identical mass fragmentation patterns. The infrared spectrum of the mixture suggested two types of carbonyl, absorbing at 5.70 and 5.83 μ. Other major absorptions occurred at 8.2 and 8.8 μ (dioxolane), at 9.9 and a broad band at 12.4 μ (CCl_3). The nmr spectrum showed that the major component (59%) contained the trichloromethyl and the acetoxy group in a *cis* arrangement with respect to the dioxolane ring, while 41% was in the *trans* form. Each peak could be assigned to its respective isomer on basis of intensity, since all resonances of the *cis* form were different from the *trans* form and fortunately of different concentration. The assignment of isomers was then based on the relative chemical shifts of these peaks. A complete interpretation of the spectrum will be included in a future publication along with a number of other cyclic derivatives of chloral.

Compound IVa was accompanied by a small amount (6%) of the addition product of 2 moles of chloral to acetoin, for which the structure 2,4-bistrichloromethyl-6,7-dimethyl-6-acetoxy-1,3,5-trioxepane (IVb) is suggested. Its infrared spectrum showed multiple sharp bands at 7.3, 8.2, 8.8, 9.8, 11.1, and 12.4 μ, with the strongest a narrow absorption at 5.72 μ. The fact that only one carbonyl band occurred indicated that the compound did not display geometrical isomerism of the type observed in IVa, which was confirmed by its nmr spectrum. The latter showed resonances at 5.59, 6.68, 4.50, 1.58, 1.41, and 2.21 ppm in approximate area ratios of 1:1:1:3:3:3, respectively, for which the following positions on the ring may be assigned: 2-H, 4-H, 7-H, 6-CH_3, 7-CH_3, and 6-$OCOCH_3$.

An alternative reaction path leading from a hemiacetal of IIIa *via* acetylation to the isomeric 4-(1-acetoxy-2,2,2-trichloroethyl) ether of IIIa cannot be ruled out on the basis of presented evidence. Structure IVb appears more probable, however, since isomerism of the type observed in five-membered rings could not be detected and since higher cyclic acetals of chloral form with great ease (to be published). See Scheme I.

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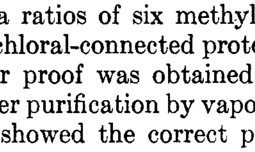
[10] W. Madelung and M. Oberwegner, *Ann.*, **526**, 226 (1936).

The removal of acetic acid from IVa was incomplete, yielding a mixture of IVa and the 2-trichloromethyl-4,5-dimethyl-2,3-dioxole (V). A degradative polymerization of V during redistillation through a spinning-band column was observed, apparently catalyzed by acidic products formed during the distillation. Therefore, only small amounts of V were obtained. Structural proof was furnished by its nmr spectrum which showed two peaks at 1.84 and 5.91 ppm, respectively, the expected area ratios of six methyl protons to approximately one chloral-connected proton, and no other protons. Further proof was obtained from the mass spectrum of V after purification by vapor phase chromatography. This showed the correct parent mass and the presence of three chlorine atoms and one acetal grouping per mole and of less predominant fragment ions which were in agreement with structure V.

In attempting to condense benzoin directly with other aldehydes, different reactions occurred. *p*-Chlorobenzaldehyde and benzoin yielded small amounts of a light yellow solid besides benzil. The elemental analysis and molecular weight showed that 2 moles of benzoin had condensed with 1 mole of *p*-chlorobenzaldehyde, retaining only two oxygen atoms per mole. The latter appeared to be present as carbonyl and as ether, suggesting aldol-type condensations as indicated by its infrared and nmr spectrum. This showed peaks at 5.29 and 7.78 ppm and a broad complex resonance with major peaks at 7.02, 7.15, and 7.39 ppm in area ratios 1:2:∼24.

