Spectrophotomer, Model DU. Analytical samples of all compounds were used for spectroscopic study.

Summary

1. The rearrangements of three 3,3′,5,5′-tetrasubstituted hydrazobenzenes, in which the substituents are methyl, bromine and chlorine, respectively, are reported. In each case, rearrangements to a benzidine, a diphenyline, and a 2,2′-diaminobiphenyl occur in 2:1 sulfuric acid medium; and disproportionation in considerable amount accompanies the rearrangements. A semidine may have been formed in one case.

2. Certain assessments of the polar and steric effects of the substituents and of medium effects upon the rates of rearrangements, the product ratios and degree of disproportionation are made.

3. The ultraviolet absorption spectra of the rearrangement products are reported and compared.

PITTSBURGH 13, PENNSYLVANIA RECEIVED MAY 26, 1949

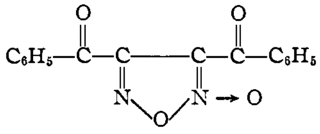
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

A Mechanism for the Formation of Dibenzoylfurazane Oxide from Phenylmethylcarbinol

BY ELLIOT R. ALEXANDER, MARK R. KINTER[1] AND JOHN D. MCCOLLUM

During another investigation, an attempt was made to carry out the nitration of phenylmethylcarbinol with fuming nitric acid in acetic acid solution. A violent reaction occurred. From the reaction mixture, benzoic acid was isolated and in addition a yellow, crystalline substance which had the molecular formula $C_{16}H_{10}O_4N_2$. Analysis by infrared spectroscopy showed a characteristic absorption in the region of a conjugated carbonyl group and of a conjugated carbon–carbon or carbon–nitrogen double bond, but none in the region to be expected of nitro, hydroxyl, amino, nitrile or nitroso groups. It formed a 2,4-dinitrophenylhydrazone and on oxidation with potassium dichromate it gave benzoic acid.

A search of the literature revealed that this compound was identical in its properties with dibenzoylfurazane oxide (I), a compound which also


I

has been prepared by dissolving acetophenone in fuming nitric acid and allowing it to stand at approximately 50° for several days.[2] We then became interested in the mechanism of this unusual transformation. Dibenzoylfurazane oxide, it will be observed, *does not have the carbon skeleton which might be expected from a preliminary self-condensation of acetophenone or phenylmethylcarbinol.* In this paper a mechanism is proposed for the formation of dibenzoylfurazane oxide from phenylmethylcarbinol or acetophenone and experiments are described in support of the intermediates which are suggested.

Experimental[3]

A. Preparation of Dibenzoylfurazane Oxide from Phenylmethylcarbinol.—Phenylmethylcarbinol (61.0 g., 0.5 mole) was dissolved in glacial acetic acid (65 ml.). This solution was placed in a one-liter three-neck flask equipped with a mechanical stirrer, a condenser and a dropping funnel. The mixture was then heated to 100°, stirring was commenced, the heating bath was removed and a solution of red fuming nitric acid (85 ml., d. = 1.59) in glacial acetic acid (50 ml.) was added dropwise. The reaction was exothermic and the heat evolved was sufficient to maintain the reaction mixture at a gentle boil. After addition was complete, stirring was continued until the flask was just warm to the touch. The contents were then poured with stirring into 500 ml. of water. A yellow oil separated and soon solidified. It was collected on a filter, washed with water and dried.

The granular solid was then ground in a mortar with excess 10% aqueous sodium carbonate solution and the resulting thin suspension was filtered. The solid material was washed with water and dried *in vacuo*. Acidification of the filtrate gave 7.3 g. (12.3%) of benzoic acid, m. p. 120–121°. A mixture of this material with an authentic sample of benzoic acid melted at 122–123°.

In order to purify the dry solid which was insoluble in sodium carbonate solution, it was taken up in a slight excess of warm ether, filtered to remove a small amount of insoluble material and evaporated until crystals began to form. On cooling, the product separated as pale yellow crystals, m. p. 82–84°. After one recrystallization from ether, 17.9 g. (24.3%) of almost white dibenzoylfurazane oxide, m. p. 85–86°,[2] was obtained.

