

Peroxide-Induced Conversions of Cyclic Acetals of Benzaldehyde to Benzoate Esters¹

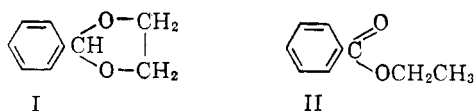
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The cyclic acetals prepared from benzaldehyde and certain 1,2- and 1,3-diols were converted to benzoate esters in reactions induced by heating the acetals with di-*t*-butyl peroxide. Benzaldehyde was formed in small amounts as a by-product in these reactions. Mechanisms involving free radical chain reactions are proposed to account for the formation of these products.

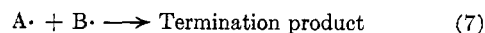
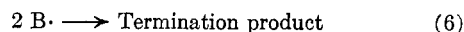
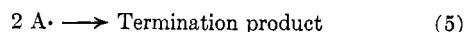
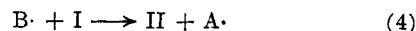
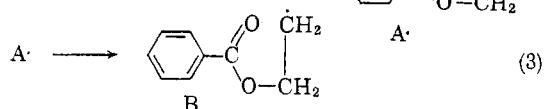
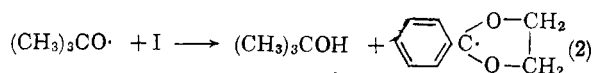
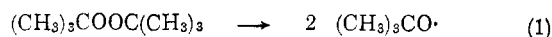
Cyclic acetals are isomeric with the appropriate carboxylic esters. For example, ethylenebenzal (I), the cyclic acetal derived from the acid-catalyzed reaction of benzaldehyde and ethylene glycol, is isomeric with ethyl benzoate (II). Any conversion of an acetal such as I to the ester would require an ox-



dation of the aldehydic carbon of the aldehyde portion of the acetal to the carboxylate oxidation state and reduction of an alcohol carbon of the diol portion of the acetal to the hydrocarbon oxidation state. We have found that such intramolecular oxidation-reduction reactions can be effected with the cyclic acetals of benzaldehyde by heating them with di-*t*-butyl peroxide. For example, ethylenebenzal was converted to ethyl benzoate in such a peroxide-induced reaction. Gas chromatographic analysis of reaction mixtures obtained by heating I with di-*t*-butyl peroxide showed that *t*-butyl alcohol and small amounts of benzaldehyde were also formed as reaction products. Ethyl benzoate was separated from one of the reaction mixtures by distillation and identified by its infrared spectra and gas chromatographic retention time, both of which were identical with those of an authentic sample of ethyl benzoate. Hydrolysis of a portion of the ester yielded benzoic acid. After removal of the ethyl benzoate and unchanged ethylenebenzal from the reaction mixture by vacuum distillation, a high-boiling residue with a molecular weight of 307 remained. This molecular weight corresponds to two ethylenebenzal units per molecule. The amount of the residue was very nearly equivalent to the amount of the peroxide used to initiate the reaction. The infrared spectra of the residue showed a strong ester carbonyl absorption band.

The mechanism of the reaction in which this cyclic benzal is isomerized to the benzoate ester presumably involves the following sequence of reactions:

(1) Abstracted from the thesis submitted by Z. Garcia in partial fulfillment of the requirements for the M.S. degree at the University of Kansas.



Reactions 3 and 4 of this reaction scheme comprise a free radical chain sequence in which the cyclic benzal is converted to the benzoate ester. The small amounts of *t*-butyl alcohol formed in the reaction result from the abstraction of a hydrogen atom from I by *t*-butoxyl radicals (reaction 2) which are formed in the thermal cleavage of the peroxide. Coupling reactions of the chain carrying radicals A \cdot and B \cdot (reactions 5, 6, and 7) terminate the chain sequence and produce the dimeric residue.

In another series of reactions, the conversion of I to II with varying amounts of the initiator was determined by gas chromatographic analysis of the reaction mixtures. The percent conversion and kinetic chain lengths of the reactions are shown in Table I.