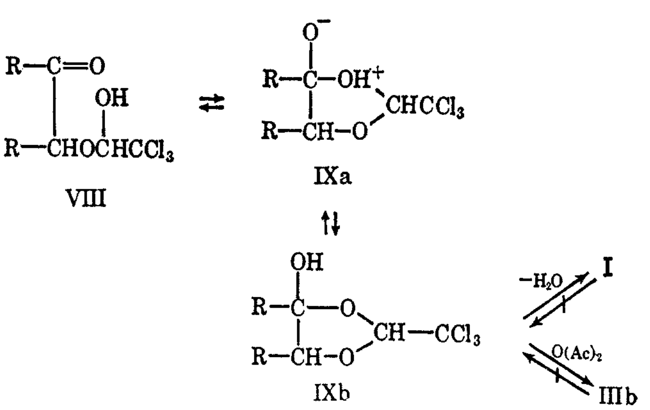
The acid-catalyzed condensation of formaldehyde resulted in 4-benzoyl-4-phenyl-1,3-dioxolane (VI). Its nmr spectrum showed a broad peak at 7.0–7.65 ppm (aromatic protons), a peak at 7.99 ppm (aromatic protons *ortho* to carbonyl), and peaks at 5.23, 5.11, 5.08, and 3.70 ppm (aliphatic protons) in area ratios 8:2:1:1:1:1, respectively. The structure of VI was established by independent synthesis from the known[11] α-hydroxymethylbenzoin and formaldehyde. Further confirmation of structure VI was obtained by studying the nmr spectrum of 4-phenyl-4-(α-hydroxybenzyl)-1,3-dioxolane (VII), obtained by hydrogenation of VI. Its nmr spectrum showed a broad resonance of ten aromatic protons at 6.75–7.31 ppm, one hydroxyl proton at 3.11 ppm, one benzylic proton at 4.81 ppm, and four aliphatic protons at 5.15, 4.76, 4.49, and 3.94 ppm, respectively, in correct area ratios. The resonance of the benzylic hydrogen appeared as a singlet, indicating that the adjacent carbon atoms were devoid of hydrogen.



VI

Discussion

Acetals of chloral are known to form with difficulty and under rather extreme conditions[12] because of the inductive and steric[13] effects of the trichloromethyl group. The unusual ease of formation of I and IIIa is presumably due to intermediates of type VIII and IX which are in equilibrium.



The shift of the equilibrium to IX is favored by the electron-withdrawing character of the trichloromethyl group which tends to increase the activity of the hydroxyl group toward the carbonyl in VIII and which is responsible for the unusual stability of acetals of chloral, once formed.[12] The reaction is completed by removal of IXb from the equilibrium as the acetate (IVa) or as the dioxole (I), in which the double bond is stabilized by conjugation with two phenyl groups.[14]

The synthesis of 4-hydroxy-1,3-dioxolanes from α-ketols will therefore be easier with negatively substituted aldehydes or ketones. When the carbonyl compound does not have electron-withdrawing substituents to enhance the basicity of the hydroxyl oxygen of the hemiacetal, the highly exothermic aldol condensation takes place, as in the case of formaldehyde → α-hydroxymethylbenzoin → VI.

Experimental Section[15]

2-Trichloromethyl-4,5-diphenyl-1,3-dioxole (I).—Pure benzoin (142 g), 250 ml of anhydrous benzene, and an excess of distilled anhydrous chloral (*ca.* 115 g) were refluxed for 10 min under nitrogen in a Dean-Stark apparatus. One gram of toluenesulfonic acid was added, and refluxing under nitrogen was continued until no more water separated (12.8 ml during 6–8 hr). The following operations were also carried out under nitrogen. The solvent was removed under vacuum. The residue was dissolved in 400 ml of hot hexane, and an excess of powdered sodium bicarbonate was added to neutralize the catalyst, followed by charcoal for adsorbing carbonyl-containing by-products. The mixture was filtered hot. Upon cooling in an ice–salt mixture, there crystallized from the filtrate 195 g (85.6%) of light yellow needles, mp 56°. Hot filtration of a methanolic solution yielded 3.2 g of 2,3,4,5-tetraphenylfuran, mp 173° (from hexane). The infrared spectrum was in agreement with the literature.[9] After crystallization of the dioxole from methanol, colorless needles were obtained, mp 59.4–59.8°, bp 162–166° (0.1–0.15 mm) with slow decomposition. The distillation was carried out in the presence of sodium bicarbonate.

Anal. Calcd for $C_{16}H_{11}Cl_3O_2$: C, 56.3; H, 3.2; Cl, 31.2; mol wt, 341.6. Found: C, 55.9; H, 3.1; Cl, 31.35; mol wt, 340.

Major infrared absorption bands occurred at 8.0, 8.9, 11.85, 12.35, 13.2, and 14.5 μ.

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(11) A. Kuzin, *Ber.*, **68**, 2169 (1935); E. Schauenstein and M. Stampfer, *ibid.*, **77B**, 19 (1944).

(12) R. Webb and A. Duke, *J. Chem. Soc.*, 4320 (1962).

(13) I. Rosen, D. Hudgin, C. Sturm, G. McCain, and R. Wilkjelm, *J. Polymer Sci.*, **A3**, 1540, 1545 (1965).

(14) C. Buehler, *Chem. Rev.*, **64**, 7 (1964).

