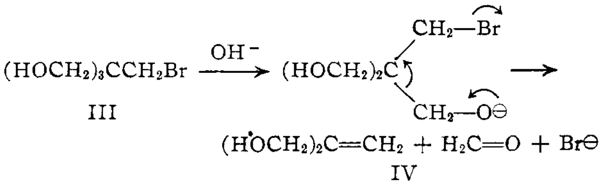
erating along the chain of the 1,3-bromohydrin moiety of III by a mechanism similar to the one postulated by Searles and Gortatowski[8] for the cleavage of 3-bromo-2,2-dimethyl-1-propanol by base.



It is interesting to note that while IV dissolved in carbon tetrachloride absorbs bromine readily, the bromine absorptive capacity of its dichloride is not appreciable, in agreement with the observation of Mooradian and Cloke.[9]

Experimental[10]

Pentaerythrityl Monobromide (III).—The procedure of Beyaert and Hansens[11] was modified using 48% in place of 66% hydrobromic acid. Recrystallization of the final product from a mixture of 2 parts by volume of ethyl acetate and 3 parts by volume of chloroform gave monobromopentaerythritol (III) melting at 75–76° (reported m.p. 70–72°,[11] 76°[12]); yield 54% of the theoretical based on pentaerythritol.

Reaction of Pentaerythrityl Monobromide (III) with Alcoholic Potassium Hydroxide.—The procedure was essentially based on the method of Govaert and Beyaert.[7] A solution of 13 g. of potassium hydroxide (0.23 mole) in 190 ml. of absolute ethyl alcohol was added to a solution of 39.8 g. (0.2 mole) of pentaerythrityl monobromide in 160 ml. of absolute ethyl alcohol. The mixture was stirred for two hours at room temperature, refluxed on the steam-bath for five minutes, cooled in an ice-bath, filtered from the precipitated potassium bromide, neutralized with acetic acid and concentrated *in vacuo* to a viscous residue. Fractionation through a Vigreux column at reduced pressure gave two fractions: fraction i, b.p. 85–100° (1–2 mm.), 4 g.; fraction ii, 3,3-bis-(hydroxymethyl)-oxetane, b.p. 135–138° (1–2 mm.), 16.5 g. (literature b.p. 128° (0.4 mm.)[7]).

Identification of Fraction (i).—Refractionation of this fraction gave a colorless liquid boiling at 93–95° (2 mm.), n^{25}_{D} 1.4731, d^{27}_{4} 1.077 (lit. b.p. for 2-methylene-1,3-propanediol 125–126° (18 mm.[9]), n^{20}_{D} 1.4758,[9] d^{20}_{4} 1.0791[9]). The compound gave positive tests for unsaturation with bromine in carbon tetrachloride and with a solution of potassium permanganate.

Acetylation was accomplished by heating on the steam-bath for 12 hours a mixture of 10 g. of 2-methylene-1,3-propanediol (IV) with 80 ml. of acetic anhydride and 1 ml. of dry pyridine. Removal of the excess acetic anhydride under reduced pressure was followed by the addition of ice and neutralization with sodium bicarbonate. Extraction with ether gave an oil which was fractionated through a Vigreux column. The yield of ester boiling at 85–87° (1 mm.) was 17.5 g. (90%), n^{25}_{D} 1.4335, d^{28}_{4} 1.072, sapon. equiv. 86 (calcd. for the diacetate of 2-methylene-1,3-propanediol, 86).

Conversion of IV to the dichloride was accomplished by addition over a period of 2 hours at 0° of 29 g. of thionyl chloride dissolved in 20 ml. of dry chloroform to a well-stirred solution of 8.8 g. of IV, 15 ml. of dry pyridine and 10 ml. of dry chloroform. The mixture was then refluxed for two hours, allowed to stand overnight and then poured onto ice and neutralized with solid sodium bicarbonate. Extraction with ether followed by washing the ether extracts with dilute sulfuric acid gave, after removal of the solvent, an oil which was fractionated to give 3.2 g. of 3-chloro-2-chloromethyl-1-propene, b.p. 137–138° (756 mm.), n^{28}_{D} 1.4720, d^{27}_{4} 1.178 (lit. b.p. 138–138.3°,[9] n^{20}_{D} 1.4754,[9] d^{20}_{4} 1.1782[9]).

Pentaerythritol Monomethyl Ether (II).—A solution of 22 g. (0.19 mole) of 3,3-bis-(hydroxymethyl)-oxetane in 60 ml. of methyl alcohol was added in the course of 5 minutes to 60 ml. of methyl alcohol containing 0.25 ml. of concentrated sulfuric acid. The mixture was kept at room temperature for 48 hours, neutralized with sodium bicarbonate, cooled in an ice-bath, filtered from the precipitated salt and concentrated *in vacuo* to a viscous residue which solidified upon standing. The crude product was dried in a vacuum desiccator, powdered and extracted exhaustively in a Soxhlet extractor with 100 ml. of dry ether. The ether extracts were cooled and filtered to give 23 g. (82%) of methyl pentaerythrityl ether (II) melting at 67–68°. One recrystallization from a mixture of 12 ml. of chloroform and 8 ml. of ethyl acetate raised the m.p. to 71–72°, recovery 90%. Two more recrystallizations raised the melting point to 72–73° (reported m.p. 72°,[4] 71–72°,[5] 70°,[6] 60–67°[13]).

