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THE PHOTOCHEMICAL ADDITION OF BENZOPHENONE TO FURAN

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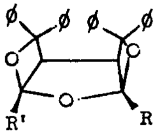
The photoaddition of benzophenone to olefins to form oxetanes is well documented (1). There are, however, only a few examples of similar reactions with dienes or aromatic compounds (2,3). One such reaction is the curious photoaddition of benzophenone to furan.* This was first observed by Schenck et al., (3) and since then the addition of carbonyl compounds to furan has been examined extensively (4,5).

Recently, Ogata et al., (6) reported that the photochemical addition of two molecules of benzophenone to furan gave two products, to which they have assigned the trioxotricyclic structures Ia and IIa.

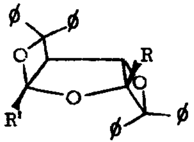


I

Ia, $R=R'=H$

Ib, $R=H$, $R'=CH_3$

Ic, $R=R'=CH_3$



II

IIa, $R=R'=H$

IIb, $R=H$, $R'=CH_3$

During our investigations (5) on the stereochemistry of oxetanodihydrofurans (the 1:1 photoadducts of ketones or aldehydes to furan), we obtained from benzophenone and furan low yields of the 2:1 adduct IIa and an isomer (IVa), in addition to the 1:1 adduct IIIa. Higher yields of IIa and IVa were obtained when a nearly equimolar benzene solution of benzophenone and furan were used according to the following procedure.

A solution of 36.2 g. (0.2 mole) benzophenone and 21.4 g (0.3 mole) furan in 230 cc benzene was purged with nitrogen for 1/2 hr. and irradiated under a nitrogen atmosphere for 8 days with a 450 watt Hg HP lamp (Hanovia) with a Pyrex filter. During the irradiation, 17.4 g. of a colorless solid precipitated; a TLC of the crude irradiation mixture indicated at least

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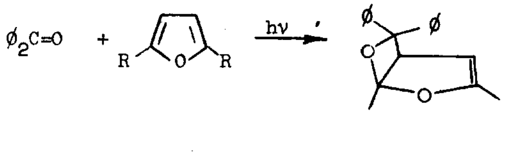
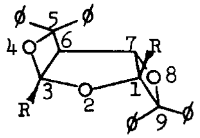
* Furan is unique in its photochemical reactivity with benzophenone in that other heterocyclic compounds (thiophene, pyrrole, isoxazole or oxazole) do not undergo analogous oxetane formation.

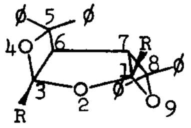
five components (R_f's - 0.57, 0.35, 0.23, 0.12 and 0.01). After filtration, concentration and recrystallization, 7.67 g. (18% yield) of crude II (R_f 0.23), m.p. 183-186° (needles from tetrahydrofuran, m.p. 192-193°) and 12.8 g. (29% yield) crude IV (R_f 0.12), m.p. 209-211° d. (needles from benzene, m.p. 211-212° d.) were obtained.* In a similar manner, the dimethyl analog IVc (needles from ether, m.p. 179-180°) was obtained after 3 days irradation in 19% yield.



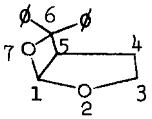
III



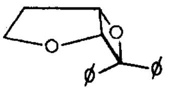
II



IV



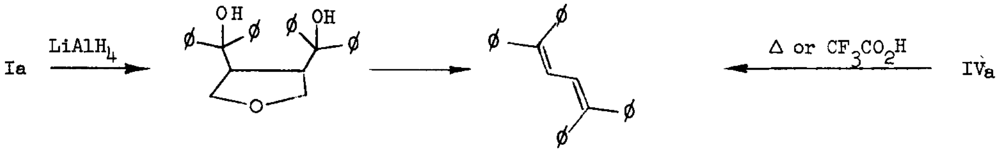
V



VI

II, III, IV, a, R=H
c, $R=CH_3$

Ogata et al., were able to demonstrate the 2,4,9-arrangement of the oxygen atoms by chemical reduction. Treatment of Ia with $LiAlH_4$ resulted in the formation of the tetrahydrofuran diol VII. Upon treatment with acetic acid-hydrochloric acid they obtained 1,1,4,4-tetraphenylbuta-1,3-diene (VIII). Similarly we have been able to reduce IVa to VII. In addition we have observed that IVa is thermally unstable; sublimation gave a 43% yield of VIII. Furthermore, treatment of IV with trifluoroacetic acid at room temperature for 10 min. afforded a 34% yield of VIII.‡



VII VIII

While the data from our products are in essential agreement with that reported (6), we assigned different structures, IVa and IVc rather than Ia and Ic, to the more symmetrical diadducts. Our assignment was based on the NMR spectrum of the skeletal protons in IVa or Ia which, as reported by Ogata et al., consists of a pair of doublets centered at 5.96 δ and 3.70 δ, and

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*The C, H and O analyses, the Mol. wt. determination, the IR and the UV spectra agree with the proposed structures and will be reported in a full paper; the NMR also agrees with the structures and it is discussed in the text.