TABLE I
REACTIONS OF ETHYLENEBENZAL WITH DI-*t*-BUTYL PEROXIDE AT 132°

[I]/[peroxide]	Time, hr.	% conversion	Kinetic chain length
5:1	18	76.8	2.0
10:1	18	43.1	2.3
21.5:1	18	36.0	3.2

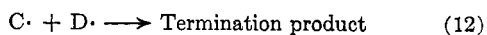
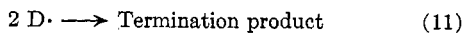
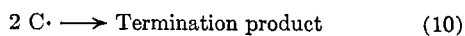
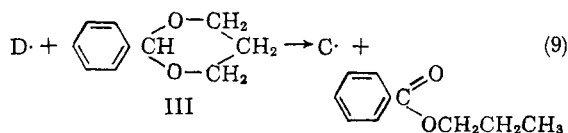
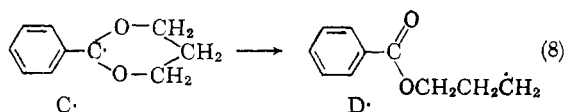
Although the kinetic chain length of the reaction is short, it is interesting that some chain character is observed. The β -elimination reactions of ether radicals resulting in the formation of a carbonyl function and an alkyl free radical are known.² The β -elimination reaction in the case of the benzal

(2) L. P. Kuhn and C. Wellman, *J. Org. Chem.*, **22**, 774 (1956); E. S. Huysen, *ibid.*, **25**, 1820 (1960).

free radical A· (reaction 3) is somewhat surprising since it involves the conversion of a resonance-stabilized benzyl type free radical to a comparatively unstable primary alkyl free radical. This reaction is quite possibly endothermic to the extent of about 15–20 kcal./mole.³ One possible explanation for the fact that the reaction does take place is the favorable increase in the entropy of the process of changing from the rather highly ordered cyclic free radical to the linear free radical. Reaction 4 of the reaction sequence should be expected to take place readily since it involves the attack of a very reactive primary alkyl free radical on a reactive benzylic hydrogen. The presence of the ester carbonyl function in the termination product indicates that this reaction does not proceed to the complete exclusion of the radical coupling reactions of this radical (reactions 6 and 7).

The increase in the kinetic chain length with the accompanying decrease in peroxide concentration is consistent with the proposed mechanism. The higher concentration of chain-carrying radicals in reactions with more chains being started by the greater amount of peroxide present should increase the rate of radical coupling and hence decrease the kinetic chain length.

Reactions of trimethylenebenzal (III), the six-membered cyclic benzal prepared in an acid-catalyzed condensation of benzaldehyde and 1,3-propanediol, induced by di-*t*-butyl peroxide yielded *n*-propyl benzoate. This ester was isolated from one of the reaction mixtures and identified by comparison of its infrared spectra, gas chromatographic retention time, both of which were the same as those of an authentic sample, as well as by hydrolysis to benzoic acid. A termination product with a molecular weight corresponding to two trimethylenebenzal units, the infrared spectra of which showed a strong ester carbonyl absorption, was also obtained. A free radical chain sequence similar to that shown for I may be proposed for these reactions.



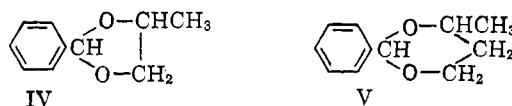
(3) For discussion of resonance stabilization of free radicals in terms of bond dissociation energies, see C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp. 40–53.