Anal.[4] Calcd. for $C_{16}H_{10}O_4N_2$: C, 65.31; H, 3.43; N, 9.52. Found: C, 65.08; H, 3.60; N, 9.79.

By infrared analysis, our sample of dibenzoylfurazane oxide showed absorption in the region characteristic of a conjugated carbon–carbon or carbon–nitrogen double bond.[5] The absorption curve also suggested the absence of nitro, hydroxyl, amino, imino, nitrile or nitroso groups in the molecule. When a solution of the compound in methanol was refluxed with hydrazine hydrochloride, an orange crystalline azine was formed, m. p. 206–207°.[6] A 2,4-dinitrophenylhydrazone was also prepared.[7] It crys-

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(1) Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

(2) Holleman, *Ber.*, **20**, 3359 (1887). For a number of references pertinent to the structure of the furazane oxide ring, see "Beilstein's Handbuch der organischen Chemie," Vol. 27, Julius Springer, Berlin, 1937, p. 562.

(3) All melting points and boiling points are uncorrected.

(4) We are indebted to Miss Theta Spoor for the microanalyses reported in this paper.

(5) We are indebted to Dr. Foil A. Miller and Mrs. J. L. Johnson for the determination and interpretation of the infrared spectra mentioned in this paper.

(6) Widman and Virgin, *Ber.*, **42**, 2794 (1909).

(7) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

tallized from ethanol or ethyl acetate as yellow needles, m. p. 184–185°.

Anal.[4] Calcd. for $C_{22}H_{14}O_7N_6$: C, 55.70; H, 2.97. Found: C, 55.97; H, 2.98.

Oxidation of dibenzoylfurazane oxide with potassium dichromate and sulfuric acid gave benzoic acid. This was identified by a mixed melting point determination.

B. **Preparation of Dibenzoylfurazane Oxide from Acetophenone.**—Acetophenone (61.0 g., 0.5 mole) was treated in the manner described above for phenylmethylcarbinol. All appearances of the reaction were the same except that the crude product obtained by pouring the reaction mixture into water was greenish-white instead of yellow and it solidified much more readily. The yield of dibenzoylfurazane oxide was 34.7 g. (47.2%). Benzoic acid (17.3 g., 28.6%) was also isolated.

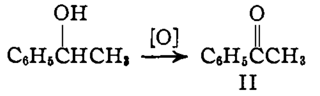
When a run was carried out with oxide-free nitric acid[8] as described in section D, no reaction occurred.

C. **Isonitrosoacetophenone.**—Isonitrosoacetophenone was prepared by the procedure used for the preparation of isonitrosopropiophenone.[9] From 420.0 g. of acetophenone 15.0 g. (2.9%) of isonitrosoacetophenone was obtained, m. p. 125–126°.[10]

D. **Preparation of Dibenzoylfurazane Oxide from Isonitrosoacetophenone.**[11]—In a 200-ml. three-neck flask fitted with a reflux condenser, a mechanical stirrer and an addition funnel were placed isonitrosoacetophenone (1.0 g., 0.0067 mole) and glacial acetic acid (5 ml.). Stirring was commenced and the flask was immersed in a bath of boiling water. To this solution was then added dropwise a mixture of 1 ml. of mineral acid and 5 ml. of glacial acetic acid. In this work runs were carried out with red fuming nitric acid (d. = 1.59–1.60), oxide-free nitric acid[8] and concentrated sulfuric acid. After addition was complete, the mixture was allowed to cool to room temperature and it was then poured into ice-water. A colloidal suspension formed which broke to yield a yellow crystalline mass on stirring and cooling in an ice–salt mixture.

