was absorbed in 3–5 hr. The catalyst was removed by filtration and washed with ether. The combined filtrates were washed with cold 3N hydrochloric acid and with cold 10% sodium hydroxide solution, and dried. The residue after evaporation of solvent was either recrystallized from pentane or distilled.

The ultraviolet spectra were determined in 95% ethanol purified before use by distillation from potassium hydroxide. The solutions were made up to give absorbance values of 0.3–0.8 at λ_{max}. A Beckman Model DK-1 spectrophotometer was used for these measurements.

Kinetic method. Basic hydrolyses were carried out in 87.8% (by volume) ethanol at 30.00 ± 0.02°, in side-arm volumetric flasks, under a positive pressure of nitrogen. The initial concentration of potassium hydroxide and of ester were about 0.04M and 0.025M, respectively. Aliquots were periodically pipetted into excess sulfuric acid, and back titrated with sodium hydroxide solution using a Sargent-Malmstadt Automatic Titrator. Consistent values of the second-order rate constants were calculated, corresponding with the first 65–80% of the reaction which was followed. An infinity-time measurement was generally used, except in calculating the few slowest rate constants, for which the zero-time concentrations were accurately determined and used.

Acknowledgment. We wish to thank Miss Ruth Ann Cook for the ultraviolet spectra, and The University of Texas Research Institute for a Summer Grant to R.F.

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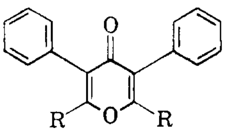
Isomeric Pyranones from Condensation of Propionic Acid with 1,3-Diphenyl-2-propanone

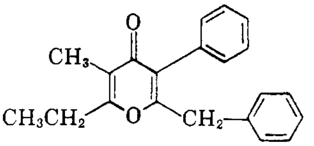
R. L. LETSINGER AND O. KOLEWE[1]

Received December 29, 1960

Acetic acid condenses with 1,3-diphenyl-2-propanone in polyphosphoric acid to give 2,6-dimethyl-3,5-diphenylpyran-4-one (I) in good yield.[2] A consideration of the possible pathways leading to this product indicated that an isomeric, unsymmetrical pyran-4-one might also have been produced under the reaction conditions; however, no such compound could be isolated. We now find that two pyran-4-ones are indeed formed in the reaction of propionic acid with 1,3-diphenyl-2-propanone. These products, m.p. 101.5–102° (21% yield) and m.p. 98–99° (24% yield), are assigned structures II and III, respectively, on the basis of the reaction type and analytical and spectral data. Evidence that both compounds are pyran-4-ones is provided by the infrared spectra, which show bands in the 6.0–6.4 μ region typical of pyran-4-ones. The NMR spectra strongly support formulas II and III and permit an unambiguous identification of the formulas with the reaction products.

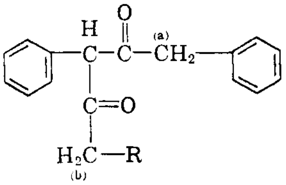


I. R = CH_3
II. R = C_2H_5



III

Formation of these pyranones may be rationalized on the basis of the pathway postulated for the analogous condensation involving acetic acid—*i.e.*, successive acylations at methylene groups α to carbonyl groups, followed by enolization and dehydration. The initial acylation would yield intermediate IV (R = CH_3, for propionic acid), or an equivalent acylated or phosphorylated enol derivative which would undergo a second acylation at either carbon (a) or carbon (b). Reaction at (a)



IV

would lead to II; reaction at (b), to III. The yields of II and III suggest that the two pathways are about equally probable for the propionic acid reaction. In the acetic acid condensation (R = H), the second acylation must occur preponderantly, if not exclusively, at position (a).

