[CONTRIBUTION FROM CHANDLER LABORATORY, COLUMBIA UNIVERSITY]

Alkoxide-catalyzed Autoxidative Cleavage of Ketones and Esters[1]

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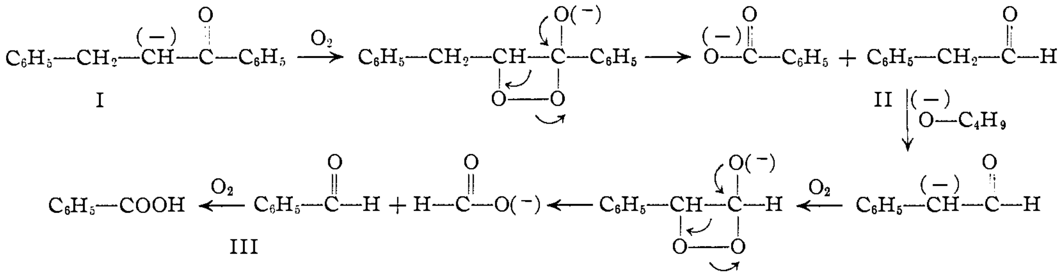
The autoxidation of several aldehydes, ketones and esters having α-hydrogen is extremely rapid in the presence of *t*-butoxide ion. The products in the main involve cleavage to acids and carbonyl compounds. Some structural limitations are placed on the reaction.

Following a study of the rapid autoxidative cleavage of quinone in the presence of alkoxide ion,[3] a number of other carbonyl-containing compounds have been investigated under similar conditions in an effort to correlate structure with ease of autoxidative cleavage. Several of the examples have been studied carefully but others, unprofitably difficult to elucidate, are reported only as examples limiting the usefulness of the autoxidative reaction.[4]

Unless otherwise stated, the substances in *t*-butyl alcohol containing potassium *t*-butoxide were oxidized by shaking with oxygen at two atmospheres. Carbonyl compounds which are sensitive to *t*-butoxide were enclosed in sealed, fragile glass vessels which were placed in the reaction mixture and liberate the carbonyl compound when shaking breaks the containing vessel. The drop in pressure was measured with a precision of ±0.2 lb. Some of the reactions were allowed to continue until the uptake of oxygen ceased completely, whereas others were interrupted shortly after the initial, rapid uptake of oxygen.

Under these conditions, benzylacetophenone (I) absorbs 1.0 equiv. of oxygen in 2.5 min. and an additional 1.1 equiv. in the following 6.3 hr. to give benzoic acid (35% based on two equivalents) and phenylbenzylglycolic acid (13%, *vide infra*). Phenylacetaldehyde (II), predicted to be the initial carbonyl compound in the conversion of I to two molecules of benzoic acid, is oxidized over a period of several hours to give benzoic acid in 70% yield. When the treatment of II with oxygen is shortened to 20 min., the temperature rises to 75° and benzaldehyde (III) is isolated. III, apparently a second intermediate, is oxidized to benzoic acid slowly, at room temperature in *t*-butyl alcohol alone and insignificantly faster in the presence of *t*-butoxide.[5]



Under the same conditions with oxygen at two atmospheres' pressure, desoxybenzoin (IV) is cleaved to benzoic acid (74%) in 2.5 min., the temperature rising to 70°. However, when oxygen is bubbled through a *t*-butanolic solution of IV and potassium *t*-butoxide, benzilic acid (60%) is isolated.

The formation of benzilic acid from desoxybenzoin and phenylbenzylglycolic acid from benzyl acetophenone[6] is explicable by analogy with the conversion of the peroxide of benzhydrylacetomesitylene to an α-diketone on treatment with alkali. Kohler and Thompson[7] suggest that the reaction be formulated through the hydroperoxide tautomers V and Va. In these terms hydroperoxides having hydrogen alpha to the carbonyl groups may decompose to hydroxide ion and α-diketones, the latter subsequently undergoing the benzilic acid rearrangement. Since both modes of cleavage are reasonably formulated as base-catalyzed, the scheme does not allow in our hands, predictable distinction between the two modes of decomposition. Cleavage of the carbon–carbon bonds seems to be favored by the higher temperature obtaining in the usual reaction conditions.

Cyclohexanone[8] reacts exothermally and very rapidly giving mainly intractable tar from which the expected cleavage product, adipaldehydic acid, could not be isolated as its known semicarbazone.[9]

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(1) Taken from a dissertation submitted May 26, 1947, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

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(3) W. von E. Doering and J. D. Chanley, THIS JOURNAL, **68**, 586 (1946).

(4) To the list of isolated examples of the slow, uncatalyzed, autoxidative reaction cited in reference 3 there may be added several more: K. v. Auwers, *Ber.*, **49**, 820 (1916); S. S. Jenkins, THIS JOURNAL, **57**, 2733 (1935); C. Dufraisse and S. Ecary, *Compt. rend.*, **223**, 1143 (1946).