The kinetic chain lengths of the reactions of III shown in Table II, although they follow the same pattern of increasing with decreasing peroxide concentration, are noticeably shorter than in the reactions with ethylenebenzal. The shorter kinetic chain lengths may very likely result in part from a lower reactivity of the benzylic hydrogens in III toward attack by radical D· (reaction 9) compared to the reactivity of the benzylic hydrogens in I toward attack by radical B· (reaction 4). This suggestion arises from the fact that the ester content in the termination products, determined by infrared analysis, is about 40% in the reactions with III and about 30% in the reactions with I. The presence of the ester function in the termination products of both reactions indicates that the seemingly more facile hydrogen abstraction is as much a factor in determining the chain length of these isomerizations as is the endothermic β -elimination reaction. The higher ester content in the termination products of the reactions with III suggests that it is even a greater limiting factor than in the reaction with I. The lower reactivity of the benzylic hydrogens in III could be accounted for on the basis of the slower rate of radical formation in six-membered ring compounds compared to that of five-membered ring compounds.⁴

TABLE II
REACTIONS OF TRIMETHYLENEBENZAL WITH DI-*t*-BUTYL PEROXIDE AT 132°

[III]/[peroxide]	Time, hr.	% conversion	Kinetic chain length
4.9:1	18	37.8	1.03
9.7:1	18	26.0	1.3
20:1	18	18.2	1.9

The di-*t*-butyl peroxide induced reactions of propylenebenzal (IV), the cyclic benzal prepared by the acid-catalyzed reaction of benzaldehyde and 1,2-propanediol, yielded a mixture of *n*-propyl benzoate and isopropyl benzoate as major reaction products. The formation of these two esters arises



from the fact that two different β -elimination reactions of radical E· are possible. One yields radical F· and the other radical G· and subsequent hydrogen abstractions from IV by these radicals yield *n*-propyl benzoate and isopropyl benzoate, respectively.

Determinations of the relative amounts of these two esters formed in the reactions were made from their gas chromatographic peak areas. The data in Table III show that *n*-propyl benzoate was formed

(4) E. L. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, ed., Wiley, New York, N. Y., 1956, pp. 148–149.

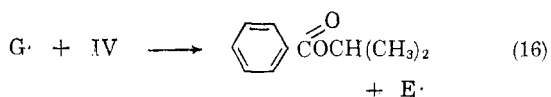
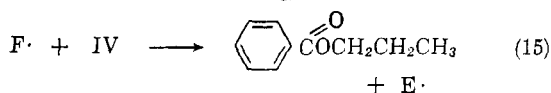
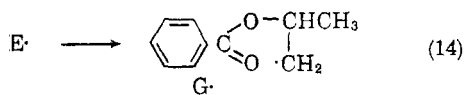
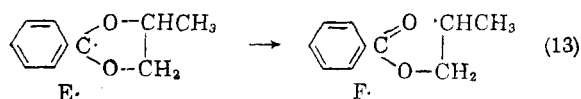


TABLE III

REACTIONS OF PROPYLENEBENZAL WITH DI-*t*-BUTYL PEROXIDE AT 132°

[IV]/[peroxide]	Time, hr.	% conversion	Kinetic chain length	<i>n</i> -Propyl ester Isopropyl ester
5.4:1	18	90	2.6	5.4
11.2:1	18	75	4.0	5.2
18.6:1	18	61	6.0	5.4

in an amount about 5.3 times greater than that of the isopropyl benzoate.

Such a distribution of the esters was not unexpected since radical E· would be expected to undergo β-elimination to form the comparatively more stable secondary radical F· faster than to form the less stable primary radical G·.

Similar reactions with 2-phenyl-4-methyl-1,3-dioxane (V), the cyclic benzal obtained from the reaction of benzaldehyde with 1,3-butanediol, yielded a mixture of *n*-butyl benzoate and *sec*-butyl benzoate. As in the reactions of IV, the *n*-alkyl ester was the predominant product (see Table IV) presumably for the same reason.

