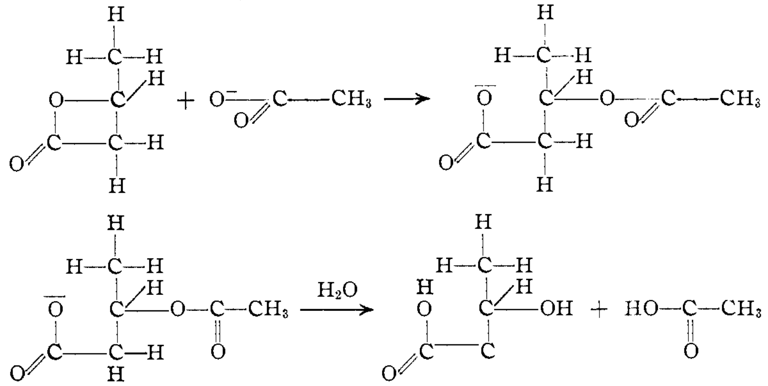
if log k_b^+ and log k_b^- are plotted against log K_b, the data for a single temperature fall fairly well on two straight lines as shown in Fig. 1. No corrections for statistical factors have been used.

In Fig. 2 we have plotted log k against log K for the reactions: (1) The nitramide decomposition,[8] (2) the mutarotation of glucose,[9] (3) the hydrolysis of ethyl ortho esters.[10] There is an arithmetical error in the value given by these authors for k_{H_2O}.

The authors of the articles usually have pointed out that graphs of this type show curvature. Thus Brønsted and Pedersen stated clearly theoretical reasons for believing that k must approach a maximum value asymptotically as K increases. For the nitramide decomposition, this was found experimentally by Tong and Olson. The present results show that in the lactone hydrolysis, the catalytic ability of a base like $CO_3^=$ must be expressed as due not to one but to two catalytic coefficients. Figure 1 demonstrates that each of these coefficients separately is compatible with an equation of the Brønsted type. Unless there is a constant proportionality between the coefficients for all catalysts, the plot of $\log(k^+ + k^-)$ against log K will not be linear.

The similarity between the lactone reactions and some of the others that have been studied, suggests that simultaneous multiple reactions may contribute to the curvatures that have been noticed in the Brønsted diagrams. Indeed the existence of at least two reactions has been demonstrated in the esterification of alcohols by thiol acids.[11]

When formate, acetate or chloroacetate buffers are used as media for the hydrolysis of β-butyrolactone, the optical rotation of the solution first decreases and then increases (Fig. 3). It is obvious that the ester which is formed hydrolyzes so slowly that the measured rotation no longer can be regarded as the resultant of the rotations of the lactone and the hydroxy butyric acids. Additional data therefore are needed for an analysis of the problem. The mechanism involved probably is



since the same optical form of hydroxybutyric acid is obtained as in hydrolysis by neutral water.

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[8] E. C. Baughn and R. P. Bell, *Proc. Roy. Soc.* (*London*), **158**, 464 (1937); L. K. J. Tong and A. R. Olson, THIS JOURNAL, **63**, 3406 (1941).

[9] J. N. Brønsted and E. A. Guggenheim, *ibid.*, **49**, 2554 (1927).

[10] J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

[11] L. S. Pratt and E. E. Reid, THIS JOURNAL, **37**, 1934 (1915); F. B. Stewart and P. V. McKinney, *ibid.*, **53**, 1482 (1931).

BERKELEY, CALIF. RECEIVED NOVEMBER 13, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

C^{14} Tracer Studies in the Rearrangement of Unsymmetrical α-Diketones. II.[1] The Alkaline Rearrangement of Benzylideneacetophenone Oxide[2,3]

BY CLAIR J. COLLINS AND O. KENTON NEVILLE

Benzylideneacetophenone oxide, labeled with carbon-14 in the carbonyl group, has been found to form 2-hydroxy-2,3-diphenylpropionic acid labeled exclusively in the carbinol group. The results are in accord with a formulation involving the benzyl-group migration of the intermediate benzyl phenyl diketone.

