

diluted with a small volume of water and the resulting mixture acidified with concentrated hydrochloric acid. An oil separated, which solidified upon strong cooling of the mixture. The solid was collected by filtration and recrystallized from boiling water, of which about 2 l. were required. Several more recrystallizations from water yielded 6.5 g. (7.3%) of white, flaky crystals of Acid A, m.p. 110–113°. The combined mother liquors were extracted with benzene. The benzene extract was concentrated under reduced pressure, petroleum ether (b.p. 30–60°) added, and the resulting mixture permitted to stand in the refrigerator. The crystals which formed were recrystallized several times from water to give 3.0 g. (3.4%) of white crystals of Acid B, m.p. 134–137°. Repeated crystallization from water gave the analytically pure acids: Acid A, m.p. 113–113.7°; Acid B, m.p. 135–137°.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.42; H, 5.65. Found: (for Acid A): C, 67.35; H, 5.67. (For Acid B): C, 67.58; H, 5.69.

Acid A in carbon tetrachloride did not decolorize 5% bromine in carbon tetrachloride. In acetone solution, Acid A gave no decoloration with a 2% solution of potassium permanganate. Acid B gave similar results with the preceding reagents. Phenylvinyl ether gave instantaneous decolorization with both reagents.

A 1-g. quantity of Acid A, m.p. 110–114°, was heated in 11.35 g. of polyphosphoric acid at 70–80° for 2 hr. with mechanical stirring and exclusion of moisture. The reaction mixture was poured into cold water and the resulting mixture extracted with benzene. The benzene solution was washed with 5% sodium bicarbonate and dried over anhydrous magnesium sulfate. Removal of the benzene revealed neither solid nor liquid residue. Acid B gave similar results with polyphosphoric acid.

Acknowledgment. The financial support of this investigation by the Research Corporation of New York is gratefully acknowledged.

AVERY LABORATORY
THE UNIVERSITY OF NEBRASKA
LINCOLN, NEB.

2,2-Diaryl-*p*-dioxanes

R. K. SUMMERBELL, JAMES P. SETTLE, AND MATHILDE KLAND-ENGLISH

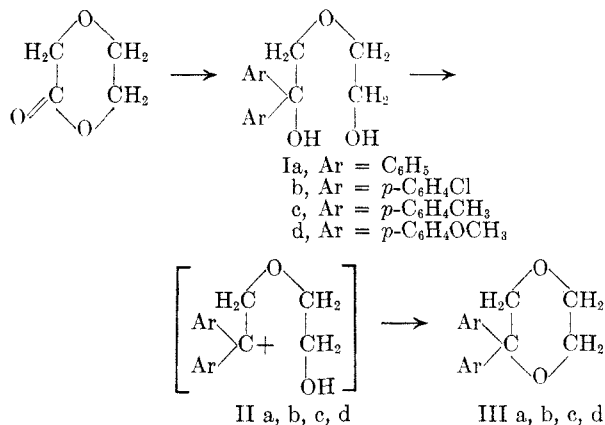
Received January 6, 1958

Two recent publications from our laboratory^{1,2} have made use of 2,2-diphenyl-*p*-dioxane as the reference compound in proving structures. This note details the original synthesis of this and other 2,2-diaryl-*p*-dioxanes.

Treatment of *p*-dioxanone with the appropriate Grignard reagent resulted in the formation of fair yields of α, α -diphenyldiethylene glycol, Ia, α, α -di-*p*-chlorophenyldiethylene glycol, Ib, and α, α -di-*p*-tolyl-diethylene glycol, Ic. These glycols were converted to dioxanes by treatment in benzene solution with anhydrous hydrogen chloride and calcium chloride at room temperature.

(1) R. K. Summerbell and Hans E. Lunk, *J. Am. Chem. Soc.*, **79**, 4802 (1957).

(2) R. K. Summerbell and Hans E. Lunk, *J. Am. Chem. Soc.*, **80**, 604 (1958).



The ease of formation of the dioxane rings contrasts with the difficulty of closing similar 4-methylmorpholine rings with acid,³ presumably because in the latter case the carbonium ion corresponding to II would have two positive charges. As would be expected from the proposed carbonium ion mechanism, Ib was not converted to the dioxane as easily as Ia or Ic. On the other hand, Id was not even isolated. Either the dioxane IIIId was formed in solvent evaporation or under the extremely mild acid conditions of the hydrolysis of the Grignard reaction product with aqueous ammonium chloride, or it was a direct product formed before hydrolysis. Such direct formation of ethers from aliphatic lactones by treatment with Grignard reagents seems to be rare.⁴

When a butyl Grignard reagent was treated with *p*-dioxanone, a compound of correct composition for the expected glycol resulted, but starting material was recovered when ring closure to the dioxane was attempted by the method successfully employed for aromatic derivatives.