The crude ether (m.p. 67–68°) was acetylated with acetic anhydride and pyridine by a procedure similar to the one described previously for the esterification of IV. The yield of ester boiling at 117–119° (1 mm.) was 71% of the theoretical based on the crude ether, n^{20}_{D} 1.4408, d^{28}_{4} 1.119.

Anal. Calcd. for $C_{12}H_{20}O_7$: C, 52.17; H, 7.30; sapon. equiv., 92. Found: C, 52.32; H, 7.23; sapon. equiv., 91.5.

Tritylation of the crude ether (1.2 g., 0.08 mole) with triphenylchloromethane (7.3 g., 0.026 mole) and dry pyridine (12 ml.) was carried out as previously reported for the monoethylene glycol ether of pentaerythritol.[2] Recrystallization from acetone gave 4.2 g. (60%) of product melting at 219–220°.

Anal. Calcd. for $C_{63}H_{56}O_4$: C, 86.26; H, 6.43. Found: C, 86.03; H, 6.50.

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[8] S. Searles and M. J. Gortatowski, THIS JOURNAL, **75**, 3030 (1953).

[9] A. Mooradian and J. B. Cloke, *ibid.*, **67**, 942 (1945).

[10] Melting points and boiling points are not corrected.

[11] M. Beyaert and M. Hansens, *Natuurw. Tijdschr. (Belg.)*, **22**, 249 (1940).

[12] F. Govaert and M. Beyaert, *ibid.*, **21**, 20 (1939).

[13] R. H. Barth (to Heyden Chem. Corp.) U. S. Patent 2,644,013 (June 30, 1953); *C. A.*, **48**, 5211b (1954).

On the Air Oxidation of 2-Phenylcyclopentanone

BY KURT MISLOW AND ALLAN K. LAZARUS

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We have had occasion to reëxamine the spectral properties[1] of 2-phenylcyclopentanone. While the infrared spectrum was identical with that earlier reported, the ultraviolet spectrum was distinctly different. We are now in a position to explain this discrepancy.

In agreement with the findings of Pascual and Crespo,[2] we have found that the ketone is rapidly oxidized by air to γ-benzoylbutyric acid. Comparison of the ultraviolet spectrum of the acid (Fig. 1, curve A) with that of freshly prepared and repeatedly crystallized ketone (Fig. 1, curve B) reveals that the acid has a maximum at 241.5 mμ, ϵ 1.2 × 10^4, precisely at a minimum point for the

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[1] K. Mislow and C. L. Hamermesh, THIS JOURNAL, **77**, 1590 (1955).

[2] J. Pascual and R. Crespo, *Anales real soc. españ. fís. y quím.*, **48B**, 273 (1952).

ketone, ϵ 50. In consequence the presence of even minute quantities of acid in the ketone causes a radical change in spectrum, which may serve as a basis for analysis; complete spectra synthesized on the basis of this single-point estimation faithfully reflect the experimental curves of deteriorated mixtures. The rapidity of the oxidation follows from our finding that a sample of ketone, on standing in air at room temperature for one month, contained *ca.* 40% of γ-benzoylbutyric acid; on the other hand, a sample of 99.9% spectrally pure ketone remained more than 99% pure after standing under nitrogen in the refrigerator for one month. The sensitivity of the method may be gauged by examination of the slight shoulder at 241.5 mμ in curve B: it can be estimated that this shoulder, if due to admixture of γ-benzoylbutyric acid, represents 0.03–0.04% contamination.

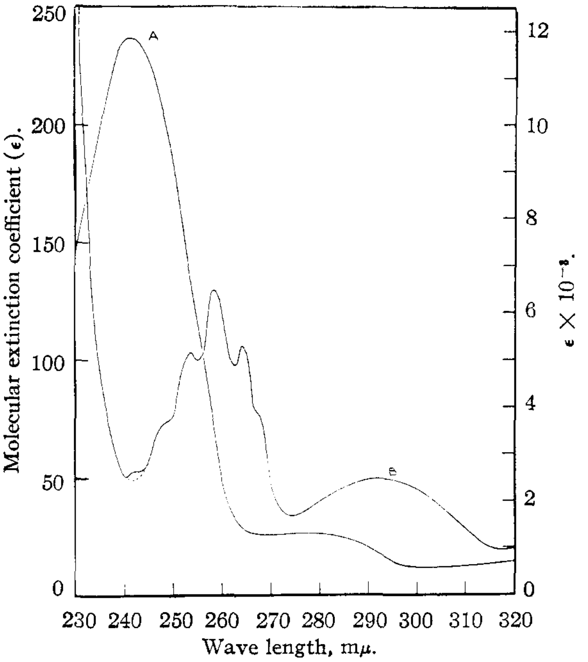

Fig. 1.—Ultraviolet spectra of γ-benzoylbutyric acid (curve A), and of 2-phenylcyclopentanone (curve B). The values of the extinction coefficients are recorded on the right-hand ordinate for A, and on the left-hand ordinate for B; solvent 95% ethanol.