‡The acid catalyzed cleavage of oxetanes to give olefins is well known and has been used by other workers for structure proof; see ref. 1a.

mutually split by 4 Hz. The spin system for either structure in question is AA'XX' (7), which involves two chemical shifts and four coupling constants. Since H-1 in the model structure V is split only by H-5 to give a doublet, it may be assumed that $J_{AA'}=J_{AX'} \simeq 0$ for either configuration Ia or IVa. The AA' or XX' part of the spectrum thus depends on the ratio of $J_{XX'}$ ($J_{6,7}$ in IV) to J_{AX} ($J_{1,7}$ and $J_{3,6}$ in IV) as shown in FIG. 1. To use this figure, one draws a horizontal line corresponding to any desired value of $J_{XX'}$ (relative to J_{AX}) and measures the frequencies from the intersections of this line with the solid curves of the upper figure. The intensities of the variable frequency transitions relative to the two fixed lines are given by the broken curve of FIG. 1. An example where $J_{XX'}=J_{AX}$ is shown in the lower figure. The spectrum will consist of two identical parts corresponding to that predicted from FIG. 1, each centered at the A and X chemical shifts. It is apparent that this spectrum will not reduce to a doublet unless $J_{XX'}$ is smaller than the limit of resolution, corresponding here to about 1/4 J_{AX} or 1 Hz. Based on the well-known (8) dependence of vicinal coupling constants on dihedral angle, we take this to be strong evidence for a <u>trans</u> ($\phi \simeq 100°$) configuration of the protons as implied by structure IVa, rather than the <u>cis</u> configuration ($\phi \simeq 15°$) required by structure Ia. Model compounds lend further support to this conclusion (9). The absence of an observable coupling between protons on C-6 and C-7 in the product II likewise led us to assign a <u>trans</u>-<u>anti</u> structure to the unsymmetrical adduct, here in agreement with Ogata et al.

The coupling in the 1,3-dimethyl derivative IVc is not directly measurable, but observation of the enhanced (3000 scans) ^{13}C satellite spectrum ($J_{CH} \simeq 140$ Hz) for the 3.62 δ signal permits us to place an upper limit of 1.0 Hz on the coupling in this compound, which again supports the <u>anti</u> structure IVc over the <u>syn</u> structure Ic by the above arguments (7,8).

Ogata et al., base their assignment of a <u>syn</u> configuration to the symmetrical diadduct on dipole moment data, their principal arguments being the following:

1. Compound Ic (but not Ia nor Ib) yields an isomer on treatment with methanolic acetic acid which has a similar NMR spectrum, but a smaller dipole moment. Ic and its rearrangement product were assumed to be <u>syn</u>-<u>anti</u> isomers, whereupon Ic was designated <u>syn</u> due to its larger dipole moment.
2. The observed dipole moment of Ia was in good agreement with group moment calculations based on tetrahydrofuran and compound V.

The purported isomerization of the <u>syn</u> adduct Ic to the <u>anti</u> adduct IVc, if true, is certainly without precedent and is more surprising in view of the acid instability of oxetanes (1a, 10). We would like to propose an alternate, more reasonable isomerization of the irradia-