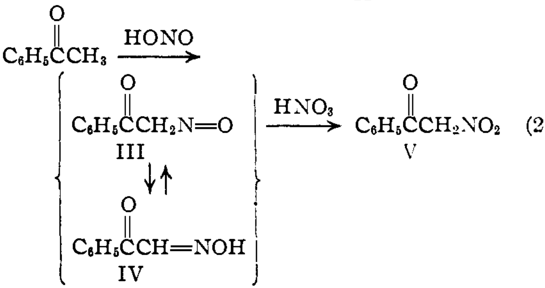
The precipitate was then collected on a filter, washed with a saturated solution of sodium carbonate and then with water. After drying, the solid was recrystallized from ether. In the runs carried out with red fuming nitric acid and oxide-free nitric acid, dibenzoylfurazane oxide separated as characteristic pale yellow crystals, m. p. 81–82°. They showed no melting point depression when mixed with an authentic sample of dibenzoylfurazane oxide. In the run with sulfuric acid, however, no dibenzoylfurazane oxide was formed. The only solid product obtained was a very small amount of material which did not melt at 300°. It was not characterized.

E. **Preparation of Dibenzoylfurazane Oxide from ω-Nitroacetophenone.**—ω-Nitroacetophenone[12] (1.0 g., 0.0061 mole) was treated with a number of different mineral acids in the manner already described for isonitrosoacetophenone. In runs with fuming nitric acid (d. = 1.59–1.60), oxide-free nitric acid[8] and concentrated sulfuric acid, dibenzoylfurazane oxide was isolated in each case and characterized by a mixed melting point determination. When concentrated hydrochloric acid or sirupy phosphoric acid (85%) was employed, almost colorless crystals separated at once when the reaction mixture was poured into water. After drying, they melted at 104–105°,[12] and showed no depression on admixture with a sample of ω-nitroacetophenone.

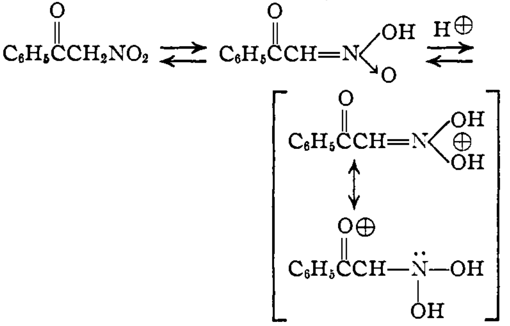


$$C_6H_5\overset{\displaystyle OH}{\overset{|}{C}}HCH_3 \xrightarrow{[O]} \underset{\text{II}}{C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}CH_3}$$

(1)



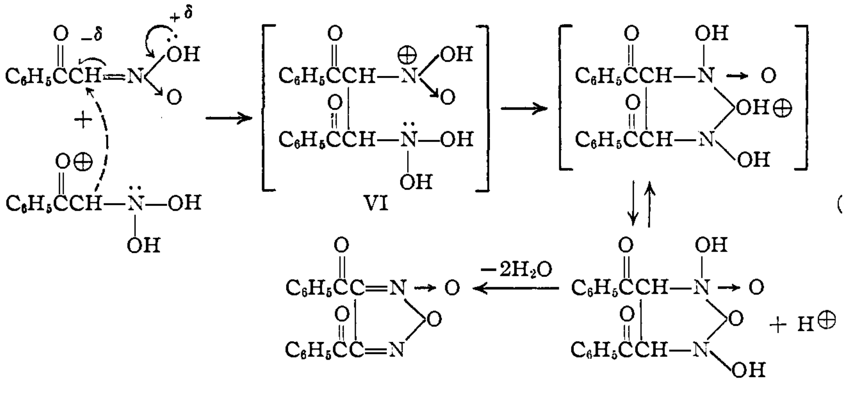
(2)



(3)

Results and Discussion

In equations 1–4 is outlined a possible mechanism for the conversion of phenylmethylcarbinol to dibenzoylfurazane oxide. Under the conditions of the reaction acetophenone (II), isonitrosoacetophenone (IV) and ω-nitroacetophenone (V) each gave dibenzoylfurazane oxide. Preliminary nitrosation (III or IV) followed by oxidation to V seems to be indicated since acetophenone underwent the reaction in the presence of red fuming nitric acid but not in the presence of oxide-free nitric acid. Similarly isonitrosoacetophenone was readily transformed into dibenzoylfurazane oxide by oxide-free nitric acid, but with concentrated sulfuric acid the reaction did not take place.



