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PHOTOCHEMICAL CYCLOADDITIONS OF ETHENE AND PROPENE TO BENZENE

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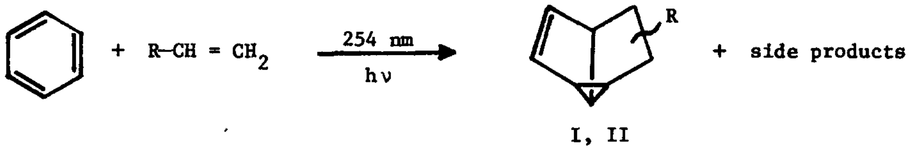
Addition of photoexcited benzene to olefins gives either 1.2-, 1.3-, or 1.4-adducts, depending on the nature of the olefin. The 1.3-addition of benzene to alkenes may proceed from the S_1 - state of benzene through a prefulvene intermediate or by a concerted meta addition.[1] In some cases an exciplex intermediate has been proposed based on kinetic investigation.[2] The 1.2-addition is believed to be the preferred product forming process when the adding olefins have certain donor or acceptor character. D. Bryce-Smith concluded from experimental results that olefins with ionization potentials of I.P. > 9.6 eV or < 8.65 eV behave as acceptors or donors, respectively, and thus undergo mainly 1.2-addition with photoexcited benzene.[3] The previously reported 1.3-addition of vinylenecarbonate[4] (I.P. = 10.08 eV) to benzene is not in agreement with D. Bryce-Smith's prediction. Since this contradiction might be explained by special properties of the vinylenecarbonate, we investigated the photochemical reaction of benzene with the simplest possible olefins, ethene (I.P. = 10.5 eV)[5] and propene (I.P. = 9.73 eV).[5] We found that both olefins add to S_1-benzene in meta-position and the 1.3-adducts I and II result as the major products. The experiments were carried out



I : R = H
II : R = CH_3

in a UV-autoclave[6] fitted with a low pressure mercury lamp (TNN 15/32, Quartzlampen GmbH, Hanau) under elevated olefin pressure in various solvents (see Table I). Compounds I and II were isolated by preparative gc (2 m x 20 mm 20% US 138 on gaschrom P 45/50 mesh and 2 m x 20 mm 20% ukon LB 1715 on gaschrom P 45/60 mesh, T 90° C). The structure of I was identified to be tricyclo $(3.3.0.0^{2,8})$ oct-3-ene by comparison with the reported nmr-spectrum.[7] Product II was a mixture of two isomers, which could not be separated. But, a comparison of the methyl group nmr signals with data of the butene adducts to benzene[8] shows that the two products are most likely the exo- and endo-isomers (II a,b) rather than one of the other possible isomers (e.g., IIc).[13]

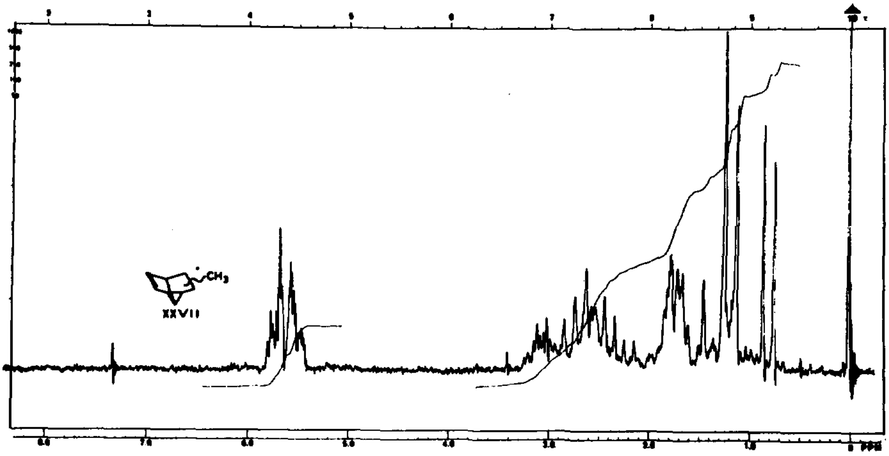
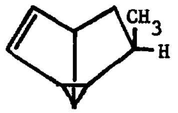
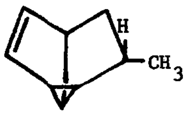
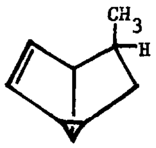


Figure I : NMR spectrum of the propene-benzene-photoadduct


IIa


IIb

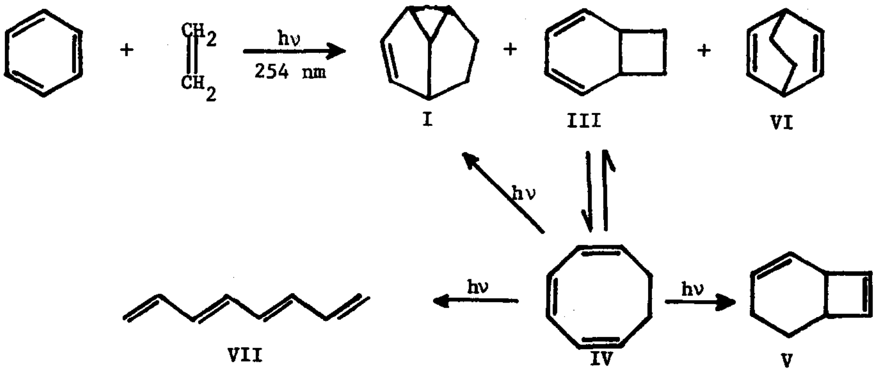

IIc

The quantum yield of formation of 1.3-adducts was directly dependent upon olefin-pressure and values of $\Phi = 0.1$ (for I and II) were obtained at 50 bar ethene (∿12 mole/l) and 14 bar propene pressure. It was impossible to achieve a higher benzene conversion than 5-10%, probably due to light absorption and/or quenching by sideproducts (see below).