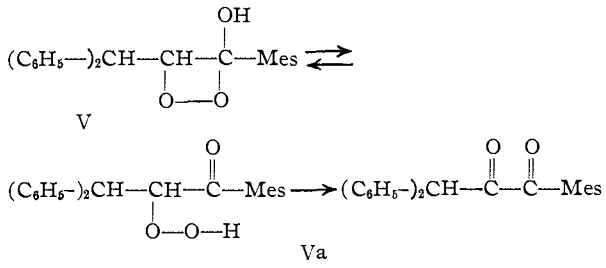
(5) That the yield of benzoic acid is not lowered by partial conversion of benzaldehyde to benzyl alcohol *via* the Cannizzaro reaction is shown by the fact that benzyl alcohol is slowly autoxidized quantitatively to benzoic acid.

(6) V. Bogdanowska [*Ber.*, **25**, 1271 (1892)] noted that phenylbenzylglycolic acid was formed in poor yield when air was passed through a warm, aqueous, potassium hydroxide solution of dibenzyl ketone and that benzilic acid was formed from desoxybenzoin upon similar treatment.

(7) E. P. Kohler and R. B. Thompson, THIS JOURNAL, **59**, 887 (1937).

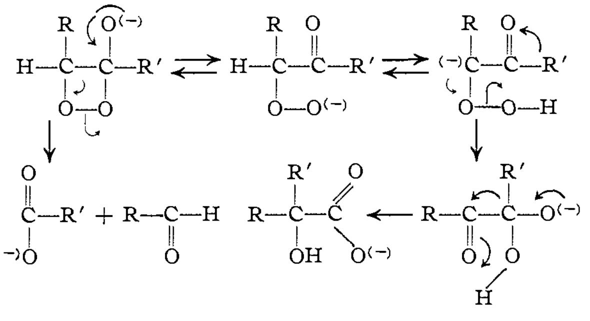
(8) Cyclohexanone, previously unoxidized under comparable conditions, is oxidized slowly at higher temperatures to adipic acid [*e.g.*, *cf.* I. V. Machinskaya and T. K. Veselovskaya, *J. Applied Chem.* (*U.S.S.R.*), **17**, 377 (1944)].

(9) W. Treibs, *Ber.*, **72**, 1194 (1939).

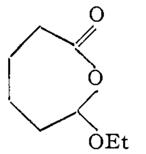


V

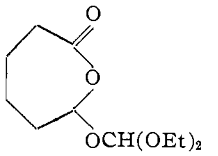
Va



However, two presumed derivatives, VI and VII, both oxidizable to adipic acid with nitric acid, are obtained by treating the crude product with ethanolic hydrogen chloride alone and with ethyl orthoformate, respectively.[10]



VI

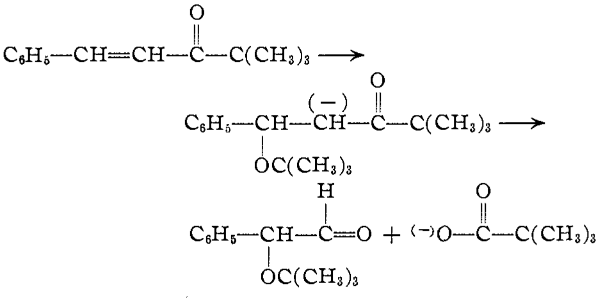


VII

In contrast to the rapid oxidation of cyclohexanone, camphor absorbs only 20% of the required amount of oxygen in 7 hr. giving camphoric acid in 5% yield.

Propiophenone, absorbing 1.5 equiv. of oxygen in 10 min., butyrophenone, absorbing 1.25 equiv. in 7 min., and acetophenone, taking up 1.25 equiv. in 2.5 hr., give benzoic acid in 63, 75 and 68% of the theoretical yield, respectively. That the anomalous rate of acetophenone might be due to condensation is excluded by experiments with dypnone. The initial oxidation of dypnone is very rapid and after 4 hr. oxidation is complete giving benzoic acid in 38% yield instead of the minimum of 68% presumably demanded if dypnone were to be an intermediate in the oxidation of acetophenone.

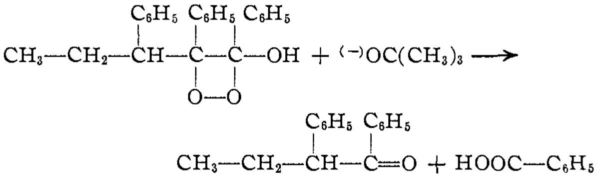
The rapid oxidation of dypnone stimulated the examination of two additional α,β-unsaturated ketones.[11] Benzalacetophenone is autoxidized very slowly to two equivalents of benzoic acid (75%). Similarly, benzalpinacolone is oxidized very slowly at room temperature and about tenfold more rapidly at 60° to pivalic acid (55%), no benzoic acid being isolated. It is suggested that dypnone is oxidized rapidly by virtue of its acidic hydrogens and that benzalicetophenone and benzalpinacolone, lacking acidic hydrogens, are oxidized only after *t*-butoxide has added to the double bond producing an oxidizable carbanion.



