allo when oxidized back to isoleucine. A recent analysis of bacitracin A of high potency from system 3 again gave 0.5 mole of alloisoleucine.

Acknowledgment. We wish to thank Mr. James Rigakos for the ultimate analyses reported in this paper. Thanks are also due Miss Gerty Walker and Mrs. Judy O'Brien for technical assistance.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

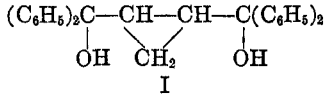
Pinacollike Rearrangement of a Cyclopropane-1,2-dimethylene Glycol*

ROBERT A. DARBY[1] AND ROBERT E. LUTZ

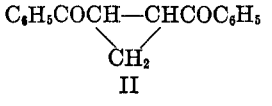
Received May 20, 1957

The cyclopropylog[2] of a 1,2-glycol, namely *trans*-1,2-di(diphenylhydroxymethyl)cyclopropane, was made by addition of phenyllithium to *trans*-1,2-dibenzoylcyclopropane. It underwent facile acid-catalyzed pinacol-type rearrangement with shift of a phenyl group to the adjacent cyclopropane carbon and concomitant cleavage of the ring, to produce the unsaturated ketone, 1,2,5,5-tetraphenyl-4-pentene-1-one. The structure of this product was demonstrated by its properties and by oxidative degradation to β-benzoyl-β-phenylpropionic acid.

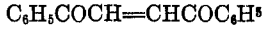
The rearrangement of the cyclopropylog[2] of a 1,2-glycol, namely *trans*-1,2-di(diphenylhydroxymethyl)cyclopropane (I), was discovered in the course of new studies on the preparation and reactions of *trans*-1,2-dibenzoylcyclopropane (II)[3,4] which had been undertaken for the purpose of comparing the conjugated system of this latter compound (II) with that of the olefinic analog, *trans*-1,2-dibenzoylethylene (III).



I

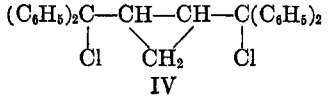


II

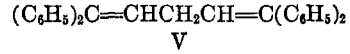


III

The cyclopropane-1,2-dimethylene glycol (I) was made by the action of phenylmagnesium bromide or phenyllithium on 1,2-dibenzoylcyclopropane (II). It had been the authors' intention to subject both this glycol (I) and the corresponding dichloride (IV) to the action of reducing agents. It was believed that possibly the conjugation between the functional groups through the cyclopropane ring might to some extent permit or favor 1,6-reduction with consequent formation of 1,1,5,5-tetraphenyl-1,4-pentadiene (V), reactions for which there are ample olefinic analogies (*cf.* the 1,6-reduction of pseudocodeine[5,6] and the 1,4-reductive-elimination of halogens from 2-butene-1,4-dihalides[7]).

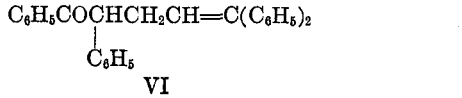


IV



V

In an attempt to prepare the dichloride (IV), the glycol (I) was subjected to the action of thionyl chloride. The crystalline product, however, proved to be halogen-free and analysis and molecular weight established the empirical formula $C_{29}H_{24}O$. The infrared absorption spectrum contained a band corresponding to a benzoyl-type carbonyl group (5.94 μ), and did not have the characteristic strong cyclopropane band in the 9.8–10 μ region. These results led to the conclusion that there had occurred a pinacol-type rearrangement with the glycol (I) functioning in the sense of a cyclopropylog[2] of a tetraphenyl-1,2-glycol, and that the product was the pinacolone partial-analog (VI).



VI

Consistent with the above formulation of the product (VI) the ultraviolet absorption spectrum of the compound showed a strong band at 248.5 mμ, ε, 16,530, which is significantly close to the summation of the expected molar absorptivities of the two independent chromophores, benzoyl and

* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

(1) Philip Francis du Pont Fellow, 1955–57. Assistance during the summer from an Office of Ordnance Research Contract, U. S. Army, is acknowledged. Present location, Experimental Station, E. I. du Pont de Nemours, Inc., Wilmington, Del.

(2) We use this term in a sense comparable with the terms homolog and vinylog.

(3) R. A. Darby, dissertation, University of Virginia, May 1957. The cyclopropanes I and II were assigned *trans* configurations on the basis of failure of II to isomerize under the action of 1% alcoholic sodium hydroxide, conditions which readily effect rearrangement of the unstable stereoisomer of 3-phenyl-1,2-dibenzoylcyclopropane. (See ref. 15).

