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STEREOCHEMISTRY OF 1,3-PHOTOADDUCTS OF BENZENE TO 2-BUTENES

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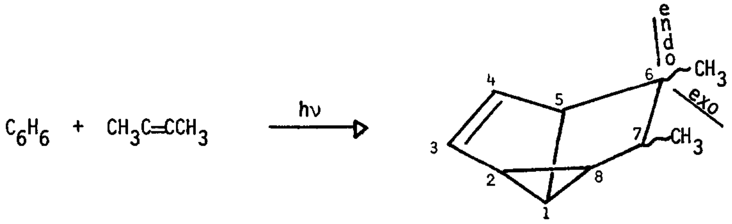
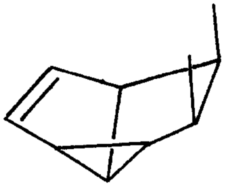
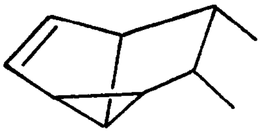
The photochemical 1,3-addition of benzene to olefins which was first described by Wilzbach and Kaplan[1] is now known to be a general reaction which proceeds with a high quantum yield in many instances. It was demonstrated even in 1966[1] that the stereochemistry of the olefin is retained in the adducts but the orientation of the olefinic group with respect to the rest of the molecule has been established in few instances. The major adduct that is formed from benzene and cyclobutene has been shown to have the *endo* structure.[2] The orientation of the methyl groups in the adducts (I, II, III and IV) from *cis* and *trans*-2-butenes has been a matter of controversy. From an analysis of the nmr spectra of the adducts, Wilzbach and Kaplan[1] concluded that the major adduct from *cis*-2-butene and benzene had the 6,7-*endo* dimethyl



(1)



I



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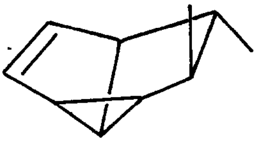

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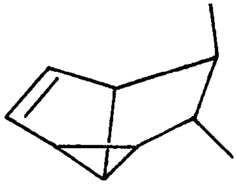
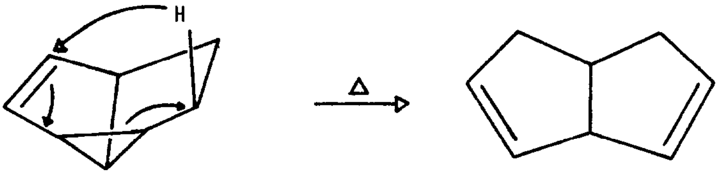


IV

structure (I). This was disputed by Morikawa, Brownstein and Cvetanovic[3] who interpreted the nmr spectra of these adducts to mean that the major adduct from cis-2-butene was II, while the stereochemistry of the major and minor adducts from trans-2-butene were assigned to be as in III and IV respectively. For the latter two compounds they claimed[3] that these structures were the reverse of the assignment that would be made if the adduct to cis-2-butene had structure I.

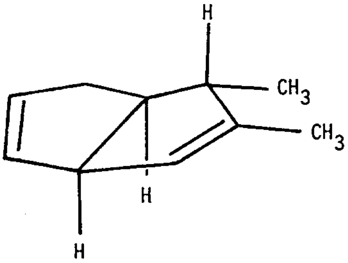
We report here results on the pyrolysis of all four of these adducts. These data help to establish the orientation of the methyl groups in these compounds.

Pyrolysis of tricyclo[3.3.0.0^{2,8}]octene-3 is known[4] to proceed according to equation (2), the reaction being an example of the well-known homo[1,5]sigmatropic shift.[5] Since the proton on C_7 that undergoes migration must be endo-oriented in order that the reaction may take place in a suprafacial manner, the occurrence of this isomerization establishes the presence of such a proton.

