[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

2-Acetoxyfuran. A Study of its Preparation and its Behavior as a Diene

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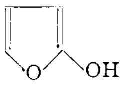
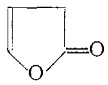
RECEIVED OCTOBER 1, 1955

The cracking of 2,5-diacetoxy-2,5-dihydrofuran to 2-acetoxyfuran, previously accomplished only by high temperature gas phase pyrolysis in 7–40% yield, has been found to proceed satisfactorily in the liquid phase at 200° in 35% yield. The reaction is acid catalyzed, being completely inhibited by a basic catalyst, whereas addition of an acid catalyst raised the yield to 81%. The reactivity of 2-acetoxyfuran as a diene in the Diels–Alder reaction is as great as, though not noticeably greater than, that of furan itself. New adducts of 2-acetoxyfuran with fumaronitrile, maleimide and dimethyl acetylenedicarboxylate are reported, as well as the aromatization of its maleic anhydride adduct to 3-acetoxyphthalic anhydride.

Despite claims to the contrary,[2] the simple hydroxy derivatives of furan appear never to have been prepared,[3] and they probably are not sufficiently stable if capable of existence to be isolated as the free enols. In particular, 2-hydroxyfuran (I) can be considered to be simply the enol form of β,γ-butenolide (II), and enol lactones containing this ring system, such as α-angelicalactone, have never been observed to exhibit enolic properties. Recently, however, a simple ester of 2-hydroxyfuran, 2-acetoxyfuran (III),[4] has been described. This substance was prepared by the vapor phase pyrolysis of 2,5-diacetoxy-2,5-dihydrofuran (IV) at 480–500° in yields varying from 40 down to 7%. The lower yields were attributed to traces of acid-forming impurities in some samples of the starting material.[4]

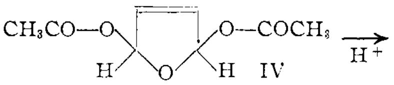


I



II

Since 2,5-diacetoxy-2,5-dihydrofuran is very readily obtained in good yield from furan,[5] it was considered of interest to find a method of preparing 2-acetoxyfuran more conveniently from this substance. It was found that the cracking reaction would proceed at a satisfactory rate in 35% yield in the liquid phase at the relatively low temperature of 200°. The effects of adding a basic or acidic catalyst were then investigated. When a large amount of potassium acetate was added to the reaction vessel the cracking process was completely inhibited at 200°. When, however, a very small amount of β-naphthalenesulfonic acid was employed as catalyst, cracking occurred readily in the temperature range 120–190° and the yield of 2-acetoxyfuran rose to 81%. This procedure, which makes 2-acetoxyfuran a readily available compound, indicates that the liquid phase cracking of 2,5-diacetoxy-2,5-dihydrofuran is clearly an acid-catalyzed process, as indicated in the equation



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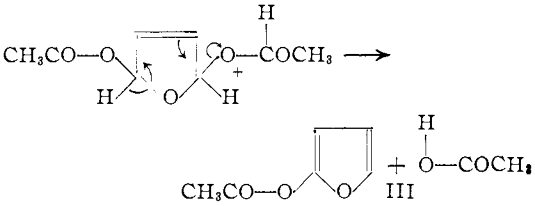
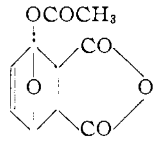


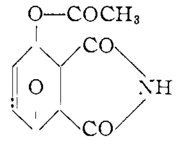
III

The fairly successful results obtained when no acid was added must be ascribed to the catalytic effect of pyrolytic acidic by-products, since the addition of potassium acetate entirely prevented the cracking reaction.

Only one Diels–Alder reaction of 2-acetoxyfuran has been reported,[4] the addition to maleic anhydride to give 3-acetoxy-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride (V). Three more examples of this reaction have now been found. Maleimide, fumaronitrile and dimethyl acetylenedicarboxylate react with 2-acetoxyfuran to give, respectively, 3-acetoxy-3,6-epoxy-Δ^4-tetrahydrophthalimide (VI), 3-acetoxy-3,6-epoxy-Δ^4-tetrahydrophthalonitrile (VII) and dimethyl 3-acetoxy-3,6-epoxy-3,6-dihydrophthalate (VIII). Furan itself is known to give adducts with all four of the dienophiles mentioned above.[6,7] Using the somewhat less reactive dienophiles citraconic anhydride, chloromaleic anhydride, acrylonitrile and *trans*-1,2-dibenzoylethylene no adducts could be obtained from either furan or 2-acetoxyfuran.[8] It appears, therefore, that the introduction of a 2-acetoxy group into the furan ring has little effect upon the reactivity of the system as a diene in the Diels–Alder reaction.