Although ethyl phenylacetate is oxidized to benzoic acid, *t*-butyl β-phenylpropionate, *t*-butyl cinnamate and ethyl γ-phenylbutyrate are not cleaved. The absorption of oxygen by this latter ester leads to phenylbutyric acid, presumably due to oxidation of ethanol liberated by transesterification.

While ethyl benzoylacetate, dimethyldihydroresorcinol, 3,3,5-trimethyldihydroresorcinol and diethyl malonate are not oxidized, diethyl phenylmalonate is converted to a mixture of ethyl phenylglyoxylate, *t*-butyl phenylglyoxylate and benzoic acid.[12]

The peroxide intermediate assumed in this paper is made reasonable by an experiment in which 1,2,3-triphenylpenten-1-ol peroxide[13] is cleaved to benzoic acid and ethyldesoxybenzoin by *t*-butoxide ion. No distinction can as yet be made between a simple two-electron step autoxidation of the carbanions which is somewhat incompatible with the paramagnetic character of oxygen and an attractive chain reaction involving a pair of one-electron steps.



Experimental[14]

Apparatus and Procedure for Autoxidation.—The solvent, *t*-butyl alcohol, was refluxed over and distilled from sodium, and immediately prior to use was redistilled from anhydrous aluminum *t*-butoxide directly into a heavy-walled, 1-l. centrifuge bottle. Potassium metal was added and caused to dissolve rapidly by agitating the mixture with a piano-wire whisk. The whisk was mounted by piercing the solid portion of a one-hole rubber stopper, boring a small well for lubricant and fitting a calcium chloride tube into a second hole.

A sealed, thin-walled glass vessel containing the substance to be oxidized was placed in the bottle which was then evacu-

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[10] Presumably, carbonyl compounds oxidizable to aliphatic aldehydes may be expected to give complex mixtures of products resulting from condensation and further oxidation of the initial aldehydes. For example, heptaldehyde is rapidly oxidized under the usual conditions to an unidentifiable mixture of substances.

[11] The results of an extended study of cyclic α,β-unsaturated ketones carried out by C. Harries [*Ber.*, **34**, 2105 (1901)] indicate that β-diketones, the main products (3–5%) of the autoxidation in the presence of alkali, are better obtained by oxidation with alkaline hydrogen peroxide.

[12] The anomalous autoxidation of diethyl phenylmalonate may involve simply the autoxidation of ethyl phenylacetate and *t*-butyl phenylacetate which may arise by cleavage of the phenylmalonic ester; *cf.* R. Connor, THIS JOURNAL, **55**, 4597 (1933).

[13] E. P. Kohler, *Am. Chem. J.*, **36**, 177 (1906).

[14] All melting points are corrected. We are indebted to Miss Lois May for the microanalyses. All samples of benzoic acid were identified by mixed m.p. with an authentic sample.

ated at the aspirator. Following the introduction of oxygen at a pressure of about two atmospheres, the reaction was initiated when the sealed vessel was broken by vigorous mechanical shaking. Agitation was continued at a rate of 100–150 oscillations per minute until the desired amount of oxygen had been absorbed or until uptake was immeasureably slow. The reaction vessel and oxygen tank had a volume of 3.6 l. corresponding to a pressure drop of 9.0 lb. per 0.1 mole of oxygen consumed. Table I gives the material data on substances oxidized.

Benzylacetophenone (I).—In expt. 1 (Table I), I, m.p. 71–71.5° (obtained from hydrogenation of benzalacetophenone using Adams catalyst), absorbed 4.5 lb. (0.05 mole) of oxygen in the first 2.5 min. and an additional 5.1 lb. (0.056 mole) in the following 6 hr. Concentration of the reaction mixture to dryness gave a residue which, after being washed with ether and acidified, yielded 11.9 g. of acid, m.p. 110–115°. Fractional crystallization from hexane and sublimation separated the crude material into two fractions: 4.32 g. (35% of the theoretical based on two equivalents) of benzoic acid, m.p. 122–122.5°, and 1.56 g. (13% yield) of phenylbenzylglycolic acid, m.p. 166.5–167° (reported[15] m.p. 165–166°).

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.4; H, 5.8; neut. equiv., 242.3. Found: C, 74.3; H, 5.6; neut. equiv., 240.0.

