The separation of the chalcone and arylidene flavanone is not easy.

The product from the reaction of 2-hydroxy-5-nitroacetophenone with benzaldehyde (V) is not 6-nitroflavanone, 5-nitroflavanol, 6-nitro-flavanone, 2-benzoyl-6-nitro-flavone, nor 2′-benzoyloxy-5′-nitrochalcone (m.p. of a mixture). The compoud is insoluble in cold ethanolic sodium hydroxyde (absence of hydroxyl groups) and does not contain halogen.

Analyses are additional proof of the structure as 3-benzylidene-6-nitroflavanone. It is similar to 3-benzylideneflavanone[12] in that the double bond is not sensitive to bromine.

Experimental[13]

Materials.—Benzaldehyde was 4-chloro-benzaldehyde, commercial grade. 5-nitro-2-hydroxyacetophenone, 4-nitro-2-hydroxy-acetophenone, and 3-nitro-4-hydroxyacetophenone were prepared by Fries reaction[14,15]; 6-nitro-3-hydroxyacetophenone was obtained by Klinke's method.[6] The preparation of the chalcones used has been described in earlier papers.[5,6,16]

Condensation of 5-Nitro-2-hydroxyacetophenone with Benzaldehyde. 3-Benzylidene-6-nitroflavanone (V).—A mixture of 5-nitro-2-hydroxyacetophenone (0.37 g.; 2 mmoles), benzaldehyde (1 ml.; 9.9 mmoles) and anhydrous ethanol (15 ml.) was saturated with hydrogen chloride at 0°. The mixture was kept at room temperature for 30 min., refluxed for 25 min., poured into water (40 ml.) and evaporated. A hot saturated solution of the residue in ethyl acetate was diluted with aqueous ethanol (60%) to turbidity and cooled. The crystals formed were collected in the cold and shaken with aqueous ethanolic sodium hydroxide (25 ml. of ethanol; 2 ml. of 2 *N* sodium hydroxide) for 3 min. The solid V, 3-benzylidene-6-nitroflavanone, was filtered (0.29 g.), washed with ethanol and subsequently with dilute acetic acid, and finally it was twice crystallized from ethanol–ethyl acetate–water (1:1:2), to give pure V (20% yield) m.p. 158°.

Anal. Calcd. for $C_{22}H_{15}NO_4$: C, 73.9; H, 4.2; N, 3.9; O, 17.9. Found: C, 73.9; H, 4.5; N, 3.9; O, 17.9.

Acidification of the alkaline filtrate gave the chalcone in 60% yield.

Only the chalcone was formed at room temperature even with a 20-fold excess of aldehyde, or if a mixture of reactants not containing an excess of aldehyde was refluxed.

If in the above experiment ketone was replaced by chalcone or flavanone the benzylidene compound was obtained in yields of 30% and 80%, respectively.

Condensation of 3-Nitro-4-hydroxyacetophenone with Benzaldehyde.—The yield of chalcone under the experimental conditions already described was 90%. Only tarry products could be isolated even when a large excess of benzaldehyde was used under refluxing conditions for 5 hr. No identifiable result was obtained in attempts to condense the 3′-nitro-4′-hydroxychalcone with benzaldehyde.

Condensation of 4-Nitro-2-hydroxyacetophenone with Benzaldehyde. 3-Benzylidene-7-nitro-flavanone.—The benzylidene flavanone and the chalcone were formed as described in experiment 1 with a refluxing time of 5 min. (25%). The benzylidene flavanone was also rapidly produced from the chalcone and aldehyde in aqueous ethanol. (30% yield). A 1.5-mmole sample of chalcone was suspended in 15 ml. 96% ethanol. The mixture of chalcone and benzylideneflavanone was separated by treatment with aqueous ethanolic sodium hydroxyde as previously described. (20 ml. of ethanol and 20 ml. of 1 *N* sodium hydroxide), m.p. 156–157°.

Anal. Calcd. for $C_{22}H_{15}NO_4$: C, 73.9; H, 4.2; N, 3.9; O, 17.9. Found: C, 73.7; H, 4.4; N, 4.1; O, 17.8.

If the refluxing period was longer than 5 min., tarry materials were formed.

Condensation of 5′-Nitro-2′-hydroxychalcone with 4-Chlorobenzaldehyde. 3-*p*-Chlorobenzylidene-6-nitroflavanone.—The chalcone (1.35 g.; 5 mmoles) and 4-chlorobenzaldehyde (1.45 g.; 10 mmoles) in ethanol (65 ml.) were saturated under cooling in an ice bath with dry hydrogen chloride. After standing for an hour, the mixture was refluxed for 5 hr. The unchanged chalcone (0.7 g.) separated from the solution on cooling in a refrigerator. After mixing the mother liquor with 30 ml. of water a pale yellow solid (0.6 g.) melting at 98° separated. After recrystallizing from carbon tetrachloride 6-nitroflavanone (0.4 g.) melting at 112° was obtained. The mother liquor of the recrystallization was evaporated to dryness and the residue obtained in this way was boiled with a small amount of methanol and filtered. The substance insoluble in methanol gave after recrystallization from ethyl acetate 3-*p*-chlorobenzylidene-6-nitroflavanone melting at 175–176°.