EXPERIMENTAL

p-Dioxanone. Small yields of this compound were obtained by each of the methods attempted.⁵⁻⁷ None was satisfactory, and our modifications did not improve matters importantly. The compound was always distilled immediately before use in order to be certain that it was in the monomeric form. A convenient method for the laboratory preparation of this compound was found later in our laboratory, and has now been published.²

(3) I. A. Geissman, M. Bassin, and E. V. Zeilberger, *J. Am. Chem. Soc.*, **73**, 5874 (1951).

(4) M. S. Kharasch and Otto Reinmuth, *Grignard Reactions of Non-metallic Substances*, Prentice Hall, New York, 1954, pp. 574–578.

(5) C. A. Bischoff and P. Walden, *Ber.*, **26**, 263 (1893); *Ann.*, **279**, 47 (1894).

(6) W. H. Carothers, C. L. Dorough, and F. J. Van Natta, *J. Am. Chem. Soc.*, **54**, 771 (1932).

(7) R. W. McNamee and C. M. Blair, U. S. Patent 2,142,033, *Chem. Abstr.*, **33**, 2542 (1939).

α,α -Diphenyldiethylene glycol, Ia. To the Grignard solution resulting from the treatment of 12.2 g. (0.5 mole) of magnesium with 78.5 g. (0.5 mole) of bromobenzene in 200 cc. of ether was added with vigorous stirring, 15.2 g. (0.15 mole) of monomeric *p*-dioxanone dissolved in 50 cc. of dry benzene. The rate of addition was such as to cause gentle reflux. The reaction mixture was hydrolyzed with ice and aqueous ammonium chloride, and the product extracted with ether which was evaporated to yield 40.9 g. of crude product. Repeated recrystallization from water-ethanol gave 19.9 g. (51% yield) of a pure product, m.p. 109.0–109.2°.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02; mol. wt. 258. Found: C, 74.63; H, 7.29; mol. wt., ebullioscopic in benzene, 250.

α,α -Di-*p*-chlorophenyldiethylene glycol, Ib. Prepared as above from Grignard reagent from 0.15 mole of *p*-bromochlorobenzene and 0.07 mole of *p*-dioxanone. Product recrystallized from ethanol-water weighed 6.2 g. (0.019 mole), yield 27%, m.p. 108.5–109°.

Anal. Calcd. for $C_{16}H_{16}O_3Cl_2$: C, 58.73; H, 4.93. Found: C, 58.95; H, 4.80.

α,α -Di-*p*-tolyl-diethylene glycol, Ic. Use of the Grignard reagent from *p*-bromotoluene as above gave a 26% yield of product recrystallized from water-ethanol, then from petroleum ether, m.p. 91–91.5°.

Anal. Calcd. for $C_{18}H_{22}O_3$: C, 75.51; H, 7.74. Found: C, 75.48; H, 7.88.

2,2-Diphenyl-*p*-dioxane, IIIa. A solution of 0.903 g. (0.0035 mole) of Ia dissolved in 50 cc. of dry benzene to which 3 g. of anhydrous calcium chloride had been added was saturated with anhydrous hydrogen chloride and allowed to stand for 24 hr. The solvent was removed by aspirator and the product recrystallized from petroleum ether to give 0.251 g. (0.00105 mole) of white crystals, m.p. 119.5–120°. Yield 30%.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.77; H, 6.65.

A melting point of 121° has been reported for 1,1-diphenylethylene glycol,⁸ a conceivable product of this reaction. The latter was prepared and shown to be different from IIIa by mixed melting point.

2,2-Di-*p*-chlorophenyl-*p*-dioxane, IIIb. The product was recrystallized from absolute ethanol, m.p., 78–79°. Yield, 12%. Unchanged starting material recovered by evaporation of the solvent amounted to 77%.

Anal. Calcd. for $C_{16}H_{14}O_2Cl_2$: C, 62.2; H, 4.53. Found: C, 61.49; H, 4.77.

2,2-Di-*p*-tolyl-*p*-dioxane, IIIc. M.p., 94.2–95.5; yield, 30%.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.46. Found: C, 80.42; H, 7.55.