Benzylideneacetophenone oxide (I) undergoes rearrangement in alcoholic alkali to yield 2-hydroxy-2,3-diphenylpropionic acid (V).[4]

The rearrangement, which has been of interest as a preparative method for certain unsymmetrical desoxybenzoins,[5] has been assumed[4,5b] to occur by a benzilic-acid type of rearrangement of the intermediate benzyl phenyl diketone (II), which can be isolated after short treatment of the epoxide with alcoholic alkali.

Since the α-diketone (II) is unsymmetrical, two possible ionic intermediates may be formulated[1]; one (III), which yields the rearranged product by benzyl-group migration, and the other (IV), in which a shift of the phenyl group must occur.[6]

The identity of the migrating group has been established by the use of carbon-14 as the labeling atom in the reaction series shown below. The radioactivities, reported in microcuries per millimole, were obtained by ion-chamber measurements of the

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[1] Paper I in this series, O. K. Neville, THIS JOURNAL, **70**, 3499 (1948).

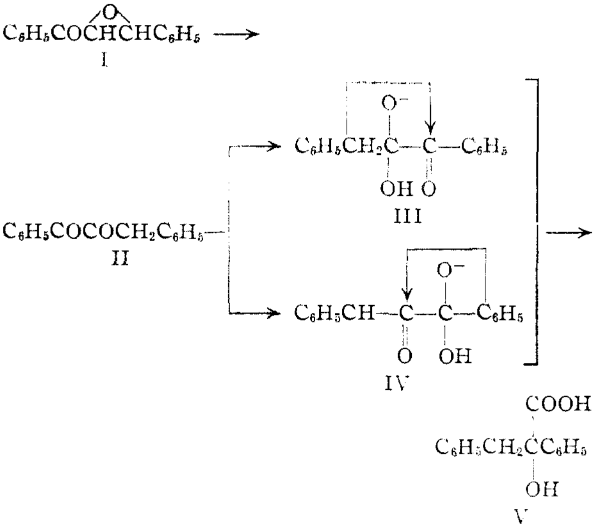
[2] This document is based on work performed for the Atomic Energy Commission at Oak Ridge National Laboratory.

[3] Presented before the Division of Organic Chemistry at the 114th Meeting of the American Chemical Society, St. Louis, Missouri, September 7, 1948.

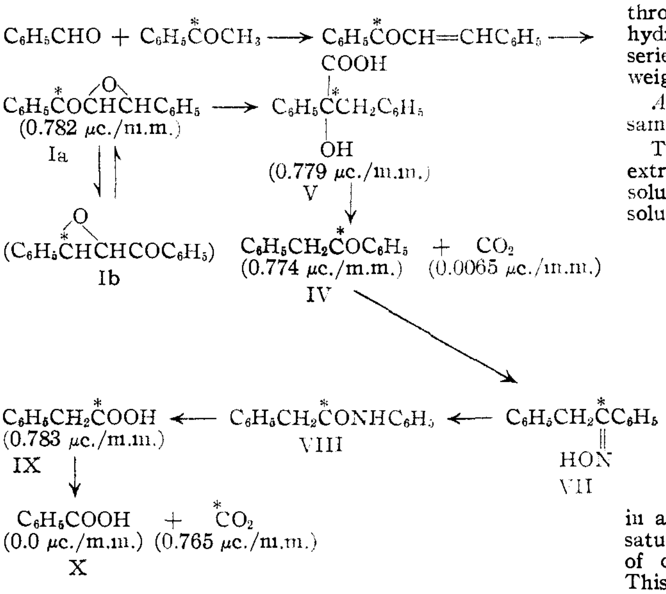
[4] O. Widman, *Ber.*, **49**, 477 (1916).

[5] (a) H. Jorlander, *ibid.*, **50**, 406, 1457 (1917); (b) W. Baker and R. Robinson, *J. Chem. Soc.*, 1798 (1932); (c) R. P. Dodwadmath and T. S. Wheeler, *Proc. Ind. Acad. Sci.*, 2438 (1935); (d) W. A. Hutchins, D. C. Motwani, K. D. Mudbhatkal and T. S. Wheeler, *J. Chem. Soc.*, 1882 (1938).