(4) J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, **49**, 1083 (1927).

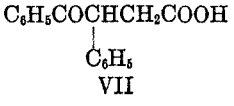
(5) R. E. Lutz, *J. Am. Chem. Soc.*, **56**, 1378 (1934).

(6) R. E. Lutz and L. F. Small, *J. Am. Chem. Soc.*, **56**, 2466 (1934).

(7) J. Thiele, *Ann.*, **308**, 339 (1899).

styryl (these chromophores in the compounds α-methyldesoxybenzoin and 1,1-diphenylpropene-1 give rise to values of *ca.* 12,000 and 12,500 at 233–242 and 248–253 mμ, respectively[8,9]).

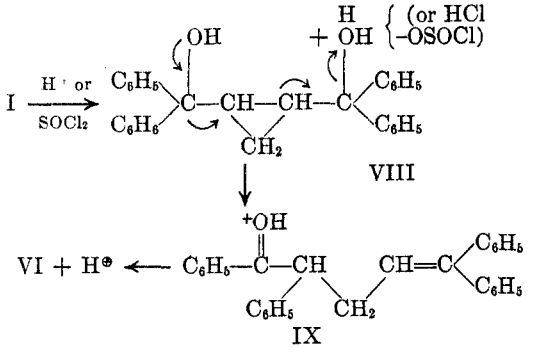
Unequivocal proof of the structure VI was obtained through oxidative degradations. With potassium permanganate in pyridine-water mixture,[10] 1.3 molar equivalents of benzoic acid and 0.32 of benzophenone were obtained, products which conclusively demonstrated the migration of one phenyl group of the glycol (I). Partial oxidation by chromic acid-acetic acid-chloroform mixture[11] gave a small but nevertheless significant yield of β-benzoyl-β-phenylpropionic acid VII which was identified by analysis, and by infrared absorption spectral comparisons and mixture melting point with an authentic synthetic sample.[12]



VII

On further study it was found that the glycol (I) could also be rearranged, readily and in 75% yield, by short heating of an acetic acid solution(refluxing for 1 min.). The fact that the glycol was recovered unchanged after fusion for 5 min. at the much higher temperature 200–210° shows that acid catalysis is important as it is in the characteristic rearrangements of simple cyclopropanes which without catalyst require relatively high temperatures.[13]

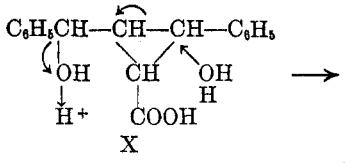
A logical representation of the mechanism of the rearrangement of the glycol (I) to the unsaturated ketone (VI), in partial analogy both with the pinacol rearrangement and with rearrangements of cyclopropanes to olefins, is as follows:



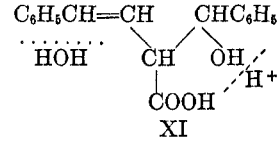
VIII

IX

In connection with the above results and discussion three other cyclopropane rearrangements should be cited as related although not fully analogous. One of these is the acid-catalyzed rearrangement of 3-phenyl-2-(phenylhydroxymethyl)-cyclopropane-1-carboxylic acid (X) to the open-chain unsaturated hydroxy acid (XI).[14]

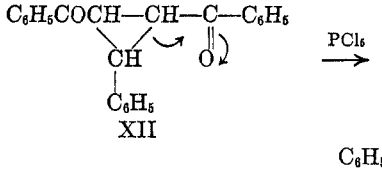


X

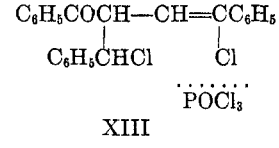


XI

The second is the reaction and rearrangement of 3-phenyl-1,2-dibenzoylcyclopropane (XII) with phosphorus pentachloride to the open-chain unsaturated dichloro ketone (XIII)[15] (analogous to the Straus reaction of α,β-unsaturated ketones[16]).

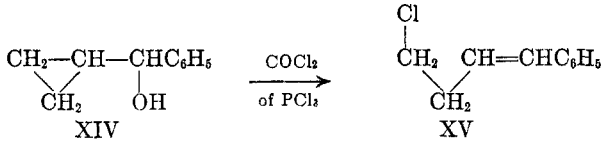


XII



XIII

The third is the recently reported rearrangement of α-cyclopropylbenzyl alcohol XIV to 4-chloro-1-phenylbutene-1 (XV).[17]



XIV XV

It will be of interest to learn of the results of experiments in progress on the action of acid on the cyclobutane analog of (I) and on 1,1,4,4-tetraphenylbutene-2-diol-1,4 which is a true vinylog of a pinacol.[18]

EXPERIMENTAL[19]

1,2-Di-(diphenylhydroxymethyl)cyclopropane (I). A solu-

(8) P. Preisweik and H. Erlenmeyer, *Helv. Chim. Acta*, **17**, 329 (1934).

