

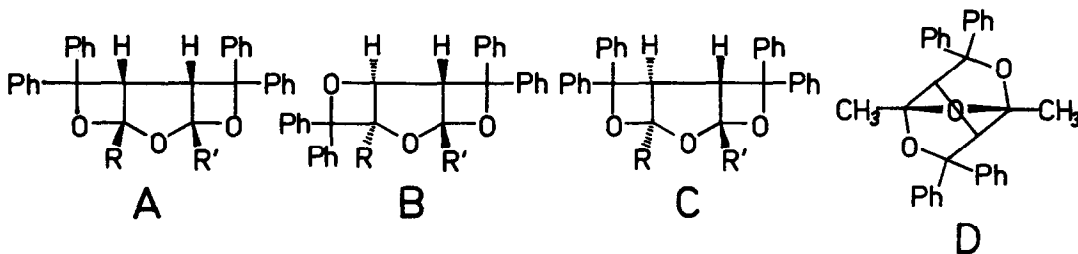
Comments on the paper  
PHOTOCHEMICAL CYCLOADDITION OF BENZOPHENONE TO FURANS<sup>1</sup>

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Ogata, Watanabe and Kano recently reported<sup>1</sup> benzophenone to give two isomeric 2:1 photoadducts with furan (IIa + IIIa), 2-methylfuran (IIb + IIIb) and one with 2,5-dimethylfuran (IIc). IIc on mild acid treatment changed into another isomer, VIII. They assigned structure A to compounds of series II, B to those of series III and C<sub>c</sub> to VIII.



a, R=R'=H  
b, R=H, R'=CH<sub>3</sub>  
c, R=R'=CH<sub>3</sub>

On the basis of the data given by the authors we should prefer to assign structure C rather than A to series II for the following reasons:

1) The n.m.r.-spectrum of IIa is reported to show two doublets ( $\tau = 4.06$  and  $6.30$ ) with  $J = 4$  cps. For an A<sub>2</sub>B<sub>2</sub>-system (as is exhibited by both A<sub>a</sub> and C<sub>a</sub>), such a type of spectrum will only be expected if the coupling between the two equivalent "upper" protons at the 3- and 4'-positions of the tetrahydrofuran ring is very small, 3 cps at most if the doublet is very "unclean", much less if it is sharp. Such a small coupling is exactly what is to be expected

for  $C_a$  where the dihedral angle between the two protons is close to  $90^\circ$ , (this is born out by the fact that in IIIa (=  $B_a$ ) the analogous coupling is also close to 0), whereas for A one should expect couplings of 7-8 cps, considering the present experience with five-membered rings and even taking into account strong distortion of the molecule.

2) Structure A when constructed as Dreiding model (using the newly supplied oxetane rings) exhibits absolutely prohibitive non-bonding interactions. In the state of least angle strain, two phenyl rings inevitably penetrate each other completely. This can be avoided by distorting the assembly but even then severe non-bonding interactions will remain. C, on the contrary, is free of such strain.

3) The authors' assignment rests on the dipole moments; they calculated 3.70 D for  $A_a$  which fits excellently with their experimental value for IIa, 3.74 D. However, using their parameters we calculated 3.33 D for structure  $C_a$ , which also fits IIa perfectly within the limits of accuracy inherent in the method; the precise agreement found by the authors is fortuitous anyway.

Since structure  $C_c$  is now no longer available for VIII, we propose a different structure, D, of the same symmetry ( $C_2$ ) for this compound which fits all its properties:

1) Formation from IIc =  $C_c$  under acidic conditions is to be expected. (D is less strained than  $C_c$ .)

2) Dreiding models show that the plane of one phenyl ring in D should lie right above one methyl group, resulting in a high field shift of the latter. This fits nicely with the abnormally high value,  $\tau = 9.15$ , found for the latter.

3) Although we could not precisely calculate the dipole moment to be expected for D it was estimated to lie somewhere between 2.36 and 2.67 D. Agree-

ment of the experimental value, 2.00 D, with this estimate is not too good, but still better than with the value to be expected for  $C_0$ , which should be greater than 2.76 D (3.33 D minus allowance for two methyl groups).

These reassignments eliminate the question why the symmetric 2:1 adduct should have formed exclusively in the syn-form A and the asymmetric adduct exclusively in the anti-form B. Rather both products are formed in the anti-forms B and C.

#### Reference

- 1 M. Ogata, H. Watanabe and H. Kano,  
Tetrahedron Letters 1967, 533