[6] T. Malkin and R. J. Robinson, *ibid.*, 371 (1925), have shown that benzyl phenyl diketone rearranges faster than benzil and, therefore, have concluded that the reaction proceeds by benzyl-group migration.



carbon dioxide from wet combustion of the organic samples.[1] The asterisk denotes the labeled carbon atom.



Since the desoxybenzoin (VI) obtained by oxidation of the rearranged product contained all of the radioactivity, the possibility of phenyl group migration was excluded. That the position of the labeled atom in the desoxybenzoin was consistent with benzyl-group migration, and that a possible isomerism, Ia ⇄ Ib, had not occurred during reaction, was shown by the subsequent degradation of desoxybenzoin to non-radioactive benzoic acid (X) and carbon-14 dioxide containing 100% of the radioactivity.

The acid-catalyzed rearrangement of benzylideneacetophenone oxide to 2-benzoylphenylacetaldehyde is presently under investigation.

Experimental

Aceto-1-C^{14}-phenone.[7]—The carbonyl-labeled acetophenone was prepared as described in a previous paper.[1]

Benzylidine-(aceto-1-C^{14})-phenone.—Ethanolic alkali was employed to condense 1.4 g. of aceto-1-C^{14}-phenone and 1.4 g. of benzaldehyde[8] to 2.35 g. (93%) of crude benzylidine-(aceto-1-C^{14})-phenone. One crystallization from alcohol yielded a material melting 51–58°, which was sufficiently pure for the subsequent preparation.

Benzylidene-(aceto-1-C^{14})-phenone Oxide (Ia).—Alkaline hydrogen peroxide[9] was used to convert 1.96 g. of benzylideneacetophenone to the epoxide; yield 2.01 g. (95%). One crystallization from alcohol yielded white crystals melting 86.5–87.5°.

Anal. 0.01095 microcurie carbon-14 per 3.14-mg. sample.

2-Hydroxy-2,3-diphenylpropionic-2-C^{14} Acid (Va).—A solution of 1.52 g. of the epoxide in 15 ml. of ethyl alcohol and 3 ml. of 6 *N* sodium hydroxide solution was heated under reflux for 90 minutes, then diluted with 60 ml. of distilled water and saturated with carbon dioxide. The solution was washed with ether and acidified with dilute HCl to yield 1.14 g. (72%) of acid.[10] One crystallization from benzene–petroleum ether produced white crystals melting 165–166°.

Anal. 0.00913 microcurie carbon-14 per 2.83-mg. sample.

Phenyl-(aceto-1-C^{14})-phenone (VI).—To 0.4635 g. of 2-hydroxy-2,3-diphenylpropionic-2-C^{14} acid (Va) in 30 ml. of glacial acetic acid, was added 0.080 g. of chromic anhydride. The reaction mixture was stirred for 30 minutes at room temperature while nitrogen gas was bubbled slowly through the solution. The released carbon dioxide was passed through a Dry Ice trap and into a half-saturated barium hydroxide solution contained in two centrifuge tubes in series. The carefully washed and dried barium carbonate weighed 0.408 g.

Anal. 0.00114 microcurie carbon-14 per 35.34-mg. sample.

The reaction mixture was added to 150 ml. of water and extracted with ether continuously for 4 hours. The ether solution was washed with aqueous sodium bicarbonate solution and concentrated. After desiccation, the solid product yielded 0.342 g. of crude phenyl-(aceto-1-C^{14})-phenone (VI), 91% of theory. Two crystallizations from alcohol produced white crystals, melting 51.0–52.5°.

Anal. 0.0101 microcurie carbon-14 per 2.56-mg. sample.