Table I

Expt.	Substance	G.	Mole	*t*-KOC_4H_9 mole	*t*-HOC_4H_9 cc.
1	Benzylacetophenone (I)	10.5	0.05	0.18	300
2	Phenylacetaldehyde (II)	9.44	.08	.24	300
3	Phenylacetaldehyde (II)	24.0	.20	.20	150
4	Benzyl alcohol	10.8	.10	.11	300
5	Desoxybenzoin (IV)	9.8	.05	.10	85
6	Cyclohexanone	20.6	.20	.20	600
7	*dl*-Camphor	15.2	.10	.20	200
8	*d*-Camphor	7.6	.05	.06	100
9	Acetophenone	6.0	.05	.17	300
10	Propiophenone	6.7	.05	.17	300
11	Isobutyrophenone	7.4	.05	.05	300
12	Dypnone	11.1	.05	.20	300
13	Benzalacetophenone	10.4	.05	.20	200
14	Benzalpinacolone	9.4	.05	.20	300
15	Ethyl phenylacetate	8.2	.05	.11	300
16	*t*-Butyl β-phenylpropionate	9.5	.046	.20	300
17	Ethyl γ-phenylbutyrate	9.83	.051	.23	250
18	*t*-Butyl cinnamate	10.0	.05	.20	300
19	Ethyl benzoylacetate	9.6	.08	.08	300
20	5,5-Dimethyldihydroresorcinol	14.0	.10	.10	300
21	2,5,5-Trimethyldihydroresorcinol	6.9	.05	.05	300
22	Diethyl malonate	8.0	.05	.05	300
23	Diethyl phenylmalonate	23.6	.10	.10	300

Phenylbenzylglycolic acid (0.7 g.) was further characterized by oxidation with 0.29 g. of potassium dichromate in a few drops of water and acetic acid. After 2 hr. at room temperature, the solution was neutralized with solid sodium carbonate and extracted with ether. Two crystallizations of the concentrated extract from 95% ethanol gave 0.21 g. of desoxybenzoin, m.p. 56–57°, which gave no depression in m.p. when mixed with an authentic sample.

Phenylacetaldehyde (II).—II in expt. 2 (Table I) absorbed 8.9 lb. (0.099 mole) of oxygen in the first 15 min. and an additional 5.1 lb. (0.056 mole) in the next 4.3 hr. The filtered precipitate was dissolved in water and on acidification gave 10.5 g. of crude benzoic acid, m.p. 119–120°, which was recrystallized from water, giving 6.64 g. of pure benzoic acid, m.p. 122–122.5° (68% yield).

In shortening the total reaction time to 20 min., II in expt. 3 (Table I) absorbed 12.5 lb. (0.4 mole) of oxygen, the temperature rising to 75°. The solution was extracted once with saturated potassium carbonate solution, the alcohol layer was separated by centrifuging and treated with saturated, aqueous sodium bisulfite, additional solid sodium bisulfite being added to maintain saturation. After remaining at 4° for two days, the solution deposited 8.06 g. of a sodium bisulfite addition product (19% yield) which was decomposed with 10% aqueous sodium carbonate. The ethereal extract was added to an alcoholic solution of 6.0 g. of 2,4-dinitrophenylhydrazine. The ether having been evaporated, 6 cc. of concentrated hydrochloric acid was added and the solution refluxed for 30 min. Upon cooling, the solution deposited 4.9 g. of benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 180–198°, which on recrystallization from 800 cc. of 95% ethanol and chloroform gave 1.99 g. of pure material, m.p. 236–237°, showing no m.p. depression on admixture with an authentic sample.

Benzaldehyde (III).—A 0.40 *M* solution of III (10 cc., 0.1 mole) in anhydrous *t*-butyl alcohol (250 cc.) was found to be 8×10^{-5} *M* in perbenzoic acid by iodometric titration with 0.0966 *M* sodium thiosulfate. After being shaken for 4 hr. under *ca.* 30 lb. of oxygen the solution had absorbed 0.025 mole of oxygen and was 0.0022 *M* in perbenzoic acid. The solution was treated with 0.4 mole of potassium *t*-butoxide in 100 cc. of anhydrous *t*-butyl alcohol and shaken with oxygen for 15 hr., 0.1 mole of oxygen being consumed. Titration of a 2-cc. aliquot showed that 0.09 mole of base had been neutralized in the reaction. Benzoic acid (10.51 g.) was isolated in 82% of the theoretical yield.

Benzyl Alcohol.—In expt. 4 (Table I) benzyl alcohol absorbed 6.0 lb. (0.066 mole) in 9 hr., affording 8.33 g. (66% yield) of benzoic acid, m.p. 119–122.5° without recrystallization.

Desoxybenzoin (IV).—In expt. 5 (Table I) IV (prepared by the method of Sudborough[16]) reacted with 0.076 mole of oxygen in 2.5 min., the temperature reaching 70°. The precipitate yielded 9.0 g. of benzoic acid (74% yield), m.p. 121–122° without recrystallization.

