Oxetan Formation from Photoexcited Charge-transfer Complexes of Anhydrides with Electron-rich Olefins

By SAMIR FARID* and S. E. SHEALER

(*Research Laboratories, Eastman Kodak Company, Rochester, New York* 14650)

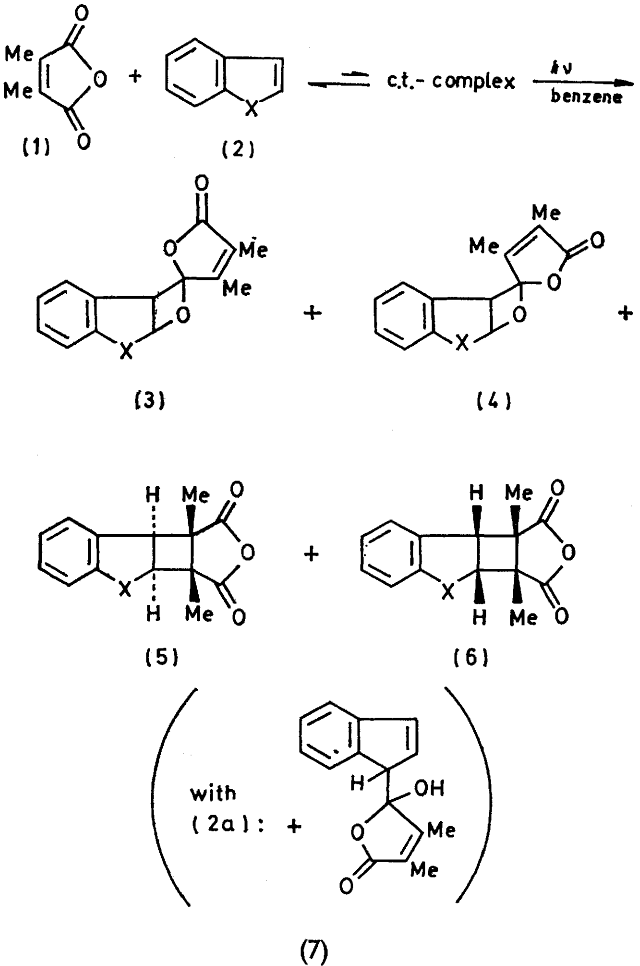
Summary Excitation of c.t.-complexes of dimethylmaleic, phthalic, and naphthalic anhydride with indene, 1,1-dimethylindene, and benzofuran in nonpolar solvents leads to oxetan and cyclobutane formation; cyclobutane production is preceded by intersystem crossing of the complex.

OXETANS are photochemically obtained from the reaction of a large variety of $n\pi^*$ triplet carbonyl compounds with olefins.[1] A few examples for oxetan formation *via* singlet excited carbonyl compounds[2] or the singlet excited olefin[3] are also known. This report describes the formation of oxetanes *via* excitation of charge-transfer complexes of the reactants.

The photoreactions of maleic anhydride and its derivatives with olefins have been studied extensively.[4] With few exceptions,[5] the major products of these sensitized or unsensitized reactions are the corresponding cyclobutane adducts. The absorption spectrum of a benzene solution of dimethylmaleic anhydride (**1**) in presence of indene (**2a**) indicated the formation of a weak c.t.-complex ($K < 0{\cdot}1$). Monochromatic irradiation of this complex (366 nm) led to the formation of the oxetans (**3a**) and (**4a**),[†] the cyclobutane (**5a**), and the RH-addition product (**7**), as well as traces of 1,1′-bi-indenyl with the major products (**3a**) and (**7**).[‡]

The triplet-sensitized reaction of (**1**) and (**2a**) is reported[6] to yield the cyclobutane (**5a**) in high yield.[§]

To explore the scope of this novel reaction leading to oxetans *via* c.t.-complex excitation, we varied both the olefin and the anhydride. 1,1-Dimethylindene (**2b**) and benzofuran (**2c**) form similar c.t.-complexes with (**1**). Excitation of these complexes in benzene led to the oxetans (**3b**), (**4b**), (**3c**), and (**4c**), together with the cyclobutanes (**5b**), (**6b**), and (**5c**), respectively. In these reactions with benzophenone as a triplet sensitizer, only the cyclobutane derivatives were obtained.



a; X = CH_2, b; X = CMe_2, c; X = O

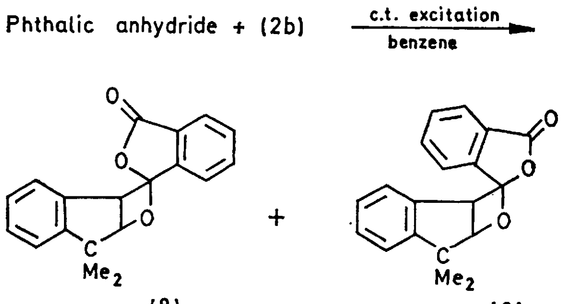
[†] The stereochemistry of the oxetans was deduced from the n.m.r spectra ($CDCl_3$) based on the pronounced shielding effect of the aromatic rings in (**4**), (**9**), and (**10**).