2,2-Di-*p*-anisyl-*p*-dioxane, IIIId. When the preparation of 2,2-di-*p*-anisyl-diethylene glycol from *p*-dioxanone and *p*-anisylmagnesium bromide was attempted, the product had a carbon content quite different from that of the glycol, but close to that of the corresponding dioxane. The yield was 54%. Repeated crystallization from ethanol, methanol, and petroleum ether gave a product of fair purity. A satisfactory analytical sample, obtained by sublimation, melted at 106.5–107.2°.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.67. Found: C, 72.30; H, 6.90.

Acknowledgment. Thanks are given to the Abbott Foundation of Northwestern University for financial aid and to Union Carbide Chemicals Corp. for a small sample of *p*-dioxanone.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILL.

Unsaturated Fatty Acids. V. Preparation of α - and γ -Linolenic-1- C^{14} Acids¹

JUDD C. NEVENZEL AND DAVID R. HOWTON

Received January 13, 1958

The decarboxylation-reconstitution technique developed² in this laboratory and employed^{3,4} in the synthesis of oleic- and linoleic-1- C^{14} acids has now been applied to the problem of labeling two trienoic acids, α - (or the common) linolenic (all-*cis*-9,12,15-octadecatrienoic) and γ -linolenic (all-*cis*-6,9,12-octadecatrienoic), with C^{14} in the carboxyl group. Use of these labeled substances in studies of *in vivo* interconversions of polyunsaturated fatty acids has been described elsewhere.⁵

EXPERIMENTAL

All melting points are corrected. Reported *trans*-contents of olefinic substances, based on infrared absorption at 10.3 μ , are considered to be within 5% of actual values.

Ultimate analyses were performed by Dr. A. Elek (Elek Micro Analytical Laboratories, Los Angeles) and infrared absorption analyses by Mr. Paul Kratz. Radioactivities were determined by Dr. J. F. Mead and by Mr. W. H. Slaton, Jr.

9,10,12,13,15,16-Hexabromostearic acid (α -I), m.p. 182.8–183.4°, was prepared by bromination of linseed oil fatty acids (kindly supplied by the Archer-Daniels-Midland Co.) essentially as described by McCutcheon,⁶ except that butanone (16.5 ml. per g.) was found to be superior to dioxane as a crystallization solvent. Treating α -I in tetrahydrofuran with diazomethane in benzene gave methyl 9,10,12,13,15,16-hexabromostearate, m.p. 154.2–155.3° (recrystallized from butanone).

Anal. Calcd. for $C_{19}H_{32}Br_6O_2$: C, 29.56; H, 4.18; Br, 62.12. Found: C, 29.68; H, 4.16; Br, 62.18.

6,7,9,10,12,13-Hexabromostearic acid (γ -I) was obtained by bromination of the mixture of fatty acids produced by saponification of the oil extracted from seeds of the evening primrose, *Oenothera Lamarckiana*,⁷ using a procedure developed by Dr. James F. Mead. In batches of about 300 g. each, 5 lbs. of dry seed (Vaughan Seed Co., Chicago) was crushed by shaking mechanically with porcelain balls (0.5–1 inch dia.) in 3 (dia.) by 10 inch tin cans for 3 hr. (Ball-mill treatment of the seeds was ineffective.) The crushed seeds were then steeped 48 hr. in 4 l. of light petroleum ether (30–60° or 60–70°), the mixture was filtered, and the dried filter cake was recrushed and reextracted twice. Evaporation of the combined yellow extracts (*in vacuo* under nitrogen) left 541 g. (23.8% by weight) of oil, which was refluxed

(1) This paper is based on work performed under Contract AT(04-1)-GEN-12 between the Atomic Energy Commission and the University of California at Los Angeles.

(2) D. R. Howton, R. H. Davis, and J. C. Nevenzel, *J. Am. Chem. Soc.*, **74**, 1109 (1952).

(3) D. R. Howton, R. H. Davis, and J. C. Nevenzel, *J. Am. Chem. Soc.*, **76**, 4970 (1954).

(4) J. C. Nevenzel and D. R. Howton, *J. Org. Chem.*, **22**, 319 (1957).

(5) G. Steinberg, W. H. Slaton, Jr., D. R. Howton, and J. F. Mead, *J. Biol. Chem.*, **224**, 841 (1957); J. F. Mead and D. R. Howton, *J. Biol. Chem.*, **229**, 575 (1957).

(6) J. W. McCutcheon, *Org. Syntheses*, **22**, 82 (1942).

(7) T. Tsuchiya, *J. Chem. Soc. Japan*, **63**, 1085 (1942) [*Chem. Abstr.*, **41**, 3754e (1947)].

(8) C. Paal and E. Weidenkaff, *Ber.*, **39**, 2063 (1906).