V



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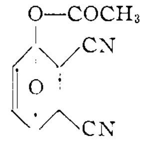
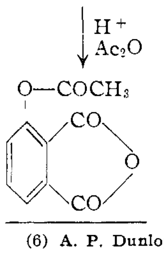
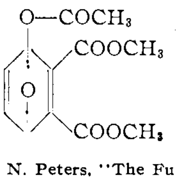


VII



IX



VIII

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[1] From the M.S. Dissertation of C. J. Williams, Jr., The Ohio State University, 1955.

[2] H. H. Hodgson and R. R. Davies, *J. Chem. Soc.*, 806 (1939).

[3] A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Co., 1953, pp. 170–175.

[4] N. Clauson-Kaas and N. Elming, *Acta Chem. Scand.*, **6**, 560 (1952).

[5] N. Clauson-Kaas, A. Lie and N. Elming, *ibid.*, **4**, 1233 (1950).

[6] A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., 1953, pp. 56–57.

[7] H. Kwart and I. Burchuk, THIS JOURNAL, **74**, 3094 (1952).

[8] The absence of reaction was determined by the constancy of the infrared spectra of the diene–dienophile mixtures.

The maleic anhydride adduct of furan is readily aromatized to phthalic acid[9] by hydrobromic acid in acetic acid. Similarly, the maleic anhydride adduct (V) of 2-acetoxyfuran is converted by sulfuric acid in acetic anhydride in 57% yield to 3-acetoxyphthalic anhydride (IX). This reaction represents a convenient new method of preparation of the latter compound.

Acknowledgment.—We gratefully acknowledge the support of this work by the Quaker Oats Company.

Experimental

Liquid Phase Pyrolysis of 2,5-Diacetoxy-2,5-dihydrofuran (IV). A. Without Catalyst.—A mixture of 2,5-diacetoxy-2,5-dihydrofuran (IV)[5] (50.9 g.) and dibutyl phthalate (50 ml.) was heated in a salt-bath at 200° under 10 mm. pressure, the reaction flask being provided with a 40-cm. helix-packed column (column temperature maintained at 120°). During a period of 120 minutes a light yellow distillate (27.3 g.) was collected. This liquid, which contained acetic acid, was diluted with ether (50 ml.) and the mixture was washed with cold saturated aqueous sodium bicarbonate (100 ml.) and dried over magnesium sulfate. Removal of the ether and distillation of the residue gave pure 2-acetoxyfuran (III) (12.7 g., 35%), b.p. 55–58° (10 mm.) (reported[4] b.p. 49–50° at 9 mm.).

B. With a Basic Catalyst.—A mixture of 2,5-diacetoxy-2,5-dihydrofuran (10.0 g.), dibutyl phthalate (25 ml.) and potassium acetate (0.5 g.) was heated at 200° for 90 minutes under conditions similar to those used without catalyst. No material distilled over. The column temperature was raised to 165° and the pressure decreased to 4 mm. A liquid, b.p. 120° (4 mm.), was collected which had an infrared spectrum identical with that of the original 2,5-diacetoxy-2,5-dihydrofuran.

C. With an Acid Catalyst.[10]—A mixture of 2,5-diacetoxy-2,5-dihydrofuran (10.0 g.), dibutyl phthalate (25 ml.) and β-naphthalenesulfonic acid monohydrate (0.05 g.) was heated in a Claisen flask under 2 mm. pressure for 45 minutes, the temperature of the heating bath being raised slowly from 100 to 190°. The distillate (9.5 g., b.p. 28–65° at 2 mm.) was redistilled through a 3-inch packed column to give 2-acetoxyfuran (b.p. 30–45° at 3 mm., 59%). Repetition of this latter experiment on a large scale using 2,5-diacetoxy-2,5-dihydrofuran (113.6 g.), dibutyl phthalate (275 ml.) and β-naphthalenesulfonic acid monohydrate (0.25 g.) gave a yellow distillate (99 g.) which on fractionation yielded 2-acetoxyfuran (62.8 g., b.p. 30–40° at 3 mm., 81.5%). The infrared spectrum of this material indicated it was essentially pure 2-acetoxyfuran.