TABLE IV

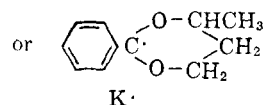
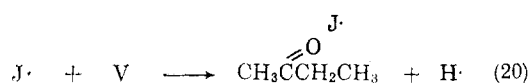
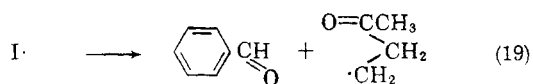
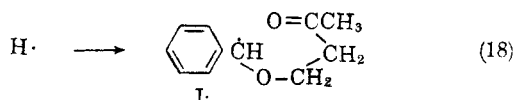
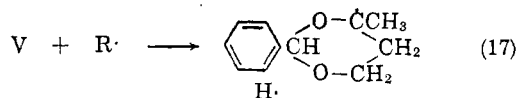
REACTIONS OF 2-PHENYL-4-METHYL-1,3-DIOXANE WITH DI-*t*-BUTYL PEROXIDE AT 135°

[V]/[peroxide]	Time, hr.	% conversion	Kinetic chain length	<i>n</i> -Butyl ester <i>sec</i> -Butyl ester
5:1	18	47	1.3	5.4
19.6:1	18	14.8	1.5	4.8
36.8:1	18	9.8	1.9	4.5

The reactions of both IV and V showed the expected increase in the kinetic chain length when the initiator concentration was decreased. Again, the chain length of the reaction is shorter in the reactions of the six-membered ring compound.

In all of the reactions of these cyclic benzals with di-*t*-butyl peroxide, benzaldehyde was formed as a reaction product. The amount ranged from less than 1% of the reaction products in the case of III to as high as 18% in some of the reactions of V. No benzaldehyde was formed when V was heated for eighteen hours at 135°. Further, heating V at this same temperature with *t*-butyl alcohol in one

case and with the butyl esters in another also failed to produce any detectable amounts of benzaldehyde. The fact that the aldehyde was found only in those reactions in which the peroxide was present suggests that the benzaldehyde was formed by a free radical reaction. One feasible reaction sequence which would yield benzaldehyde is the following:



Thus, the radical formed by abstraction of a hydrogen bonded to a carbon alpha to an ether oxygen, such as H· in the case of V, could undergo two β-elimination reactions and yield benzaldehyde. The isolation of methyl ethyl ketone along with benzaldehyde from a peroxide-induced reaction of V supports this mechanism for the formation of the aldehyde. Further, the relatively large amount of benzaldehyde formed in the case of V compared to III would also be expected if the mechanism outlined above is correct. One of the hydrogens that must necessarily be abstracted from V to yield benzaldehyde is bonded to a branched carbon and is comparatively more susceptible to abstraction than the similarly placed hydrogens in III.

Experimental⁵

Preparation of the Cyclic Acetals of Benzaldehyde.—The cyclic acetals used in this study were prepared by refluxing a benzene solution of the appropriate diol with an equivalent amount of benzaldehyde in the presence of a catalytic amount of *p*-toluenesulfonic acid. As fast as water was formed in the reaction, it was distilled as an azeotrope with benzene and collected in a Dean-Stark trap. The cyclic acetals prepared in 70–100% yield using this procedure were the following: ethylenebenzal, from benzaldehyde and ethylene glycol, b.p. 115–116° at 16 mm., n_D^{20} 1.5182; trimethylenebenzal, from benzaldehyde and 1,3-propanediol, b.p. 128–129° at 14 mm., m.p. 48°, reported, 49–51°; propylenebenzal, from benzaldehyde and 1,2-propanediol, b.p. 125° at 24 mm., n_D^{20} 1.5068; 2-phenyl-4-methyl-1,3-dioxane, b.p. 102–103° at 4 mm., n_D^{20} 1.5118, $C_{11}H_{14}O_2$; C, 74.13; H, 7.91; found, C, 74.34; H, 7.95.

(5) All boiling points and melting points are uncorrected.

(6) E. Fisher, *Ber.*, **27**, 1537 (1894).