(4)

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[8] Oxide-free nitric acid was prepared by refluxing nitric acid with urea; see Houben, "Die Methoden der organischen Chemie," Vol. IV, Edwards Bros., Inc., Ann Arbor, Michigan, 1941, p. 139.

[9] Hartung and Crossley, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 363.

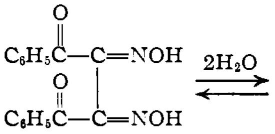
[10] Claisen, *Ber.*, **20**, 656 (1887).

[11] See also Holleman, *ibid.*, **21**, 2837 (1888).

[12] Jakubowitsch, *J. prakt. Chem.*, [2] **142**, 37 (1935).

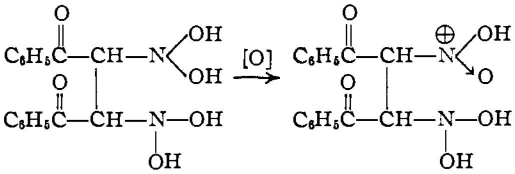
In equations 3 and 4 are shown the intermediates which seem probable to us for the acid-catalyzed self-condensation of ω-nitroacetophenone. Dehydration might, of course, occur earlier in equation 4, but it would not alter the general nature of the step. It is interesting that a strong acid is required for the reaction. With concentrated sulfuric acid or oxide-free nitric acid, ω-nitroacetophenone gave dibenzoylfurazane oxide, but when concentrated hydrochloric or sirupy phosphoric acids were employed the nitro compound was recovered unchanged.

Support for the conversion of an intermediate such as VI to dibenzoylfurazane oxide is to be found in the observation that the dioxime VII can be converted to dibenzoylfurazane oxide on heating with nitric acid.[13] Although it is impossible to decide what the actual intermediate is just before ring closure, it can be seen that the dioxime VII is related to the intermediate V by the steps:



$$\begin{array}{l} C_6H_5\overset{O}{\overset{\|}{C}}-C=NOH \\ \qquad\quad\;\; | \\ C_6H_5\overset{O}{\overset{\|}{C}}-C=NOH \end{array} \quad \underset{\longleftarrow}{\xrightarrow{2H_2O}}$$

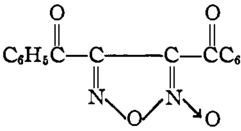
VII



$$\begin{array}{l} C_6H_5\overset{O}{\overset{\|}{C}}-CH-N\begin{smallmatrix}OH\\ OH\end{smallmatrix} \\ \qquad\quad\;\; | \\ C_6H_5\overset{O}{\overset{\|}{C}}-CH-N-OH \\ \qquad\qquad\qquad\;\; | \\ \qquad\qquad\qquad\; OH \end{array} \xrightarrow{[O]} \begin{array}{l} C_6H_5\overset{O}{\overset{\|}{C}}-CH-\overset{\oplus}{N}\begin{smallmatrix}OH\\ \searrow O\end{smallmatrix} \\ \qquad\quad\;\; | \\ C_6H_5\overset{O}{\overset{\|}{C}}-CH-N-OH \\ \qquad\qquad\qquad\;\; | \\ \qquad\qquad\qquad\; OH \end{array}$$

Summary

When phenylmethylcarbinol, acetophenone, isonitrosoacetophenone or ω-nitroacetophenone is treated with red fuming nitric acid in boiling glacial acetic acid solution, the principal product is dibenzoylfurazane oxide.



Of the four possible starting materials, only ω-nitroacetophenone will undergo the reaction in the presence of oxide-free nitric acid or concentrated sulfuric acid. It is suggested that all of these reactions involve the intermediate formation of ω-nitroacetophenone and a mechanism is proposed for the transformation.