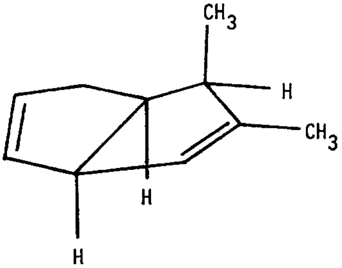


(2)

Of the two 1,3-photoaddition products from cis-2-butene and benzene, the major one was recovered unchanged after heating to 300° for 20 min. as a vapor. The minor adduct, under identical conditions, was converted quantitatively to an isomer (Mol. Wt. by mass spectrum: 134) whose nmr spectrum (solv. CCl_4; tetramethyl silane as internal reference) consisted of absorptions at δ, 5.51-2H-singlet; 5.18-1H-broad; 3.58-1H-v. broad; 2.7-1.9-4H-complex; 1.62-3H-broad singlet; 1.36-3H-doublet, J = 7 Hz. The spectrum would fit structure V which is



V

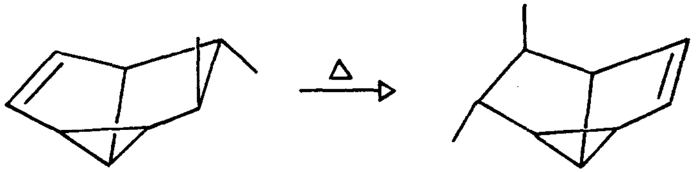


VI

the product that can be expected by a 1,5-H shift from C_7 to C_4 in structure II. The major 1,3-adduct must therefore have structure I. This assignment would agree with that made by Wilzbach and Kaplan.[1]

Of the two 1,3-addition products of benzene to trans-2-butene,[6] the major one was stable to heating to 250° for 20 mins. Under the same conditions, the minor adduct was transformed quantitatively to an isomer (Mol. Wt. by mass spectrum: 134) whose nmr spectrum consisted of absorptions at δ, 5.54-2H-broad singlet; 5.17-1H-broad; 3.45-1H; 3.2-2.4-2H; 2.25-2H; 1.63-3H-broad singlet; 0.98-3H-doublet, J = 7Hz. The spectrum would fit structure VI which is the product that can be expected by the 1,5-H shift from C_7 to C_4 in structure IV. Since V and VI differ only in the stereochemistry of the methyl group at C_4, it is to be expected that their nmr spectra would be similar as, indeed, they are.

The major 1,3-photoadduct of benzene to trans-2-butene which must have structure III proved to be unstable to pyrolysis at a higher temperature, i.e., 310°. The only product under these conditions was VI. This is understandable since III can rearrange to IV by a vinylcyclopropane rearrangement (equation 3) and the latter would in turn give VI. A similar sequence of a vinylcyclopropane rearrangement followed by a 1,5-sigmatropic shift has been observed in the closely related 1,3-photoadducts of m-xylene to cyclobutene.[7]



(3)

These pyrolytic transformations suggest that the stereochemistry that was assigned to the 1,3-adducts of trans-2-butene to benzene by Morikawa, Brownstein and Cvetanovic[3] is correct.

The data that are available at present indicate that when benzene adds 1,3 to a small olefinic molecule, the products show a preferential 6,7-endo orientation of the substituents on the olefin. Bulky olefins such as norbornene, favor an exo-orientation[8] in the adduct probably due to steric considerations.

References

1. K. E. Wilzbach and L. Kaplan, J. Amer. Chem. Soc., 88, 2066 (1966).
2. R. Srinivasan, IBM J. Res. Dev., 15, 34 (1971).
3. A. Morikawa, S. Brownstein and R. J. Cvetanovic, J. Amer. Chem. Soc., 92, 1471 (1970).
4. W. R. Roth and B. Peltzer, Ann., 685, 56 (1965).
5. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr, Germany, 1970, p. 132.
6. If the numbering used in ref. 3 to identify the adducts is followed, the major and minor 1,3-adducts from trans-2-butene would be 4 and 5; the major and minor 1,3-adducts from cis-2-butene would be 8 and 7. The chromatograms reported earlier[3] were well-reproduced in this work.
7. R. Srinivasan, J. Amer. Chem. Soc., 93, 3555 (1971).
8. R. Srinivasan, J. Phys. Chem. (in press).