Oxygen at atmospheric pressure was bubbled into 200 cc. of anhydrous *t*-butyl alcohol containing 0.2 mole of potassium *t*-butoxide for one hour. IV (20 g., 0.1 mole) was added and the treatment with oxygen was continued for 1.5 hr. The filtered precipitate was washed with ether and acidified with 2 *N* hydrochloric acid, giving 15.5 g. of material, m.p. 146–149°. The latter was partially dissolved in 500 cc. of boiling water, treated with sodium carbonate and filtered from 1.95 g. of material, m.p. 200–201.5°, which was not investigated further. Acidification of the alkaline solution precipitated 7.37 g. of benzilic acid, m.p. 147° (no depression with an authentic sample). Ether extraction of the aqueous mother liquor afforded 2.29 g. of crude acid. From the alcoholic filtrate of the reaction mixture additional benzilic acid (1.1 g.) was obtained, bringing the total yield to 60%.

Cyclohexanone.—In 4 min. the temperature rose to 83° and 0.18 mole of oxygen was absorbed in expt. 6 (Table I) when cyclohexanone was oxidized. Removal of most of the solvent by distillation left a yellow precipitate which was washed with anhydrous ether and added to a solution of 100 cc. of anhydrous ethanol and 45 cc. of ethyl orthoformate (0.27 mole). Hydrogen chloride was bubbled through the cooled (−10°) solution for 20 min. After standing for 3 hr., the solution was neutralized with excess anhydrous sodium bicarbonate, diluted with ether and washed successively with cooled, saturated sodium chloride. Concentration of the dried, ethereal solution left a viscous residue which gave, after flash distillation, 4 g. of an orange-yellow liquid, presumably ϵ-(diethoxymethoxy)-hexanolactone (VII, 8.7% yield). A portion of VII which had been evaporatively distilled four times had the following physical constants: $n^{22.5}D$ 1.4319, $d^{22.5}$ 1.0471; M_D calcd. 57.38, found 57.49.

Anal. Calcd. for $C_{11}H_{20}O_5$: C, 56.9; H, 8.7; C_2H_5O, 38.8. Found: C, 56.6; H, 8.6; C_2H_5O, 38.8.

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[15] O. Widman, *Ber.*, **49**, 477 (1916).

[16] J. J. Sudborough, *J. Chem. Soc.*, **71**, 218 (1897).

A small amount of VII treated with concentrated nitric acid gave adipic acid, m.p. 149–150°, identical with an authentic sample.

The solid yellow residue obtained as above from the oxidation of 0.1 mole of cyclohexanone was washed thoroughly with anhydrous ether, suspended in 80 cc. of anhydrous ethanol, cooled in a salt–ice-bath and treated with hydrogen chloride gas for 20 min. By proceeding as above, a viscous material was obtained from which vacuum distillation separated 0.6 g. and evaporative distillation afforded an additional 1.2 g. (total yield 11%) of a colorless liquid, presumed to be ε-ethoxyhexanolactone (VI), b.p. 76–79° (3 mm.). Two evaporative distillations gave purer VI: $n^{26}\text{D}$ 1.4440, $d^{26.5}$ 1.0457; $M\text{D}$ calcd. 40.24, found 40.18.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.3; H, 8.3.

A small amount of VI treated with concentrated nitric acid gave adipic acid, m.p. 149–150°.

dl-**Camphor**.—In expt. 7 (Table I), oxygen was bubbled through the reaction mixture for 4 hr. After the addition of water, the aqueous layer was extracted with ether, acidified and again extracted with ether. Concentration of this ether extract gave 2 g. (10% yield) of crude camphoric acid, m.p. 197–198°; after recrystallization from acetic acid, m.p. 199–200° (reported[17] m.p. 202–203°).

d-**Camphor**.—In expt. 8 (Table I) *d*-camphor ($[\alpha]^{23}\text{D}$ +43°) absorbed 0.012 mole of oxygen in 7 hr. The reaction product, obtained by removing the solvent, was dissolved in water, extracted with ether, acidified and extracted again with ether giving 0.53 g. (5.3% yield) of *d*-camphoric acid; after recrystallization from acetic acid, m.p. 184–185° (reported[18] m.p. 187°).

Acetophenone.—Acetophenone, in expt. 9 (Table I), was oxidized slowly, 0.062 mole being consumed in 2.5 hr. The aqueous solution of the concentrated reaction mixture was extracted with ether, and acidified, giving 3.8 g. of benzoic acid, m.p. 115–121°, and an additional 0.5 g. by ether extraction (total yield 68%). Recrystallization from *n*-heptane gave 3.44 g. of benzoic acid, m.p. 120–122°.

Propiophenone.—In expt. 10 (Table I) propiophenone consumed 0.061 mole of oxygen in 10 min., affording 3.85 g. of benzoic acid, m.p. 120–121° (63% yield).

Isobutyrophenone.—In expt. 11 (Table I), isobutyrophenone absorbed 0.063 mole of oxygen in 7 min. to yield 6.6 g. of dark colored acid, m.p. 116–121°, a *n*-heptane solution of which, after filtration from 0.29 g. of unidentified material, deposited 4.58 g. of benzoic acid, m.p. 121–122.5° (75% yield).