Phenyl-(acet-1-C^{14})-anilide (VIII).—To 0.528 g. of crude oxime (VII) (m.p. 85–93°) prepared from 0.5 g. of labeled desoxybenzoin (VI) and 0.5 g. of hydroxylamine hydrochloride, was added 5 ml. of benzene and 0.311 g. of PCl_5. After the solution was heated under reflux for 15 minutes, 20 ml. of water was added and the benzene was evaporated in an air stream. The ether extract, after washing with saturated bicarbonate solution and water, yielded 0.481 g. of crude phenyl-(acet-1-C^{14})-anilide, melting 105–113°. This was dissolved in 4.0 ml. of benzene and placed on an alumina (80–200 mesh) column (11 × 140 mm.). The column was developed with 30 ml. of benzene. The first 14 ml. through the column contained a viscous oil, and was discarded. The phenyl-(acet-1-C^{14})-anilide was then washed from the column with ethanol, which was evaporated, yielding 0.379 g. of crude product (79%). Recrystallization from ether–petroleum ether after treatment with Norite gave 0.328 g. of white crystals melting 114–115°; yield 68%.

Phenyl-(acetic-1-C^{14}) Acid (IX).—A sealed tube containing 0.102 g. of phenylacetanilide, 2.5 ml. of glacial acetic acid and 0.5 ml. of concd. hydrochloric acid was heated for 8 hours at 190–197°. The contents of the tube were washed with acetic acid into a 50-ml. flask, and evaporated to dryness. The solid white crystals were dissolved in 3.0 ml. of 6 *N* hydrochloric acid, and this solution was extracted with two 5-ml. portions of ether. The ether layer was con-

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[7] The name "aceto-1-C^{14}-phenone" is derived by considering acetophenone a derivative of acetic acid, and employing the I.U.C. numbering system for ethanoic acid. This is consistent with decisions made at the meeting of the International Union of Pure and Applied Chemistry, Amsterdam, September, 1949. Other compounds in this paper have been named similarly, placing the labeled atom position number immediately after the part of the designation which includes the carbon-14. Where a possible ambiguity exists, parentheses have been employed.

[8] E. P. Kohler and H. M. Chadwell, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 78–80.

[9] E. Weitz and A. Scheffer, *Ber.*, **54**, 2338 (1921).

[10] O. Widman, *ibid.*, **49**, 484 (1916).

centrated and desiccated yielding 0.0645 g. of crude phenyl-(acetic-1-C^{14}) acid (IX) melting 69–73°; yield 100%. Several preparations gave similar results. When the reaction temperature was allowed to rise above 200°, the yield was considerably decreased. Recrystallization from water yielded white crystals melting 73–74.5°.

Anal. 0.0249 microcurie carbon-14 per 4.32-mg. sample.

Benzoic Acid and Carbon-14 Dioxide.—A 0.030-g. sample of phenyl-(acetic-1-C^{14}) acid was treated with 0.050 g. of chromic anhydride and 0.01 g. of sulfuric acid at 100° for one-half hour. The evolved carbon dioxide was passed into half-saturated barium hydroxide solution. The carefully washed and dried barium carbonate weighed 0.031 g. or 71% of the theoretical amount.

Anal. 0.1185 microcurie carbon-14 per 30-mg. sample.

The oxidation solution was diluted with water and extracted with ether; the ether was evaporated. The residue which contained traces of phenyl-(acetic-1-C^{14}) acid and benzaldehyde was oxidized at 100° in a 1-ml. aqueous solution containing 0.01 g. of potassium hydroxide and 0.020 g. of potassium permanganate. After being heated under reflux for 1 hour, the solution was acidified and extracted with ether. The recovered benzoic acid weighed 0.022 g. or 82% of theory; m.p. 121°.

Anal. A 3.425-mg. sample contained activity indistinguishable from background.

OAK RIDGE, TENNESSEE RECEIVED OCTOBER 14, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SWARTHMORE COLLEGE]

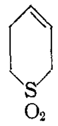
Thiapyran Derivatives. II. The Preparation, Properties, and Reactions of Δ^3-Dihydrothiapyran 1,1-Dioxide[1]