EXPERIMENTAL

Reaction of 1,3-diphenyl-2-propanone with propionic acid. A solution containing 2.2 g. of 1,3-diphenyl-2-propanone and 25 ml. of propionic acid in 40 g. of polyphosphoric acid[3] was heated at reflux (138–145°) for 1.5 hr.; then it was cooled to room temperature, diluted with water and extracted with ether. The ether solution was washed with 10% sodium hydroxide solution, dried, and evaporated to yield a brown oil which failed to crystallize at 0°. On chromatography on alumina with petroleum ether (b.p. 60–71°)–benzene mixtures as eluent, a pale yellow band developed. Elution of this band yielded 2.0 g. of tan product, m.p. 70–93°, which was dissolved in ether and decolorized with charcoal. Recrystallization from hexane afforded 0.9 g. of product III, m.p. 90–95°. Concentration of the mother liquors gave 0.8 g. of product II, m.p. 95–100°. After several recrystallizations from pentane, III melted at 98–99°; weight, 0.8 g. (24% yield). Product II, after recrystallization from pentane, melted at 101.5–102°; weight, 0.7 g. (21%). A mixture of pure II and III melted over a range from 75–90°.

Anal.[4] Calcd. for $C_{21}H_{20}O_2$: C, 82.85; H, 6.62. Found: Compound II. C, 82.67; H, 6.57. Found: Compound III. C, 82.62; H, 6.13.

Spectral data. Both II and III exhibited absorption in the 6.0–6.4 μ region characteristic of pyrones[2]; The infrared spectrum of II had sharp peaks at 6.06, 6.16, and 6.22 μ; that of III, peaks at 6.09 and 6.22 μ and a shoulder at 6.33 μ. Otherwise the spectra differed in numerous respects. In

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[1] National Science Foundation Undergraduate Summer Research Participant, 1960.

[2] R. L. Letsinger and J. D. Jamison, *J. Am. Chem. Soc.*, **83**, 193 (1961).

[3] The polyphosphoric acid was kindly supplied by the Victor Chemical Company.

[4] Carbon and hydrogen analyses were made by H. Beck.

particular, III absorbed strongly at 10.0, 12.65, and 13.5 μ whereas II showed no bands in these regions, and II absorbed strongly at 12.3 μ, a region in which III was transparent.

The NMR spectra were determined at 60 Mc. in chloroform solvent with tetramethylsilane as a reference. The spectrum of II was relatively simple, with a peak at 441 c.p.s. (aromatic hydrogens), a quadruplet centered at 141 c.p.s. (methylene hydrogens) and a triplet centered at 74.3 c.p.s. (methyl hydrogens). In good agreement with the structure assigned II, the relative areas of these bands were 10.0, 4.0, and 5.8. The spectrum of III contained five band areas; a doublet with peaks at 434 and 442 c.p.s. (hydrogens of the two phenyl groups), a singlet at 213 c.p.s. (hydrogens of the benzyl methylene group), a quadruplet centered at 140 c.p.s (methylene hydrogens of the ethyl group), a singlet at 97.3 c.p.s. (methyl hydrogens of the methyl group joined to the pyranone ring), and a triplet centered at 57.6 c.p.s. (methyl hydrogens of the ethyl group). The relative areas of these bands were, respectively, 8.5, 2.2, 2.4, 3.0, and 2.8, which compares favorably with the number of protons associated with these resonances (10, 2, 2, 3, and 3).

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Reactions of Anthracene Lithium Derivatives with Diethyl Ketone and Anthraquinone[1]

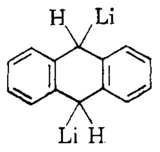
PETER WALKER[2]

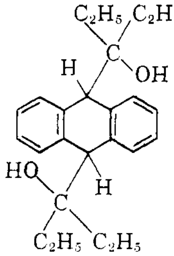
Received December 30, 1960

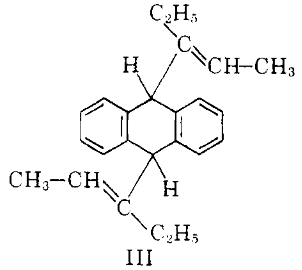
Anthracene lithium derivatives are well known in the literature but have been little used in synthesis.[3] The adduct resulting from anthracene and sodium, perhaps more suitable for large scale use than the anthracene-lithium adduct, has yielded several 9,10-disubstituted esters and acids of anthracene.[4]

9,10-Dilithio-9,10-dihydroanthracene (I) reacted with diethyl ketone in ether to give 9,10-di(3-hydroxy-3-pentyl)-9,10-dihydroanthracene (II), which was dehydrated by the action of hydriodic acid to 9,10-di-(2-penten-3-yl)-9,10-dihydroanthracene (III).