Dypnone.—In expt. 12 (Table I) dypnone (prepared by the method of Kohler[19] absorbed 0.11 mole of oxygen in 12 min. The concentrated reaction mixture was dissolved in water and thoroughly extracted with ether giving an undistillable dark brown tar. Acidification and ether extraction of the aqueous solution gave a solid residue which upon sublimation yielded 4.0 g. of benzoic acid, m.p. 119–121° (33% based on two equivalents).

Benzalacetophenone.—In expt. 13 (Table I) benzalacetophenone, m.p. 56–57°, absorbed 9.3 lb. (0.103 mole) of oxygen in 18.5 hr. The reaction mixture was concentrated to about 50 cc. and diluted with water dropwise until the precipitate had dissolved. The ethereal extract was washed several times with water, the aqueous washings being combined with the main aqueous phase. Acidification of the aqueous solution gave 1.16 g. of benzoic acid, m.p. 119–122° (75% based on two equivalents). Concentration of the ethereal layer afforded 0.17 g. of material, m.p. 218–220°, not further identified.

Benzalpinacolone.—Benzalpinacolone[20] (expt. 14, Table I) absorbed 5.4 lb. (0.06 mole) of oxygen in 42 hr. at 27° and 6.1 lb. (0.066 mole) in 4 hr. at 60°. The latter reaction mixture, after concentration, was diluted with ether, and extracted with water. Distillation of the dried, ethereal extract of the combined, acidified washings gave 2.8 g. of trimethylacetic acid, m.p. 33–35° (55% yield).

Ethyl Phenylacetate.—Ethyl phenylacetate (expt. 15, Table I) absorbed 0.11 mole of oxygen in 8.5 hr., affording 3.5 g. of benzoic acid (56% yield).

Preparation and Oxidation of *t*-Butyl β-Phenylpropionate.—*t*-Butyl β-phenylpropionate, b.p. 86–88° at 1.5 mm., $n^{25}\text{D}$ 1.4801, was prepared in 55% of the theoretical yield by the method of Abramovitch, *et al.*[21]

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 75.7; H, 8.7. Found: C, 75.8; H, 8.8.

In expt. 16 (Table I) this ester absorbed 0.01 mole of oxygen in 43 hr. Bubbling carbon dioxide into the reaction mixture precipitated a thick paste which was dissolved in water. The solution was brought to *p*H 8 by treating with solid carbon dioxide and extracting with ether. Acidification and ether extraction of the aqueous phase gave dark brown material which was sublimed to yield 0.16 g. of β-phenylpropionic acid, m.p. 46–47°. The dried ethereal extract was distilled giving 3.66 g. of *t*-butyl β-phenylpropionate, b.p. 80–85° at 1 mm. (39% recovery). No products of oxidation could be isolated.

Ethyl γ-Phenylbutyrate.—Ethyl γ-phenylbutyrate, prepared by the method of von Braun,[22] in expt. 17 (Table I), reacted with 7.3 lb. (0.081 mole) of oxygen in 23 hr. The residue obtained from concentration of the reaction mixture, upon acidification with concentrated hydrochloric acid, gave 3.83 g. of γ-phenylbutyric acid, m.p. 50–51°, mixed m.p. 50–51°, representing a recovery of 41.7% of the starting material.

***t*-Butyl Cinnamate**.—In expt. 18 (Table I) *t*-butyl cinnamate (prepared by the method of Abramovitch, *et al.*[21]) failed to react with oxygen over a period of 5.5 hr. There was recovered 6.0 g. (54%) of the ester and 2.55 g. of cinnamic acid, m.p. 132–133°, representing a total recovery of 88% of the starting material.

Ethyl Benzoylacetate.—In expt. 19 (Table I), ethyl benzoylacetate gave a precipitate and failed to absorb oxygen. The precipitated potassium salt was removed by centrifugation, dissolved in 250 cc. of 2 *N* potassium hydroxide and shaken under *ca.* two atmospheres of oxygen. No oxygen was absorbed.

5,5-Dimethyldihydroresorcinol.—In expt. 20 (Table I), a homogeneous solution absorbed no oxygen in 17 hr. Even at 60° for 4 hr. no oxygen was taken up, 5,5-dimethyldihydroresorcinol being recovered in 87% yield.

2,5,5-Trimethyldihydroresorcinol.—In expt. 21 (Table I), a homogeneous solution of 2,5,5-trimethyldihydroresorcinol (prepared by the method of Desai[23]) absorbed no oxygen.

Diethyl Malonate.—Neither a heterogeneous mixture (expt. 22, Table I) of diethyl malonate nor the homogeneous solution of 8.0 g. (0.05 mole) of diethyl malonate in 300 cc. of 2 *N* aqueous potassium hydroxide absorbed any oxygen.