Anal. Calcd. for $C_{22}H_{14}NO_4Cl$: C, 67.4; H, 3.6; N, 3.6; Cl, 9.0. Found: C, 67.2; H, 4.0; N, 3.8; Cl, 8.6.

Starting from 4′-nitro-2′-hydroxychalcone in this experiment a yellow crystalline substance melting at 221–222° (N, 4.7; Cl, 10.6) was obtained, which was not the expected benzylidene compound and gave a melting point depression with the 4′-nitro-2′-hydroxy-4′-chlorochalcone.

Condensation of 6-Nitro-3-hydroxyacetophenone with Benzaldehyde. 6′-Nitro-3′-hydroxychalcone.—The ketone (0.28 g.; 1.5 mmoles) was dissolved in 13 ml. of anhydrous ethanol, then saturated for half an hour under cooling in ice with hydrogen chloride, kept standing for half an hour, and finally boiled under reflux for an other half hour. After distilling the solvent the dry residue was recrystallized from benzene to give 6′-nitro-3′-hydroxychalcone melting at 177–81° (75% yield). After a repeated recrystallization the melting point rose to 185°.[17]

Condensation of 5′-Nitro-2′-hydroxy-4-chlorochalcone with Benzaldehyde. 3-Benzylidene-6-nitro-4′-chloroflavanone.—A mixture of the chalcone (0.2 g.; 0.66 mmole) and benzaldehyde (0.72 ml.; 7 mmoles) in 30 ml. of 96% ethanol was saturated with hydrogen chloride in the manner described above and after standing for half an hour refluxed for 2.5 hr. The unchanged chalcone, which separated on cooling was removed by filtration. On mixing the filtrate with water (15 ml.) the crude 2-benzylidene-6-nitro-4′-chloroflavanone melting at 130° separated (40% yield).

This product was recrystallized three times from a mixture of ethyl acetate–ethanol and 1–2 drops of water so that in every case the first fraction of crystals separating from the lukewarm ethyl acetate–ethanol solution was filtered off and 1–2 drops of water added to the filtrate just after this operation. In this way ivory-colored leaflets insoluble in alkali were obtained; m.p. 165°. The mixture of chalcone and benzylideneflavanone could be separated also with the aid of an alkaline methanolic solution.

Anal. Calcd. for $C_{22}H_{14}NO_4Cl$: C, 67.4; H, 3.6; N, 3.6. Found: C, 67.0; H, 3.7; N, 3.9.

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[13] The melting points are uncorrected.

[14] T. Széll, *Chem. Ber.*, **91**, 2609 (1958); A. S. U. Chaughulay and G. C. Amin, *Sci. Cult.* (Calcutta), **91**, 614 (1954); Sh. S. Joshi and J. Singh, *J. Am. Chem. Soc.*, **76**, 4993 (1954).

[15] Á. Gerecs, T. Széll, and M. Windholz, *Acta Chim. Acad. Sci. Hung.* **3**, 459 (1953).

[16] C. M. Christian and G. C. Amin, *Chem. Ber.*, **90**, 1287 (1957); G. S. Chhaya, P. L. Trivedi, and G. V. Jadhav, *J. Univ. Bombay*, **25** (5) 8 (1957).

[17] Sipos and Széll also have found this melting point.[5]

The Pyrolysis of 3-Acetoxytetrahydrofuran

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There are very few examples of the effect of an adjacent hetero atom on the direction of pyrolysis of esters.

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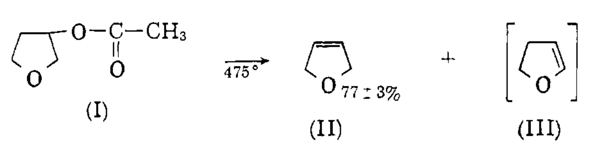
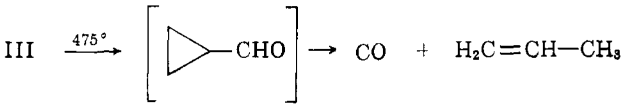
[1] National Science Foundation Summer Research Participant, 1959.

Of these few examples, two bear on the effect of an adjacent oxygen atom. Burchfield[2] found that on pyrolysis of the diacetate of propane-1,2-diol the secondary acetate was eliminated the more rapidly, and 75% of the olefinic product was allyl acetate and 25% propionaldehyde enol acetate. DePuy, King, and Froemsdorf[3,4] pyrolyzed 2-acetoxy-1-methoxypropane, and found an approximately 50–50 mixture of the 1- and 2-olefins to be formed.