[‡] Compounds (**3a**) and (**4a**) undergo acid-catalysed oxetan → enone rearrangement to the corresponding aldehyde. During column and gas chromatographic work-up, compound (**7**) rearranges to the 3-substituted indene derivative and dehydrates to the corresponding triene.

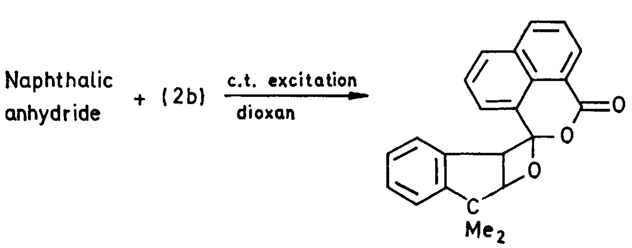
[§] We found that the only other product of this sensitized reaction is the isomeric cyclobutane (**6a**). The ratio (**6a**) : (**5a**) is 1 : 36 in benzene and 1 : 15 in acetonitrile.

Phthalic anhydride and naphthalic anhydride also formed c.t.-complexes with (**2b**), although the reduction potentials of these anhydrides are higher than that of (**1**). Analogously, c.t.-excitation of these complexes led to the oxetans (**8**), (**9**), and (**10**), respectively. The reaction of the phthalic anhydride–(**2a**) complex yielded a similar mixture of the corresponding oxetans and R–H addition products.

It is interesting that whereas the ratio (**3**) : (**4**) from all three olefins ranged between 8 : 2 and >9 : 1, the ratio of the corresponding oxetans from phthalic anhydride and (**2a**) or (**2b**) is *ca.* 1 : 1 and the reaction of naphthalic anhydride afforded only the more sterically hindered isomer (**10**). This implies that overlap between the aromatic rings of the anhydride and the olefin molecules is favoured in the intermediate leading to these products. The ground-state complex seems to possess, at least partly, this configuration with π-overlapping orbitals since irradiation in the crystalline state of frozen indene solutions (−50°) of dimethylmaleic anhydride and phthalic anhydride yielded (**3a**) as the only major product in the first case and *ca.* 1 : 1 mixture of the two oxetans in the latter, which is similar to the solution reaction. The fact that the products reflect the stereochemistry of the ground-state complex indicates that the oxetans are formed directly from the excited complex rather than being preceded by a geminate radical-ion pair formation. In these systems the formation of the solvated radical ions would be expected to take place in polar media. This was found to be the case and the chemistry of the resultant indene radical cation is discussed in a future communication.



(8) (9)



(10)

The formation of the cyclobutanes is most probably preceded by intersystem crossing of the excited c.t.-complex. Support for this view is obtained from the fact that both the c.t.-excitation reaction and the benzophenone-sensitized reaction provided the same ratio of (**6b**) : (**5b**) and, more important, the dependency of this ratio¶ on the solvent in both the sensitized and unsensitized reactions was the same. It is very unlikely that both the same product ratio and the same solvent dependency would be observed if different reacting species were involved in the two reactions.

(*Received*, *5th March* **1973**; *Com.* **293**.)

¶ The ratio (**6b**) : (**5b**) from both sensitized and unsensitized reactions is 1 : 5·8 (in benzene), 1 : 5 (in chlorobenzene), 1 : 3·6 (in 1,2-dichloroethane), and 1 : 2 (in acetonitrile, only from the sensitized reaction).

[1] *Cf.* D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301; and references therein.

[2] N. C. Yang, R. Loeschen, and D. Mitchell, *J. Amer. Chem. Soc.*, 1967, **89**, 5465; N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, 1970, **92**, 320; and references therein.

[3] S. Farid, J. C. Doty, and J. L. R. Williams, *J.C.S. Chem. Comm.*, 1972, 711.

[4] G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.*, 1963, **96**, 498; R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, 1965, **98**, 3854; H. D. Scharf and F. Korte, *Chem. Ber.*, 1965, **98**, 764; *cf.* also R. Steinmetz, *Fortschr. Chem. Forsch.*, 1967, **7**, 445.

[5] J. A. Barltrop and R. Robson, *Tetrahedron Letters*, 1963, 597; C. H. Krauch and H. Küster, *Chem. Ber.*, 1964, **97**, 2085; H. D. Scharf and F. Korte, *Tetrahedron Letters*, 1966, 2033.

[6] W. Metzner, H. Partale, and C. H. Krauch, *Chem. Ber.*, 1967, **100**, 3156.