Diethyl Phenylmalonate.—In expt. 23 (Table I), diethyl phenylmalonate consumed 0.1 mole of oxygen in 1 hr. After concentration to approximately 100 cc. and addition of ether, the reaction mixture was washed with water until neutral. The aqueous washings were combined, acidified and extracted with ether to give, after recrystallization from *n*-hexane, 1.63 g. of benzoic acid, m.p. 119–120°. The dried ethereal extract was distilled giving three fractions: (a) 0.77 g., b.p. below 50° at 0.2 mm., $n^{25}\text{D}$ 1.4982; (b) 3.46 g., b.p. 82° at 0.2 mm., $n^{25}\text{D}$ 1.5011; and (c) 5.61 g., b.p. 82–112° at 0.3 mm., $n^{25}\text{D}$ 1.4880.

Hydrolysis with concentrated hydrochloric acid of 0.39 g. of fraction (a) gave 0.02 g. of benzoic acid, m.p. 120–121°. Evaporative distillation of 1.96 g. of fraction (b) gave 0.14 g. of material evaporating at room temperature at 0.05 mm., and 0.94 g. of ethyl phenylglyoxylate evaporating at 45° at 0.05 mm. (see analysis) leaving a residue of 0.26 g. of higher boiling material.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.4; H, 5.7. Found: C, 67.1; H, 5.4.

The 2,4-dinitrophenylhydrazone of fraction (b) was prepared from 0.33 g. of un-redistilled liquid, giving 0.44 g. of yellow-orange needles, m.p. 148–176°. The derivative, recrystallized first from ethanol and then from benzene, m.p. 183–184.8° dec., is apparently the 2,4-dinitrophenylhydrazone of *t*-butyl phenylglyoxylate.

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: C, 56.0; H, 4.7; N, 14.5. Found: C, 55.8; H, 4.5; N, 14.7.

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(17) O. Aschan, *Ann.*, **316**, 196 (1901).

(18) O. Aschan, *Ber.*, **27**, 2001 (1894).

(19) E. P. Kohler, *Am. Chem. J.*, **31**, 658 (1904).

(20) Prepared by the method described in "Organic Syntheses," Coll, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 81.

(21) B. Abramovitch, J. C. Shivers, B. E. Hudson and C. R. Hauser, THIS JOURNAL, **65**, 986 (1943).

(22) J. v. Braun, *Ber.*, **44**, 2867 (1911).

(23) R. D. Desai, *J. Chem. Soc.*, 1079 (1932).

Evaporative distillation of 2.1 g. of fraction c gave 1.5 g. of material distilling at 45° at 0.05 mm., n^{25}_D 1.4952, d^{21} 1.1416, and 0.29 g. of higher boiling liquid. The 2,4-dinitrophenylhydrazone of fraction c was prepared from 0.33 g. of un-redistilled material, giving 0.06 g. of orange needles, m.p. 186–189.5° (rapid heating), m.p. 184–185° dec. after recrystallization from ethanol and then from benzene. A mixed m.p. with the 2,4-dinitrophenylhydrazone of fraction b was 184–185° dec.

A small portion of fraction c was heated with concentrated hydrochloric acid for several hours. Concentration of an ethereal extract of the acidic solution gave an oil which was treated with an alcoholic solution of phenylhydrazine hydrochloride. A small amount of a yellow phenylhydrazone was obtained, which after recrystallization from ethanol melted at 158–159° dec. (reported by Dilthey and Böttler[24] for the phenylhydrazone of phenylglyoxylic acid, m.p. 160–161°).

1,2,3-Triphenylpenten-1-ol Peroxide. (a) Preparation.—1,2,3-Triphenylpenten-1-ol was prepared according to Kohler[13] by instantly treating a moist ethereal solution of the decomposed Grignard addition product of ethylmagnesium bromide and benzaldesoxybenzoin with air. Kohler reported the isolation of two isomers, m.p. 166° and m.p. 109° (no decomposition), neither of which liberated iodine from potassium iodide. Repeated crystallization, first from an acetone–heptane mixture and finally from acetone gave a product, m.p. 149–149.5° dec., which liberated iodine from an alcoholic solution of potassium iodide.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.8; H, 6.4. Found: C, 79.6; H, 6.2.

(b) **Cleavage.**—A solution of 0.01 mole of potassium *t*-butoxide and 3.46 g. (0.01 mole) of 1,2,3-triphenylpenten-1-ol peroxide in 100 cc. of dry *t*-butyl alcohol was sealed in a bottle under nitrogen, shaken for 2 hr., and then allowed to remain overnight. After neutralization with 2 *N* hydrochloric acid and distillation of the solvent, first water and then ether were added to the solution. The ethereal layer was washed twice with a 2 *N* sodium carbonate solution, the washings being added to the aqueous fraction which was then acidified, yielding 0.52 g. of benzoic acid, m.p. 122–122.5°. Ether extraction of the mother liquor afforded an additional 0.19 g. of acid (total yield 58%). The ethanolic solution of the red oil resulting from concentration of the ethereal fraction yielded 1.27 g. (54% yield) of ethyldesoxybenzoin, m.p. 56–57°, reported m.p. 58°.[25]

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.2. Found: C, 85.6; H, 7.1.