3-Acetoxy-3,6-epoxy-Δ⁴-tetrahydrophthalimide (VI).—To 2-acetoxyfuran (1.0 g.) was added a solution of freshly sublimed maleimide (0.80 g.) in benzene (4 ml.). Within 5 minutes, white needles began to separate. After standing overnight the product was filtered and recrystallized from benzene to give the imide VI (1.1 g., 61%), m.p. 191–192°.

Anal. Calcd. for $C_{10}H_9NO_5$: C, 53.81; H, 4.06; N, 6.28. Found: C, 54.34; H, 4.24; N, 6.35.

3-Acetoxy-3,6-epoxy-Δ⁴-tetrahydrophthalonitrile (VII).—To 2-acetoxyfuran (1.0 g.) was added a solution of freshly sublimed fumaronitrile (0.8 g.) in benzene (4 ml.). After standing overnight the precipitate was filtered and recrystallized from benzene–petroleum ether to give fine white needles of the nitrile VII (0.50 g., 31%), m.p. 130.0–130.6°.

Anal. Calcd. for $C_{10}H_8N_2O_3$: C, 58.82; H, 3.95; N, 13.72. Found: C, 58.79; H, 3.97; N, 13.80.

Dimethyl 3-Acetoxy-3,6-epoxy-3,6-dihydrophthalate (VIII).—To 2-acetoxyfuran (0.670 g.) was added dimethyl acetylenedicarboxylate (0.733 g.). Within one day the mixture became viscous, but after one week no solid had separated. Benzene (1 ml.) was added and the mixture warmed. On cooling and rubbing, a solid (900 mg.) slowly separated. After recrystallization from benzene the diester VIII (0.70 g., 50%), formed fine white crystals, m.p. 152.2–152.8°.

Anal. Calcd. for $C_{12}H_{12}O_7$: C, 53.73; H, 4.51. Found: C, 53.85; H, 4.55.

3-Acetoxyphthalic Anhydride (IX).—A mixture of 3-acetoxy-3,6-epoxy-Δ⁴-tetrahydrophthalic anhydride (V)[3] (2.0 g.), acetic anhydride (20 ml.) and sulfuric acid (4 drops) was heated at 120° for one hour. The acetic anhydride was removed by distillation at 1 mm. and the dark residue was boiled with benzene (25 ml.) and activated charcoal. The filtered benzene solution was concentrated and cooled to give yellowish crystals (1.3 g.), m.p. 112–113° (sealed tube). Recrystallization from benzene–petroleum ether gave the pure anhydride (1.1 g., 57%), m.p. 116.0–116.2° (sealed tube) (reported[11] 113.5–115.5°).

Anal. Calcd. for $C_{10}H_6O_5$: C, 58.26; H, 2.93. Found: C, 58.12; H, 3.04.

COLUMBUS 10, OHIO

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[9] Reference 6, p. 59.

[10] The exact conditions of method B were not appropriate with an acid catalyst, since cracking occurred too rapidly to be controlled.

[11] D. S. Pratt and G. A. Perkins, THIS JOURNAL, **40**, 227 (1918).

[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE]

Reversible Formation and Eradication of Colors by Irradiation at Low Temperatures. A Photochemical Memory Model

BY YEHUDA HIRSHBERG

RECEIVED AUGUST 29, 1955

It has been found that the colored forms of three spiropyrans and of one bianthrone derivative, produced by ultraviolet irradiation at low temperatures, at which they are stable, could nevertheless be reversibly eradicated, on irradiation with different visible monochromatic lights even at those temperatures. The eradication strength of each of the monochromatic visible lights was measured for the four compounds dissolved in different media. A mechanism for the energy transitions during the formation and eradication of color is proposed. On the basis of the experimental results, for the different media, the chemical course for the whole cycle studied is discussed and presented schematically. The cycle of the appearance of the color on ultraviolet irradiation and the disappearance of the color by irradiation with visible light is proposed for the first time as a photochemical memory model.

Introduction

The reversible formation of colors when colorless solutions of certain compounds are irradiated at room temperature was first reported by Lifschitz.[1] The occurrence of this phenomenon in rigid media solutions of some compounds has been found by Lewis and Lipkin.[2]

In 1950 Hirshberg reported that compounds belonging to the bianthrone series, either thermochromic or non-thermochromic, produce reversibly stable colors when their solutions are irradiated with

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[1] J. Lifschitz, *Ber.*, **52**, 1919 (1919); **61**, 1463 (1928); *Z. physik. Chem.*, **97**, 426 (1921).

[2] G. N. Lewis and D. Lipkin, THIS JOURNAL, **64**, 2801 (1942).