(15) Melting points are corrected. The following instruments were used in spectral analyses: a grating infrared spectrometer from Perkin-Elmer, Model 521; a single-focusing mass spectrometer from Consolidated Electrodynamic Corp., Model 21-103-C; and an nmr spectrometer from Varian, Model A-60. The molecular weights were determined in a vapor pressure osmometer from Mechrolab, Inc., Model 302.

Hydrolysis of I.—Ethanol (50 ml), concentrated hydrochloric acid (20 ml), and I (11.4 g) were refluxed under nitrogen for 0.5 hr. After dilution with water, 6.8 g (97%) of benzoin and 1.5 g of chloral hydrate were isolated.

Oxidation of I.—The solid dioxole (I) formed benzil and acidic vapors in air within less than 1 hr. Ethanolic solutions (0.2 *M*, 100 ml each) were stirred in an oxygen atmosphere at room temperature. Solution A (blank) showed an induction period of 5.1 hr and absorbed approximately 0.5 mole of oxygen/mole of I after 33 hr, with an initial rate of approximately 0.035 M hr^{-1} (M of I)$^{-1}$. Solution B, which was 0.01 *M* in hydrochloric acid, showed an induction period of 3 hr, an absorption of 0.5 mole of oxygen after 24 hr, and an initial rate of 0.05 M hr^{-1} (M of I)$^{-1}$. Solutions C and D, which were 0.01 *M* in hydroquinone and in 1,4-diazabicyclo[2.2.2]octane, respectively, did not turn yellow or absorb oxygen during 1 week, even after stirring at 60° during an 8-hr period. An almost quantitative yield of benzil, mp 93° (lit. 95°), confirmed by its infrared spectrum, and 39% of chloral hydrate were isolated from solution A.

Benzoin Dichloroacetate (IIb).—Compound IIa, obtained by storing I for 5 months in a nitrogen-filled glass flask at room temperature, was dissolved in benzene under nitrogen. To this solution was added gradually aqueous sodium bicarbonate with agitation until carbon dioxide formation ceased. The organic phase was separated, dried, and evaporated. The residue yielded IIb after several recrystallizations from ethanol as fine, white needles, mp 79–80°, without noticeable by-products. The yield was not determined.

Anal. Calcd for $C_{16}H_{12}Cl_2O_3$: C, 59.5; H, 3.72; Cl, 22.0; mol wt, 323. Found: C, 59.53; H, 3.52; Cl, 22.2; mol wt, 316.

The infrared spectrum showed major bands at 5.78, 5.98, 7.85, 8.02, 8.18, 10.3, 10.6, 12.3, 13.1, 13.25, and 14.4 μ.

Transesterification of IIb.—Anhydrous methanol (15 ml), IIb (2 g), and seven drops of concentrated sulfuric acid were heated for 4 hr. After crystallization in a refrigerator overnight, 1.1 g (82%) of benzoin was filtered off and the filtrate was fractionated through an 8-in. spinning-band column. A fraction distilling from 130 to 135° (lit. 135°) showed the same major absorptions in its infrared spectrum as an authentic sample of methyl dichloroacetate.

2-Trichloromethyl-4,5-dimethyl-5-acetoxy-1,3-dioxolane (IVa).—To a mixture of 189 g of acetoin, 660 ml of benzene, and 200 ml of pyridine was added slowly, with stirring, under nitrogen, 295 g of anhydrous chloral, causing a temperature increase from 25 to 66°. The mixture was refluxed for 3.5 hr. After cooling, 222 g of acetic anhydride was added slowly under nitrogen, and the mixture was boiled for 2 hr. Most of the solvents were removed by distillation up to bp 105°. The residue was extracted five times with water, taken up in chloroform, dried, and distilled through a spinning-band column. The fraction boiling at 72–74° (0.3 mm) comprised 336 g (60.5%).

Anal. Calcd for $C_8H_{11}Cl_3O_4$: C, 34.63; H, 3.95; Cl, 38.4; mol wt, 278.5. Found: C, 35.1; H, 4.06; Cl, 38.75; mol wt, 281.

2,4-Bistrichloromethyl-6,7-dimethyl-6-acetoxy-1,3,5-trioxepane (IVb).—From the distillation residue of IIIa an addition product of 2 moles of chloral to acetoin (acetoxylated) crystallized in 6.2% yield (based on acetoin) as colorless crystals, mp 144° (from methanol).

Anal. Calcd for $C_{10}H_{12}Cl_6O_5$: C, 28.34; H, 2.83; Cl, 50.15; mol wt, 425. Found: C, 28.24; H, 2.79; Cl, 50.00; mol wt, 439.