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[24] W. Dilthey and Th. Böttler, *Ber.*, **52**, 2040 (1919).

[25] V. Meyer and L. Oelkers, *ibid.*, **21**, 1295 (1888).

[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

β-Propiolactone. XIV.[1] β-Isovalerolactone

BY T. L. GRESHAM, J. E. JANSEN, F. W. SHAVER AND W. L. BEEARS

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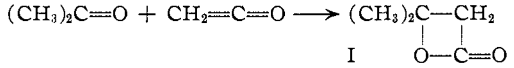
The reactions of β-isovalerolactone are similar to those of β-propiolactone except for a rapid loss of carbon dioxide in polar solvents and a greater difficulty of substitution at the β-tertiary carbon atom. Polymerization, hydrolysis and reactions of β-isovalerolactone with halogen acids, alcohols, phenols, amines, dithiocarbamic acid salts and thionyl chloride are discussed.

In the continuation of our work on β-lactones,[1] it was of interest to compare the reactivity of a β-lactone disubstituted in the β-position. For this purpose, β-isovalerolactone[2] (I) was prepared from ketene and acetone.

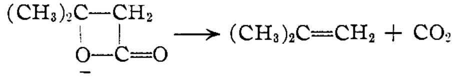


$$(CH_3)_2C{=}O + CH_2{=}C{=}O \longrightarrow \begin{array}{l}(CH_3)_2C{-}CH_2\\ \quad\ \ |\qquad |\\ \quad\ \ O{-}C{=}O\end{array}$$

I

This β-lactone I exhibits the characteristic shift of carbonyl absorption to shorter wave length,[3] and is reasonably stable at ordinary temperatures.

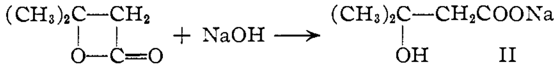
In water at room temperature, I decomposes rapidly to carbon dioxide and isobutylene to the near exclusion of hydrolysis. This is probably due to a tendency for ionization at the tertiary carbon–oxygen bond with subsequent shift of electrons and expulsion of carbon dioxide occurring more rapidly



$$\begin{array}{l}(CH_3)_2\overset{+}{C}{-}CH_2\\ \quad\ \ |\qquad |\\ \quad\ \ \underset{-}{O}{-}C{=}O\end{array} \longrightarrow (CH_3)_2C{=}CH_2 + CO_2$$

than attack of an ion at the tertiary carbon. This ease of loss of carbon dioxide in polar solvents and the difficulty of attack at the β-tertiary carbon atom limits the yields of products obtained by this type of reaction. These are the only significant differences in the reactions of I as compared to the unsubstituted β-lactone. Reactions due to attack at the carbonyl group with ordinary ester type ring opening occur in a normal manner.

The very rapid reaction of hydroxyl ion with β-propiolactone is attributed[4] to normal ester hydrolysis at the carbonyl group. This interpretation is confirmed by the hydrolysis of I which occurs rapidly and completely provided decarboxylation is avoided by adding I to the aqueous base. II was identified by reduction to isovaleric acid.

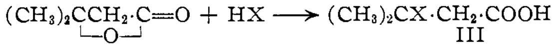


$$\begin{array}{l}(CH_3)_2C{-}CH_2\\ \quad\ \ |\qquad |\\ \quad\ \ O{-}C{=}O\end{array} + NaOH \longrightarrow \begin{array}{l}(CH_3)_2C{-}CH_2COONa\\ \qquad\quad |\\ \qquad\ \ OH\end{array}$$

II

Polymers of I are formed similar to those for β-propiolactone[5] and are polyesters of low molecular weight. They are characterized by pyrolysis to β,β-dimethylacrylic acid, hydrolysis to β-hydroxyisovaleric acid and alcoholysis to β-hydroxyisovalerates.

Attempts to prepare β-bromoisovaleric acid from I and sodium bromide in water resulted in poor yields due to loss of most of I to carbon dioxide and isobutylene. However, fairly good yields of β-halogen acids III were obtained by addition of I to concentrated aqueous halogen acids.



$$\underbrace{(CH_3)_2CCH_2{\cdot}C}_{O}{=}O + HX \longrightarrow (CH_3)_2CX{\cdot}CH_2{\cdot}COOH$$

III

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[1] For paper XIII of this series, see THIS JOURNAL, **74**, 1323 (1952).

[2] β-Isovalerolactone was first prepared from β-bromoisovaleric acid by Sidney M. Hagman, Inaugural Dissertation, Lund University, 1924. Hydrolysis studies with acids and bases were reported also.

[3] Unpublished data from this Laboratory.

[4] P. D. Bartlett and Gilbert Small, Jr., THIS JOURNAL, **72**, 4868 (1950).

[5] T. L. Gresham, J. E. Jansen and F. W. Shaver, *ibid.*, **70**, 998 (1948).