Obviously earlier preparations[3] of 2-phenylcyclopentanone had yielded, in fact, γ-benzoylbutyric acid; of more immediate interest is the observation that the particular sample used for the earlier determination of the ultraviolet spectrum[1] was contaminated by γ-benzoylbutyric acid to the extent of about 14%. Any slight oxidation of the optically active ketone[1] which might have gone unrecognized would have had the effect of lowering its specific rotation, the product of oxidation being itself optically inactive. The conclusions advanced[1] therefore retain their validity. However, it is unlikely that the relative magnitude of the rotation of the cyclic ketone can be attributed, as originally felt, to a large difference in the ultraviolet absorption spectra of 3-phenyl-2-butanone and of 2-phenylcyclopentanone; the spectra of these two compounds are in fact closely similar. We shall reserve further comment pending an examination of the rotatory dispersions of these compounds.

Experimental

2-Phenylcyclopentanone.—This compound was prepared[1] by treatment of 2-chlorocyclopentanone with phenylmagnesium bromide. In the workup of the chloroketone care was taken to isolate the fraction boiling at 75° (11 mm.), it being known[4] that the chlorination of cyclopentanone results in a variety of products. Freshly distilled 2-phenylcyclopentanone, b.p. 96° (0.4 mm.), was recrystallized from ligroin five times, m.p. 36.5–37.5°. Its ultraviolet spectrum (curve B) was determined three hours subsequent to the final crystallization. A sample was sealed under nitrogen and kept in the refrigerator for one month; its spectrum after storage was substantially unchanged.

Air Oxidation of 2-Phenylcyclopentanone.—A sample of 2-phenylcyclopentanone was allowed access to air for a period of six weeks. During this time spectra were determined at intervals of 11, 21 and 33 days, revealing successively increasing amounts (4.8, 7.4, 39%) of γ-benzoylbutyric acid. Over this period the material changed from large, flat, colorless, transparent plates to a liquid, which gradually turned light yellow, and eventually to an oily, high-melting solid. The last product was triturated with a mixture of carbon tetrachloride and 5% sodium carbonate; the aqueous layer was acidified and the resulting solid, recrystallized from benzene–ligroin and water, melted at 127–127.5°, mixed m.p. with authentic γ-benzoylbutyric acid 126.5–127°.

The semicarbazone melted at 210–212° dec. The ultraviolet spectrum is reproduced in curve A.[5]

A sample of ketone was allowed to stand, with intermittent access to air, in the refrigerator for one month. In appearance the material consisted of large, lustrous plates characteristic of the ketone. Recrystallized three times from ligroin, the material melted at 36–37°. Its spectrum, recorded three hours subsequent to its last crystallization, revealed that it was 9.8% contaminated by γ-benzoylbutyric acid. Appearance and melting point cannot, therefore, be employed as sole criteria of purity in the case of this ketone.

Acknowledgment.—The authors gratefully acknowledge assistance afforded them by Dr. Alvin I. Kosak in the determination of the spectra. A grant from Research Corporation supported a part of this work.

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[3] V. M. Mitchovitch, *Compt. rend.*, **200**, 1601 (1935); J. Pascual, J. Sanchez and R. Crespo, *Anales real soc. españ. fis. y quim.*, **45B**, 583 (1949).

[4] H. W. Wanzlick and G. Gollmer, *Chem. Ber.*, **88**, 281 (1955).

[5] C. D. Gutsche and K. L. Seligman, THIS JOURNAL, **75**, 2579 (1953), report λ_{max}^{EtOH} (ϵ) 242 mμ (12,200), 280 (1180).

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The Structure of 2-Methyl-1,4-naphthoquinone Addition Compounds with Bisulfites

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RECEIVED AUGUST 15, 1955

In a previous paper,[1] the structure of the antihemorrhagically active addition compound of menadione with bisulfites was formulated as I rather than II, III or IIIa (M represents a metallic or ammonium cation).

Additional confirmation of this structure now has been obtained from infrared spectrosopic data on a purified specimen of the potassium salt, synthe-

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[1] M. Carmack, M. B. Moore and M. E. Balis, THIS JOURNAL, **72**, 844 (1950).