Table I. Quantum Yields of Addition Products of the Irradiation of Benzene with Ethene and Propene.
Lamp: TNN 15/32 (Quarzlampen GmbH Hanau)
Benzene - Conc.: 1 mol/l. T.: 25° C

Olefin pressure bar	Quantum yield 1.3-adducts	Others	Irradiation time hrs	Solvent	Olefin
15	0.02	0.015	1.5	CH_2Cl_2	ethene
27	0.08	0.07	1.5	"	"
50	0.11	0.08	1.5	"	"
21	0.06	trace	16	cyclohexane	"
40	0.09	0.01	16	"	"
50	0.10	0.02	16	benzene	"
14	0.1	--	16	cyclohexane	propene

After short irradiation times (90 min) the major sideproducts were the 1.2-adduct III and its tautomer IV, as could be shown by comparison of the gc retention times with authentic samples.[9] But at higher conversion III and IV were present only in small amounts, whereas their photoproducts (V, VI, VIII) could now be identified by their retention times in gc (V, VI)[10] or by its characteristic uv - spectrum (VII).[11] Several other unidentified sideproducts were formed in small amounts. Compared with ethene the propene addition to benzene was a rather clean reaction. Except for a small amount of polymer, no side products were detectable.



Our results are not in accord with predictions based on D. Bryce-Smith's generalizations.[3] In spite of high ionization potentials of 10.5 eV and 9.73 eV respectively, ethene and propene clearly prefer a 1.3-addition to benzene rather than the predicted 1.2-addition. Their high ionization potentials and the low electron affinities (E.A. = -1.8 eV)[12] of ethene and propene make these olefins both poor electron donors and poor electron acceptors. Therefore the 1.2 addition of these olefins to benzene is only of minor importance. Thus, although D. Bryce-Smith's prediction is probably based on the right idea, it is necessary to consider electron affinities, not ionization potentials, in order to predict acceptor properties of olefins, since a high I.P. cannot always be equated with a high E.A.

REFERENCES

1. D. Bryce-Smith and A. Gilbert, Tetrahedron Letters, 32, 1309-26 (1976).
   D. Bryce-Smith, Chem. Comm., 806 (1969).
2. V.Y. Merrit, J. Cornelisse and R. Srinivasan, J. Am. Chem. Soc., 95, 8250 (1973).
3. D. Bryce-Smith, A Gilbert, B. Orger, H. Tyrell, Chem. Comm., 1974, 334.
4. H.G. Heine and W. Hartmann, Angew. Chem., 87, 708 (1975); Intern. Ed., 14, 698 (1975).
5. A.J. Gordon and R.A. Ford, "The Chemist Companion", Wiley, (1972).
6. A. Saus, CZ - Chemie Technik 1973, 19
7. O.L. Chapman, G.W. Borden, R.W. King and B. Winkler, J. Am. Chem. Soc., 86, 2660 (1964).
8. A. Morikawa, S. Brownstein and R.J. Cvetanovic, J. Am. Chem. Soc., 92, 1471 (1970).
9. Compounds III and IV were prepared independently by the procedure described by A.C. Cope, A.C. Haven, F.L. Ramp and E.R. Trumbull, J. Am. Chem. Soc., 74, 4867 (1952).
10. The retention times of V and VI were identical with those of the photoproducts in the sensitized reaction of 1,3-cyclohexadiene with acetylene. These results are to be published elsewhere. After hydrogenation of the reaction mixture V was identified as cis-bicyclo (4.2.0) octane (IX) and VI as bicyclo (2.2.2) octane (X) by gc comparison with independently prepared samples. For preparation of IX see R.S.H. Liu, J. Am. Chem. Soc., 89, 112 (1967) and for X see J. Hine, J.A. Brown, L.H. Zalkow, W.E. Gardner and M. Hine, J. Am. Chem. Soc., 77, 595 (1955).
11. G.F. Woods and L.H. Schwartzman, J. Am. Chem. Soc., 71, 1396 (1949).
12. A. Henglein, W. Schnabel and J. Wendenburg, "Einfuehrung in die Strahlenchemie", Verlag Chemie, Weinheim (1969).
13. The methyl group doublets are centered at 0.78 ppm (j = 7hz) and 1.15 ppm (j = 7 hz) compared with 0.78 and 1.11 ppm for methyl groups in 7-position of the benzene-butene-adduct given in ref. 8. The corresponding methyl groups in the 6-position are reported[8] to be at 0.98 ppm and 0.73 ppm respectively. A more detailed assignment will be presented elsewhere.

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