2-Trichloromethyl-4,5-dimethyl-1,3-dioxole (V).—A mixture of 55.5 g of IVa and 33.6 g of barium oxide was refluxed under nitrogen and vacuum at 180–200° (bath temperature) for 5 hr. A flash distillation at 18 mm yielded 5–10 g of liquids, boiling below the starting material (130° at 18 mm). Redistillation through a spinning-band column yielded a small fraction of colorless liquid, boiling at 80–85° (18 mm). Most of the material underwent degradative polymerization during the redistillation. The mass spectrum was carried out with material purified by vapor phase chromatography. It showed the presence of a compound having a molecular ion observed at a mass to unit charge ratio of 216 along with isotope peaks at *m/e* 218, 220, and 222, which were in the correct ratio for a compound containing three chlorine atoms. A major fragment ion at *m/e* 99 resulting from the loss of the trichloromethyl group was found characteristic for trichloromethylacetals. This was confirmed by comparison with the mass fragmentation patterns of 2-trichloromethyl-1,3-dioxolane and of other acetals. Less predominant fragments were compatible with structure V. The infrared spectrum showed unsaturation at around 5.7 to 6.1 μ, which is characteristic for haloalkyl-substituted dioxols or 4-methylenedioxolanes.

Reaction of *p*-Chlorobenzaldehyde and Benzoin.—*p*-Chlorobenzaldehyde (28.1 g) was condensed with 42.4 g of benzoin in the same manner as described for chloral. A yellow, crystalline material (12.9 g) was obtained from a benzene–ethanol (1:1) mixture: mp 210–213°. After several recrystallizations from methanol and methyl ethyl ketone there remained 5.5 g, mp 217–218° dec.

Anal. Calcd for $C_{35}H_{27}ClO_2$: C, 81.7; H, 5.26; Cl, 7.12; mol wt, 516.6. Found: C, 81.16; H, 5.15; Cl, 6.81; mol wt, 535.

The infrared spectrum appeared complicated, showing major sharp bands at 5.9, 7.9, 8.1, 8.8, 9.2, 12.1, 12.9, 13.1, and at around 14.4 μ.

4-Benzoyl-4-phenyl-1,3-dioxolane (VI). A.—Benzoin (63.6 g), paraformaldehyde (18 g), 150 ml of dry toluene, and 2.0 g of *p*-toluenesulfonic acid were refluxed for 8 hr, the eliminated water being collected in a Dean-Stark trap. Evaporation of the solvent and recrystallization from methanol produced 10.0 g of light yellow crystals of VI, mp 66.8°.

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.59; H, 5.51; mol wt, 254. Found: C, 76.16; H, 5.28; mol wt, 254.

The infrared spectrum showed a strong carbonyl absorption at 5.96 μ and major bands at 7.9, 9.3, 10.5, and 14.3 μ. As by-products 1.5 g of 2,3,4,5-tetraphenylfuran, mp 173–174°, and small amounts of benzil were obtained.

B.—α-Hydroxymethylbenzoin (36.2 g), obtained in 82% yield,[11] was refluxed for 2 hr with 7.5 g of paraformaldehyde and 0.30 g of *p*-toluenesulfonic acid in 250 ml of dry benzene, the eliminated water being collected in a Dean-Stark trap. After neutralization with solid sodium bicarbonate and filtration (hot), the solvent was removed under vacuum, yielding 43.4 g (90%) of impure crystals, mp 50–55°. Several recrystallizations from toluene yielded pure VI, mp 66–67°; with the product of method A mmp 66–67°, and showing a congruent infrared spectrum with the latter.

4-Phenyl-4-(α-hydroxybenzyl)-1,3-dioxolane (VII).—Compound VI (3.63 g) dissolved in 100 ml of ethanol was hydrogeneted at room temperature with 0.2 g of palladium on charcoal as a catalyst, until no more hydrogen was consumed (*ca.* 0.02 mole of hydrogen). A quantitative yield of product was recovered, divided into two fractions by repeated recrystallizations from petroleum ether (bp 30–60°) and petroleum ether–methanol mixtures, melting at 58 and 72–73°. Both compounds showed identical infrared spectra, indicating that they were isomers. The infrared spectrum showed hydroxyl of medium intensity at 2.85 μ, the absence of carbonyl, and major bands at 9.25, 10.5, and 14.3 μ. The nmr spectrum was confirming.

Anal. Calcd for $C_{16}H_{16}O_3$: C, 75.0; H, 6.25. Found: C, 75.18; H, 6.45.

Acknowledgment.—The authors are indebted to Messrs. W. Harple, H. Hoberecht, and G. Vickers from Olin Central Analytical Research Department for determining and interpreting spectral data, and to Dr. R. Rittner and co-workers for performing instrumental and microanalytical work.