(9) R. Lucas and M. J. Hoch, *Bull. soc. chim. France*, (5) **2**, 1376 (1935).

(10) D. A. Shirley, *Preparation of Organic Intermediates*, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 219.

(11) B. Riegel, R. B. Moffett, and A. V. McIntosh, *Org. Syntheses*, **Coll. Vol. III**, 234–236 1955.

(12) A. Ali, *et al.*, *J. Chem. Soc.*, 1013 (1937).

(13) G. E. Egloff, G. Hulla, and V. I. Komarewsky, *Isomerization of Pure Hydrocarbons*, Reinhold Publishing Corp., New York, N. Y., 1952, pp. 95–97.

(14) C. F. H. Allen and R. Boyer, *Can. J. Research*, **9**, 159 (1933).

(15) E. P. Kohler and W. N. Jones, *J. Am. Chem. Soc.*, **41**, 1249 (1919).

(16) C. F. H. Allen and A. H. Blatt, *Organic Chemistry. An Advanced Treatise*, H. Gilman, ed., Vol. I, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 680.

(17) W. J. Close, *J. Am. Chem. Soc.*, **79**, 1455 (1957).

(18) C. F. Dickerson, dissertation, University of Virginia, May 1954; and further experiments which are in progress.

(19) Microanalyses by B. J. Williamson and Mrs. T. C. Jensen. Ultraviolet absorptivities were determined using a Beckman DU quartz spectrophotometer and 2×10^{-5} molar absolute ethanol solution. Infrared determinations were made on a Perkin-Elmer Model 21 double beam spectrophotometer using potassium bromide pellets.

tion of phenyllithium was prepared under nitrogen from 0.9 g. of lithium in 25 ml. of dry ether by dropwise addition of 5.3 ml. (0.05 mole) of distilled, dried bromobenzene in 25 ml. of dry ether over a period of 20 min. with stirring and slight warming to initiate the reaction. After stirring for an additional 1.5 hr. a solution of 5 g. (0.02 mole) of 1,2-dibenzoylcyclopropane (II) in 250 ml. of ether was added under gentle refluxing over a period of 30 min. Hydrolysis, washing with water, drying the ether solution over sodium sulfate, and evaporating under reduced pressure, gave a colorless solid which was recrystallized from benzene-ligroin mixture, m.p. 169.5–171.5°, yield 6.26 g. (77%).

Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.37; H, 6.19. Infrared absorption: 2.8, 9.93 μ.

In a similar experiment using phenylmagnesium bromide, except that hydrolysis was with 10% sulfuric acid, the yield of the glycol (I) was 33%.

One gram of the glycol after heating at 200–210° for 5 min. was recovered almost quantitatively.

1,2,5,5-Tetraphenyl-4-pentene-1-one (VI). A suspension of 0.5 g. (0.00123 mole) of the glycol (I) in 10 ml. of acetic acid was brought rapidly to boiling and refluxed for one min. Upon cooling a white precipitate of VI formed and was recrystallized from absolute ethanol, m.p. 130.5–132.5°; yield 0.36 g. (75%).

Anal. Calcd. for $C_{29}H_{24}O$: C, 89.65; H, 6.22; mol. wt. 388.5. Found: C, 89.43; H, 5.91; mol. wt. (Rast), 408. Ultraviolet absorption in absolute ethanol (2.02×10^{-5} *M*): λ_{max}, 248.5; ϵ, 16,530. Infrared absorption: 5.94, 6.23, 6.67, 6.9, very slight peak at 9.95 μ.

In another experiment, 5 g. (0.0123 mole) of the glycol (I) dissolved rapidly in 40 ml. of thionyl chloride with the evolution of gas. The red solution was warmed on a steam bath for 20 min., and the excess thionyl chloride was evaporated under reduced pressure. Ligroin was added and evaporated. The residue was recrystallized from benzene-ligroin mixture or from absolute ethanol; m.p. 131.5–132.5°; yield 3.0 g. (61%).

Numerous *ozonolysis* attempts were unsuccessful.