A third ester with a beta oxygen has also been pyrolyzed. This ester is 3-acetoxytetrahydrofuran (I), which is readily prepared from the commercially available 3-hydroxytetrahydrofuran. Olsen[5] noted that pyrolysis of this ester gave no 2,3-dihydrofuran (III), but instead gave 3,4-dihydrofuran (II) and furan.



It had previously been shown, however, that 2,3-dihydrofuran decomposes when heated on glass[6] with the ultimate production of propylene and carbon monoxide. The following scheme has been suggested.



If this decomposition reaction of the enol ether were taking place during the pyrolysis reaction, a simple product analysis would give misleading results with respect to the direction of elimination. As a consequence we have re-examined this pyrolysis. At 475–500° only a single dihydrofuran is formed in the pyrolysis of I, and this olefin is 3,4-dihydrofuran, as shown by its spectral properties and its retention time on gas chromatography. In addition, two low-boiling products are formed, and these have been identified as propylene and carbon monoxide. We therefore believe that the 2,3-dihydrofuran is destroyed during the pyrolysis. In order to get an accurate measure of the relative amounts of the two olefins formed, we have made use of gas chromatography with an internal standard. A known mixture of the ester (I) and chlorobenzene was pyrolyzed to about 50% conversion. This conversion was determined accurately by the relative amounts of chlorobenzene and ester in the product. The amount of 3,4-dihydrofuran formed was also determined accurately from the chlorobenzene–olefin ratio in the product. By this method it was determined that pyrolysis of I gives 77 ± 3% of II. By difference it is assumed that the other 23% is III.

Experimental

3-Acetoxytetahydrofuran (I).—This ester was prepared from 3-hydroxytetrahydrofuran obtained from the Aldrich Chemical Company. Careful fractionation gave a fraction; b.p. 71.5–72.5°, 19 mm. [lit.,[7] b.p. 64° (2 mm.)].

3,4-Dihydrofuran (II).—This olefin was prepared by treating 2-butene-1,4-diol (25 g.) with sulfuric acid (1 g.) in a distilling flask at 20 mm. The product distilled as soon as formed, and was collected in a Dry Ice trap. Fractionation gave a pure fraction, b.p. 65–66° (lit.,[7] b.p. 67°).

Pyrolysis.—The pyrolyses were carried out as described previously.[3] In a typical run a mixture of 6.61 g. of chlorobenzene and 3.93 g. of I was analyzed by g.p.c. and the relative peak area determined. A portion of the mixture (3.27 g.) was pyrolyzed at 450°. At the temperature and flow rate chosen only about 50% conversion was obtained. A low boiling gas, identified as propylene by its g.p.c. retention time was obtained, along with higher boiling products. The higher boiling products were analyzed by g.p.c. using the chlorobenzene as an internal standard. From the decrease in ester–chlorobenzene ratio the amount of ester decomposed could be determined. From the olefin–chlorobenzene ratio the amount of 3,4-dihydrofuran was determined. Corrections were made for differences in thermal conductivities between the olefin and chlorobenzene, as determined by the analysis of known mixtures. By this method it was determined that pyrolysis of I gives 77 ± 3% II.

Gas Chromatography.—A 1-m. column of THEED[8] 1:3 on 60/80 firebrick in series with a 1-m. column of THEED on Fluoropak was used at 125°.

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[4] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 433 (1960).

[5] S. Olsen, *Acta Chem. Scand.*, **4**, 473 (1950).

[6] J. Wilson, *J. Am. Chem. Soc.*, **69**, 3002 (1947).

[7] W. Reppe, *Ann.*, **596**, 1 (1955).

[8] N,N,N',N'-Tetrakis(2-hydroxyethyl)ethylenediamine.

Half-lives of Some Inert Oxiranes in Acetic Acid–Pyridinium Hydrobromide at 30°

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Epoxysuccinic acids have been prepared by a variety of methods. Earlier stereochemical studies involved their interconversion to the corresponding chloromalic and tartaric acids.[1–3] Both the *trans*-racemate and the *cis,meso*-forms can be prepared from fumaric and maleic acids, respectively, by a sodium tungstate-catalyzed hydrogen peroxide oxidation.[4] The *cis,-meso*-form has been prepared also by the hydrogen peroxide oxidation of benzoquinone[5] and by nitric acid oxidation of the macrolide antibiotic, carbomycin.[6] To obtain the pure (−)-*trans* isomer, however, a fermentative preparation is convenient since good yields have been reported from the fermentation of dextrose by *Aspergillus fumigatus*.[7–10]

These prior publications, particularly some of the oxidative preparations and the formation of an acid chloride from the *cis* isomer by prolonged heating with phosphorus pentachloride,[11] suggested a remarkable

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