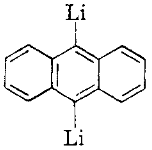
The ultraviolet spectrum of this product (III) indicates about 25% of anthracenoid material presumably formed by dehydration in the *meso* positions of the nucleus followed by rearrangement.

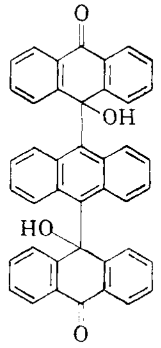

I

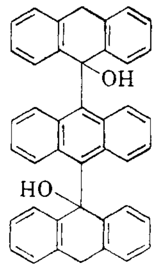

II


III

Anthraquinone failed to react with 9,10-dilithio-9,10-dihydroanthracene (I) but added to 9,10-dilithioanthracene (IV) in boiling di-*n*-butyl ether to give 9,10-di-9′-(9′-hydroxyanthronyl)anthracene (V). Reduction with zinc dust in boiling pyridine gave 9,10-di-9′-(9′-hydroxy-9′,10′-dihydroanthryl)anthracene (VI), the structure of which was confirmed by ultraviolet absorption and a molecular weight determination.


IV


V


VI

Attempts to cyclize these products to polycyclic compounds, using aluminum trichloride or ultraviolet irradiation, have resulted in rupture of the *meso* links to yield anthracene.

EXPERIMENTAL[5]

9,10-Di(3-hydroxy-3-pentyl)-9,10-dihydroanthracene (II). 9,10-Dilithio-9,10-dihydroanthracene[3] was prepared by adding a solution of 2.0 g. (0.011 mole) of anthracene in 200 ml. of dry benzene under an atmosphere of nitrogen to a suspension of 0.4 g. of finely-cut lithium in 200 ml. of ether containing a few pieces of broken glass. A red-brown solution resulted after 3 days shaking which was treated with a solution of 1.8 g. (0.02 mole) of diethyl ketone in 100 ml. of ether during 2 hr. with stirring. Saturated ammonium chloride was slowly added and the organic layer separated, washed with water, dried over sodium sulfate, and evaporated to small bulk. On standing the liquid deposited a solid which was crystallized from a 1:1 ether-benzene mixture giving colorless needles (II), m.p. 215–216°, yield 2.1 g. (70%); $\lambda_{max}^{C_2H_5OH}$ 258 mμ (ε 670), 266 (1050) and 274 (1,300).

Anal. Calcd. for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15; mol. wt. (Rast) 352. Found: C, 81.70; H, 9.25; mol. wt., 321.

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(1) Abstracted from the Ph.D. thesis of the author, Imperial College, 1957.

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(3) B. M. Mikhailov, *Bull. Acad. Sci. U.S.S.R.*, 619 (1946); 420 (1948). M. Maienthal, M. Hellmann, C. P. Haber, L. A. Hymo, S. Carpenter, and A. J. Carr, *J. Am. Chem. Soc.*, **76**, 6392 (1954). E. Müller and T. Töpel, *Ber.*, **72**, 273 (1939).

(4) C. S. Rondestvedt and I. Nicholson, *J. Org. Chem.*, **20**, 346 (1955). A. H. Beckett and B. A. Mulley, *J. Chem. Soc.*, 4159 (1955).

(5) Melting points were determined on a Kofler block and are corrected. Analyses by Miss J. Cuckney, Imperial College, London.