Potassium permanganate oxidation (cf. Ref. 10). A solution of 4 g. of VI (0.0103 mole) in 100 ml. of pyridine and 30 ml. of water on a steam bath was treated with six 2.1-g. portions of potassium permanganate (a total of 0.08 mole) at 1-hr. intervals. Upon steam distillation 0.69 g. (32%) of benzophenone, m.p. 44–46.5°, was obtained and identified by a mixture melting point determination. Work-up of the residue from steam distillation produced 1.6 g. (64%) of the calculated two equivalents of benzoic acid, m.p. 119–120° (identified by a mixture melting point determination).

Chromic acid oxidation.[11] A solution of 5 g. (0.0128 mole) of VI in 30 ml. of chloroform and 39 ml. of acetic acid at 45–50° was treated dropwise over 10 min. under stirring with a solution of 4.8 g. (0.048 mole) of chromic acid in 4 ml. of water and 26 ml. of acetic acid. After stirring for an additional 20 min. at this temperature and treatment dropwise with methanol to destroy excess reagent, the reaction mixture was concentrated on a steam bath under reduced pressure and evaporated to near dryness at room temperature under reduced pressure. The residue was triturated with ether, filtered, and placed in 150 ml. of water. Extraction of ether, washing with 10% hydrochloric acid, drying over sodium sulfate, evaporation under reduced pressure, and trituration of the viscous residue with ether, gave 0.9 g. of a white crystalline solid, m.p. 153–160°; recrystallized from dilute ethanol, m.p. 163–165°. It was identified as VI by a correct analysis, and by mixture m.p. with, and identity of the infrared absorption spectrum with that of an authentic sample prepared as described below.

β-Benzoyl-β-phenylpropionic acid. This synthesis is based on a procedure outlined briefly by Ali, *et al.*[12] To a solution of 0.5 g. of sodium in 15 ml. of absolute ethanol was added portion-wise 5 g. (0.0254 mole) of desoxybenzoin (m.p. 52–5°). After all of the ketone had been added, the mixture was treated with 2.8 ml. (4.2 g., 0.0252 mole) of distilled ethyl bromoacetate and was refluxed for 5 hr.; the alcohol was then evaporated. A solution of the residue and 1.5 g. of sodium hydroxide in 25 ml. of ethanol was refluxed for 30 min., cooled, diluted with water, and neutralized with concentrated hydrochloric acid. The resulting white precipitate was recrystallized from dilute ethanol; m.p. 163–165°; (A[12], m.p. 168°); yield 3.6 g. (55%).

CHARLOTTESVILLE, VA.

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Lead Tetraacetate Oxidations of 2,5-Diarylfurans*,[1a]

CHI-KANG DIEN[1b] AND ROBERT E. LUTZ

Received February 4, 1957

Lead tetraacetate in chloroform solution oxidized five 2,5-diarylfurans to the *cis* unsaturated 1,4-diketones and converted three β-acetoxy-2,5-diarylfurans into the corresponding 2-acetoxy-3-furanones. 2,5-Dimesitylfuran and 3,4-dichloro-2,5-diphenylfuran did not react under these conditions.

In refluxing concentrated acetic acid lead tetraacetate, behaving differently, brought about two-stage oxidations of three 2,5-diarylfurans to the 2-acetoxy-3-furanones. In one of these cases the reaction could be stopped at the first stage of oxidation with production of the 3-acetoxyfuran. Four 3-acetoxy-2,5-diarylfurans were oxidized to 2-acetoxy-3-furanones.

These reactions are consistent with expectations based on known behaviors of the reagent, effects of different types of substituents, and present views of mechanism.

Numerous 2,5-diarylfurans (I), including one carrying a sterically hindering mesityl group at one of the two α-positions, undergo oxidative-cleavage by nitric-acetic acids to *cis* unsaturated 1,4-diketones (II),[2] but 2,5-dimesitylfurans (Ij)[3] resist this

* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

(1) (a) This investigation was supported in part by a contract with the Office of Ordnance Research, U. S. Army, and in part by a grant-in-aid from the National Science Foundation. (b) Present location, National Aniline Div. Allied Chemical & Dye Corp., Buffalo, N. Y.

(2) (a) A. P. Dunlap and F. N. Peters, *The Furans*, Reinhold Publishing Corp., N. Y., 1953, and references cited therein; see especially p. 50. (b) R. E. Lutz and F. N. Wilder, *J. Am. Chem. Soc.*, 56, 978 (1934); (c) R. E. Lutz and W. P. Boyer, *J. Am. Chem. Soc.*, 63, 3189 (1941).