BY EDWARD A. FEHNEL AND PATRICIA A. LACKEY

An unsaturated, six-membered heterocyclic sulfone, Δ^3-dihydrothiapyran 1,1-dioxide, has been prepared by the abnormal Clemmensen reduction of tetrahydro-1,4-thiapyrone 1,1-dioxide. The addition reactions of the unsaturated sulfone with hydrogen, bromine, hydrogen iodide, hydrogen bromide and methanol are described, and the hydrogen halide addition products are characterized as 4-halotetrahydrothiapyran dioxides. Dehydrohalogenation of 3,4-dibromotetrahydrothiapyran 1,1-dioxide yields an unsaturated bromosulfone from which Δ^3-dihydrothiapyran 1,1-dioxide may be obtained by hydrogenolysis. The base-catalyzed addition of methanol to the unsaturated sulfone to give 3-methoxytetrahydrothiapyran 1,1-dioxide is considered to proceed *via* the tautomeric rearrangement of the Δ^3-dihydrosulfone to the Δ^2-isomer, but all attempts to prepare the latter compound by isomerization of the Δ^3-form have been unsuccessful. 2,2,6,6-Tetramethyl-Δ^3-dihydrothiapyran 1,1-dioxide and several of its derivatives have been prepared and their properties compared with those of the unmethylated analogs in the parent series.

The ability of the sulfone function to promote prototropic rearrangement in an adjacent allylic system has been demonstrated in studies of several unsaturated heterocyclic and acyclic sulfones.[2,3] Thus the facile interconversion of the Δ^α- and Δ^β-forms of the so-called butadiene sulfones in the presence of dilute aqueous alkali has been known for some time, and recently it has been found possible to bring about the isomerization of allyl benzyl sulfone to propenyl benzyl sulfone by refluxing with anhydrous tertiary amines.[3b] Since earlier studies with heterocyclic sulfones have been limited to the more or less readily available five-membered rings, little is known about the effects that structural variations might have upon the tautomeric mobility and position of equilibrium in systems of this type, and it would be of interest to have information on the properties of the unsaturated six-membered heterocyclic sulfones. The preparation, properties and reactions of one of the simplest representatives of this previously unexplored class of compounds is described in the present paper.

An unsaturated sulfone having the empirical formula $C_5H_8SO_2$ and presumably corresponding, therefore, either to structure I or II or to a tautomeric mixture of these was unexpectedly obtained as the major product (*ca.* 85%) of an attempted Clemmensen reduction of tetrahydro-1,4-thiapyrone 1,1-dioxide (III), along with a small amount (*ca.* 15%) of the expected tetrahydrothiapyran 1,1-dioxide (IV).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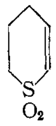
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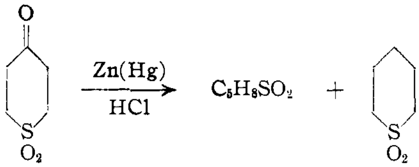

III IV

Variations in the conditions under which the reduction was carried out, such as changes in time, acid concentration, physical form of the zinc, etc., failed to alter the results significantly, and, in view of the rather similar results obtained in the reduction of 2,2,6,6-tetramethyltetrahydro-1,4-thiapyrone 1,1-dioxide (see below), it appears that this mode of reduction is the usual course of the reaction in this series of ketosulfones. Attempts to effect a separation of the mixture of saturated and unsaturated sulfones obtained in the reduction of III by repeated recrystallization from ligroin or cyclohexane proved to be impractical. The purification of the product was therefore carried out by treating the crude reduction product with an excess of bromine in glacial acetic acid, collecting and recrystallizing the precipitated dibromide and regenerating the unsaturated sulfone by treatment of the dibromide with zinc dust in ethanol. The unchanged saturated sul-

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[1] For the preceding paper in this series, see E. A. Fehnel and M. Carmack, THIS JOURNAL, **70**, 1813 (1948).

[2] (a) H. J. Backer and J. Strating, *Rec. trav. chim.*, **54**, 170, 618 (1935); (b) J. Böeseken and E. de Roy van Zuydewijn, *Proc. Acad. Sci.* (Amsterdam), **40**, 23 (1937) [*C. A.*, **31**, 4953 (1937)]; (c) E. de Roy van Zuydewijn, *Rec. trav. chim.*, **56**, 1047 (1937).

[3] (a) E. Rothstein, *J. Chem. Soc.*, **309**, 317 (1937); (b) H. J. Backer and G. J. de Jong, *Rec. trav. chim.*, **67**, 884 (1948); (c) C. C. J. Culvenor, W. Davies and W. E. Savige, *J. Chem. Soc.*, 2198 (1949).