Reaction of Ethylenebenzal with Di-*t*-butyl Peroxide.—A solution consisting of di-*t*-butyl peroxide (2.0 g., 0.014 mole) in ethylenebenzal (25 g., 0.16 mole) was heated at 130–132° for 18 hr. The infrared spectra of the resulting reaction mixture showed a strong carbonyl absorption at 1718 cm.⁻¹. Gas chromatographic analysis of the reaction mixture indicated the presence of materials with retention times the same as those of *t*-butyl alcohol, benzaldehyde, ethyl benzoate, and the unchanged ethylenebenzal. Distillation of the reaction mixture yielded 12 g. of ethyl benzoate, b.p. 209–213, *n*_D²⁰ 1.5032. The infrared spectra of the ester was identical with that of an authentic sample of ethyl benzoate. Hydrolysis of a portion of the ester yielded benzoic acid, m.p. 121–122°.

In another run under the same conditions with a solution consisting of 7.3 g. (0.05 mole) of the peroxide and 75.1 g. (0.50 mole) of the cyclic acetal, the same reaction products were found. After removing the *t*-butyl alcohol, benzaldehyde, ethyl benzoate, and unchanged ethylenebenzal by vacuum distillation, a high-boiling residue with a molecular weight of 307 (determined cryoscopically in benzene) amounting to 18.5 g. (0.06 mole) remained. The infrared spectra of this residue showed a carbonyl absorption at 1718 cm.⁻¹, and hydrolysis of the residue with 25% sodium hydroxide gave benzoic acid, m.p. 121°. Calculation of the ester content in this residue based on the carbonyl absorption band, using the carbonyl absorption of ethyl benzoate as a standard, showed that 31% of the residue consisted of benzoate ester.

Reaction of Trimethylenebenzal with Di-*t*-butyl Peroxide.—A reaction mixture consisting of 25 g. (0.15 mole) of trimethylenebenzal and 4.4 g. (0.03 mole) of di-*t*-butyl peroxide was heated for 18 hr. at 135°. Distillation of this reaction mixture yielded 8.8 g. of *n*-propyl benzoate (b.p. 112° at 5 mm., *n*_D²⁰ 1.5170). Hydrolysis of the ester gave benzoic acid, m.p. 121–122°. The infrared spectra and gas chromatographic retention time of the ester obtained in the reaction were identical with those of an authentic sample of *n*-propyl benzoate.

In another run, 88.0 g. (0.50 mole) of the benzal was heated for 18 hr. at 135° with 8.5 g. (0.054 mole) of the peroxide. Removal of *t*-butyl alcohol, benzaldehyde, *n*-propyl benzoate, and unchanged benzal by vacuum distillation left a residue with a molecular weight of 332 (determined cryoscopically in benzene) amounting to 14.9 g. (0.045 mole). The infrared spectra of the residue showed a strong ester carbonyl absorption at 1718 cm.⁻¹. Determination of the ester content from the infrared spectra, using the carbonyl absorption of *n*-propyl benzoate as a standard, indicated 41% of the residue was benzoate ester.

Determination of Kinetic Chain Lengths.—Samples of ethylenebenzal and di-*t*-butyl peroxide in the mole ratios indicated in Table I were placed in sealed tubes and heated for 18 hr. at 132° in a refluxing chlorobenzene bath. A weighed aliquot of each reaction mixture was added to a weighed amount of chlorobenzene and the resulting mixture gas chromatographed on a 5 ft. × 1/4 in. column packed with Tide. The areas of the ethyl benzoate and chlorobenzene peaks were found with a planar compensating planimeter. Knowing the moles of chlorobenzene in the sample chromatographed, the moles of ester could be calculated from the following relationship

$$\frac{\text{Moles of ester}}{\text{Moles of chlorobenzene}} = 0.78 \frac{\text{Peak area of ester}}{\text{Peak area of chlorobenzene}}$$

The correction factor, 0.78, was previously determined from the peak areas observed in the gas chromatograms of known mixtures of ethyl benzoate and chlorobenzene.

The same procedure was employed for the kinetic chain length determinations for the reactions of trimethylenebenzal shown in Table II. The correction factor used for converting the peak area ratios to mole ratios, previously found from known mixtures of chlorobenzene and *n*-propyl benzoate, was 0.72.