URBANA, ILLINOIS RECEIVED JULY 20, 1949

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[13] Angeli, *Ber.*, **26**, 528 (1893).

[CONTRIBUTION FROM ROHM & HAAS COMPANY]

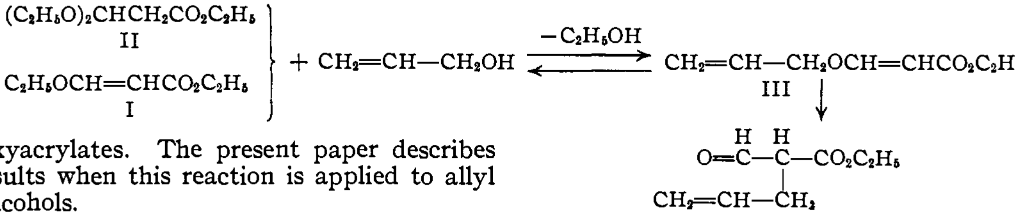
Transetherification Reactions. Preparation and Rearrangement of β-Alloxyacrylates[1]

BY W. J. CROXALL AND J. O. VAN HOOK

In a previous paper it was reported that the transetherification of ethyl β-ethoxyacrylate (I) and ethyl β,β-diethoxypropionate (II) with alcohols[2] produced ethyl β-alkoxyacrylates and alkyl β-alkoxyacrylates. The present paper describes our results when this reaction is applied to allyl type alcohols.

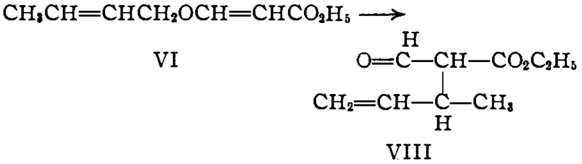
Allyl alcohol and the acrylate (I) or propionate (II) react in the presence of acidic or basic catalysts to give ethyl β-alloxyacrylate (III) and allyl β-alloxyacrylate (IV), respectively. Other allyl type alcohols react in a similar manner. Table I lists the various allyl ether esters which were prepared from these alcohols.

These esters which possess an allyl vinyl ether group[3] undergo a Claisen rearrangement on heating. Thus, the alloxyacrylate (III) is converted to ethyl α-formylallylacetate (V). The equation illustrates the transetherification and rearrangement.



$$\left.\begin{array}{c} (C_2H_5O)_2CHCH_2CO_2C_2H_5 \\ \text{II} \\ C_2H_5OCH=CHCO_2C_2H_5 \\ \text{I} \end{array}\right\} + CH_2=CH-CH_2OH \underset{\longleftarrow}{\xrightarrow{-C_2H_5OH}} \begin{array}{c} CH_2=CH-CH_2OCH=CHCO_2C_2H_5 \\ \text{III} \;\downarrow \\ \begin{array}{l} \overset{H}{O=C}-\overset{H}{C}-CO_2C_2H_5 \\ \qquad\quad\; | \\ CH_2=CH-CH_2 \end{array} \\ \text{V} \end{array}$$

In a similar manner ethyl β-crotoxyacrylate (VI) and methallyl β-methalloxyacrylate (VII) were rearranged to ethyl α-formyl-3-methyl-4-pentenoate (VIII) and methallyl α-formylmethallylacetate (IX), respectively.



$$\begin{array}{c} CH_3CH=CHCH_2OCH=CHCO_2H_5 \longrightarrow \\ \text{VI} \end{array} \quad \begin{array}{l} \overset{H}{O=C}-CH-CO_2C_2H_5 \\ \qquad\qquad\; | \\ CH_2=CH-\underset{H}{C}-CH_3 \end{array}$$

VIII

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[1] For the previous paper in this series, see Croxall, Van Hook and Luckenbaugh, THIS JOURNAL, **71**, 2741 (1949).

[2] Croxall, Van Hook and Luckenbaugh, *ibid.*, **71**, 2736 (1949).

[3] Tarbell, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 4.