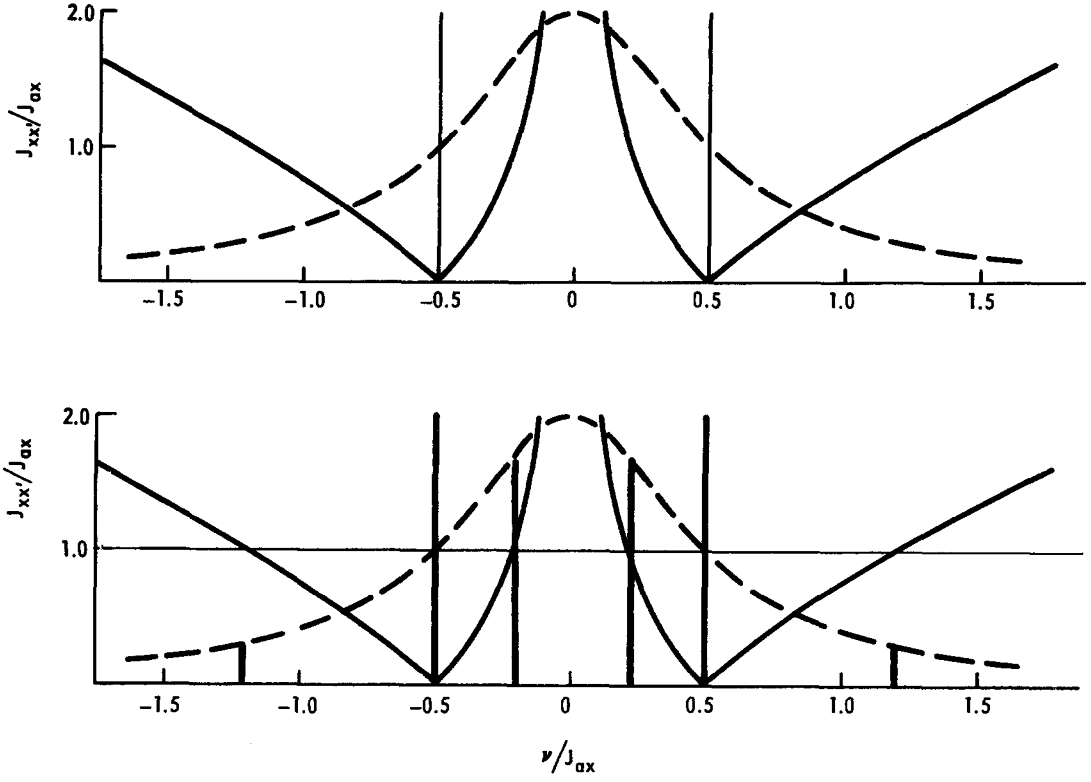

FIGURE 1

TOP: CALCULATED FREQUENCIES (RELATIVE TO J_{ax}) AND INTENSITIES OF EITHER GROUP IN AN AA'XX' SPECTRUM WITH $J_{AA'} = J_{A'X} = J_{AX'} = 0$.

BOTTOM: CALCULATED LINE SPECTRUM FOR $J_{XX'} = J_{AX}$.

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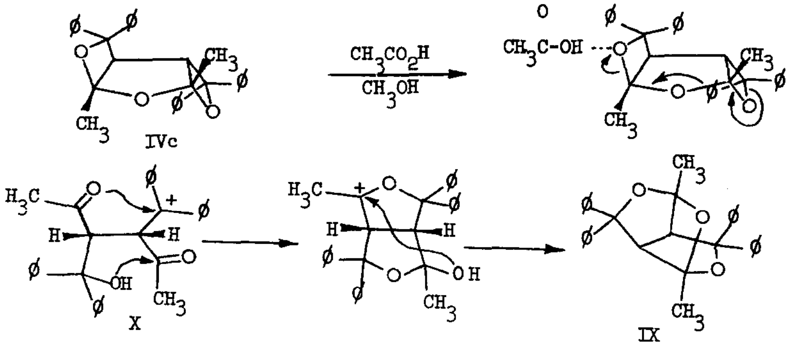
tion product IVc (or Ic) to the structure IX which is also consistent with the reported data (6).

The acid catalyzed decomposition from IVc via the dicarbonyl carbonium ion X has the correct geometry to give the tricyclic product IX. By this mechanism a rearrangement of Ia or Ib



would be less likely since intermediate aldehydes would be formed and hemi-acetal formation might be favored with the solvents (methanol-acetic acid) employed.

The NMR of the acid catalyzed rearrangement product of IVc has a 2H singlet at 3.52 δ and a 6H singlet at 0.85 δ. However the ^{13}C sattelites ($J_{CH} \simeq 150$ Hz) of the 3.52 δ signal reveals a vicinal coupling constant of 1.8 Hz, consistent with the dihedral angle of ~60° expected from models of X but inconsistent with the <u>anti</u> structure ($J \leq 1$ Hz) proposed by Ogata et al.

The other evidence cited by Ogata et al., is the close agreement between the observed dipole moment of Ia (3.74 D) and that (3.70 D) calculated for a <u>syn</u> configuration of group moments derived from furan and V. Group moment calculations are tenuous, however, as witnessed by the fact that consistently good agreement is not obtained for the <u>pair</u> of isomers involved. Using Ogata's model, we calculated a lowering of 0.4 D on going from a <u>syn</u> to an <u>anti</u> configuration, but yet the observed difference in dipole moments of the dimethyl analog Ic and its isomer is 1.17 D. We therefore consider the agreement of the calculation for Ia to be fortuitous. The lack of appropriate models does not permit us to calculate a dipole moment for IX that we feel would have any bearing on the argument.

We believe we have isolated the same products that Ogata et al., have isolated, and we agree on the structure of the product IIa. On the other hand, their arguments for the structure of compounds Ia and Ic are invalidated by the NMR evidence that we cited. Hence, we must conclude from the data that products IVa and IVc have the <u>anti</u>-configuration.

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