In the gas chromatograms of both sets of reactions, small peaks with retention times identical to that of benzaldehyde were present. Rough calculations of the benzaldehyde content based on these peak areas showed that it amounted to less than 1% of the total products in the case of trimethylenebenzal and 5–10% in the reactions of ethylenebenzal.

Reactions of Propylenebenzal with Di-*t*-butyl Peroxide.—Samples of propylenebenzal and the peroxide in the mole ratios shown in Table III were sealed in glass-stoppered tubes. The reaction mixtures were heated for 18 hr. at 132–133° in a refluxing chlorobenzene bath. Gas chromatographic analysis of the reaction mixtures on a 10 ft. × 1/4 in. column packed with 15% polyethylene succinate on Chromasorb W showed peaks with retention times identical with those of *t*-butyl alcohol, benzaldehyde, *n*-propyl benzoate, and isopropyl benzoate. The ratio of the two esters was determined from their peak areas (correction factor for converting peak area ratios to mole ratios was equal to one). The benzaldehyde content in these reaction mixtures was estimated from the peak area of this component with respect to the total area of the two esters and ranged from 1–12% of the reaction products.

Reactions of 2-Phenyl-4-methyl-1,3-dioxane with Di-*t*-butyl Peroxide.—Samples of 2-phenyl-4-methyl-1,3-dioxane and the peroxide in the mole ratios indicated in Table IV were placed in glass-stoppered tubes and heated for 18 hr. at 135° in a constant temperature oil bath. Gas chromatographic analysis of the reaction mixtures on the same column described in the previous experiment indicated the presence of *t*-butyl alcohol, benzaldehyde, *n*-butyl benzoate, and *sec*-butyl benzoate. The ratio of the two benzoates formed in each case was determined from their peak areas (correction factor for converting peak area ratio to mole ratio was one). An estimate of the benzaldehyde content with respect to the amount of the esters formed in the reactions was determined from the peak areas of these components and the amount of benzaldehyde ranged from 4–18% of the total products.

Identification of Methyl Ethyl Ketone and Benzaldehyde as Products in the Reaction of 2-Phenyl-4-methyl-1,3-dioxane with Di-*t*-butyl Peroxide.—A solution consisting of 12.2 g. (0.087 mole) of 2-phenyl-4-methyl-1,3-dioxane and 1.08 g. (0.007 mole) of di-*t*-butyl peroxide was heated in a sealed tube at 135° for 18 hr. Distillation of the resulting reaction mixture gave a low-boiling fraction (b.p. 80–90°) which showed a strong carbonyl absorption in the infrared spectra at 1710 cm.⁻¹. Gas chromatographic analysis of this distillation fraction showed a peak with retention time identical to that of methyl ethyl ketone. Reaction of a portion of this fraction with 2,4-dinitrophenylhydrazine yielded the 2,4-dinitrophenylhydrazone of methyl ethyl ketone (m.p. 117–118°; reported m.p. 117°).⁷ The next distillation fraction with a boiling temperature up to 80° at 45 mm. contained the benzaldehyde (m.p. of 2,4-dinitrophenylhydrazone, 242–243°; reported m.p., 237°).⁸ A mixture of *n*-butyl benzoate and *sec*-butyl benzoate was distilled from the reaction mixture at 90° at 1 mm. No attempt was made to separate these esters by distillation.

No benzaldehyde was detected by either infrared analysis or gas chromatographic analysis of samples of 2-phenyl-4-methyl-1,3-dioxane which had been heated without peroxide for 18 hr. at 135°. Other experiments in which this cyclic acetal was heated at the same temperature with *t*-butyl alcohol in one case and the benzoate esters in another also failed to yield any detectable amounts of benzaldehyde.

Acknowledgment.—The authors wish to acknowledge with appreciation the support of this research by a grant from the National Science Foundation.

(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., Wiley, New York, N. Y., 1956, p. 316.

(8) Ref. 7, p. 287.