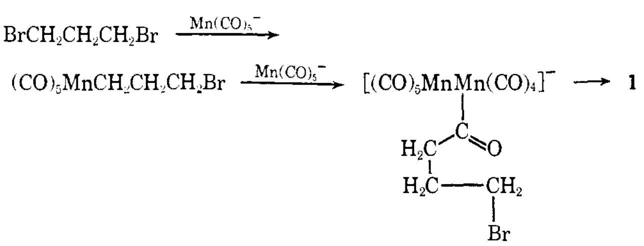
limed at 25° (40 mm) in a closed system to give $\mathrm{CH_3Mn(CO)_5}$ (0.24 g 48% recovery). The residue from this sublimation was chromatographed on silica gel with pentane–benzene to give a small amount of $\mathrm{Mn_2(CO)_{10}}$ and a slower moving orange solid further purified by sublimation at 50° (0.01 mm), identified as the methylmethoxycarbene complex **6** (0.24 g, 24% yield, mp 78–81°, lit.[6] mp 81°). Compound **6** was identical in physical and spectral properties with an authentic sample of the methylmethoxycarbene complex prepared according to Fischer's procedures.[6]

In contrast to Fischer's facile isolation of mononuclear acyl anions as their tetralkylammonium salts,[7] our attempts to isolate the acetyl anion **4** led to the formation of $\mathrm{(CH_3)_4N^+Mn(CO)_5^-}$ and $\mathrm{CH_3Mn(CO)_5}$.

The formation of the cyclic metal carbene complex **1** from 1,3-dibromopropane and $\mathrm{NaMn(CO)_5}$ can now be rationalized according to the reaction sequence presented in Scheme II. The key step in the sequence is the attack of $\mathrm{Mn(CO)_5^-}$ on an intermediate alkylmanganese compound to give a dinuclear acylmanganese anion similar to the adduct **4** obtained above. The dinuclear acylmanganese anion is trapped by intramolecular alkylation of the acyl oxygen atom by the alkyl bromide functionality.

Scheme II



$$\mathrm{BrCH_2CH_2CH_2Br} \xrightarrow{\mathrm{Mn(CO)_5^-}} \mathrm{(CO)_5MnCH_2CH_2CH_2Br} \xrightarrow{\mathrm{Mn(CO)_5^-}} [\mathrm{(CO)_5MnMn(CO)_4}]^- \longrightarrow \mathbf{1}$$

We are presently investigating the generality of this new reaction and its potential in the synthesis of other dinuclear metal–carbene complexes.

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(7) E. O. Fischer and A. Maasbol, *Chem. Ber.*, **100**, 2445 (1967).

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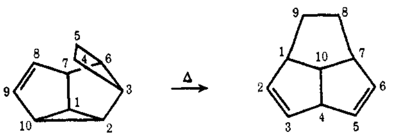
Orientation of Substituents in the Photochemical 1,3 Addition of Benzene to Cyclobutene

Sir:

The first report by Wilzbach and Kaplan[1a] on the photochemical 1,3 addition of benzene to olefins has been followed by a number of others[1–5] which have demonstrated the generality of this reaction with respect to a variety of linear and cyclic olefins. While it is known[1b] that the excited state of benzene that takes part in this reaction is the singlet ($^1\mathrm{B}_{2u}$) state or a structure derived from it, its geometry is a matter for speculation. Two observations which are pertinent to this problem are: (i) the addition is a concerted reaction,[1a] and (ii) the 1,2 and 1,4 additions of benzene to olefins may also occur from the same precursor since, in a given system, the relative quantum yields of 1,2 and 1,4 additions to the 1,3 addition are invariant with experimental conditions.[1d,5]

We report here data on the modes of photochemical 1,3 addition of toluene and the three xylenes to cyclobutene. These results seem to provide a clue to the structure of the excited state of the benzene when it undergoes 1,3 addition.

The choice of cyclobutene as the olefin was advantageous for three reasons: first, the addition proceeded with as high a quantum yield as between benzene and cyclobutene and with the same chemical yield (~20%).[5] Secondly, it was possible to establish that the stereochemistry of the adducts was 3,6 endo (in structure I) in all cases because all of them underwent the (2′-vinylcyclopropyl)cyclobutane rearrangement (reaction 1)[6] to give derivatives of tricyclo[5.2.1.0^{7,10}]deca-2,5-diene (II). Thirdly, the location of the methyl groups in these structures was, for the most part, readily done merely by noting the chemical shifts of these protons in the nmr spectra of the photoadducts and their thermally rearranged products.[7] A cross-check was provided by the number of olefinic protons that were missing from these spectra when compared to the spectra of I or II. To illustrate, the 3,6-endo adduct obtained from *o*-xylene could have one of six structures according to the positions of the two methyl groups. Since the product had two olefinic protons, and neither of its methyl groups was located on a double bond, the substituent groups can only be (in structure I) at positions 10,2 or 2,1 or 1,7. Based on these three probable structures, pyrolysis of this adduct can give one of three tricyclic products in which the methyl groups would be (in structure II) at positions 3,5 (two olefinic protons–two allylic methyls) or 4,5 (three olefinic protons–one allylic methyl) or 4,10 (four olefinic protons–no allylic methyl). The product actually corresponded to the second one.



I II (1)

A unique structure assignment based on these data alone was not possible in every instance. The structures of the adducts from *p*-xylene, toluene, and one of the adducts from *m*-xylene could be narrowed down to two possibilities. The final choice was based on the following consideration. In the nmr spectra of all five of the adducts that were obtained in this work, it was noticed that the absorption at *ca.* δ 3.1 due to a proton originating from the benzene ring was missing.

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(1) (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2066 (1966); (b) K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, **90**, 1116 (1968); (c) L. Kaplan and K. E. Wilzbach, *ibid.*, **90**, 3291 (1968); (d) K. E. Wilzbach and L. Kaplan, *ibid.*, **93**, 2073 (1971). The author wishes to thank Drs. Wilzbach and Kaplan for sending him a preprint of this communication.

(2) (a) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966); (b) D. Bryce-Smith and H. C. Longuet-Higgins, *ibid.*, 593 (1966); (c) D. Bryce-Smith, *Pure Appl. Chem.*, **16**, 47 (1968); (d) D. Bryce-Smith, *Chem. Commun.*, 806 (1969).

(3) (a) K. Koltzenburg and K. Kraft, *Tetrahedron Lett.*, 389 (1966); (b) K. Draft, Doctoral Dissertation, University of Bonn, 1968.

(4) A. Morikawa, S. Brownstein, and R. J. Cvetanovic, *J. Amer. Chem. Soc.*, **92**, 1471 (1970).

(5) R. Srinivasan, *IBM J. Res. Develop.*, **15**, 34 (1971).

(6) R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 7542 (1970).

(7) We judge it unlikely that free-radical migrations of methyl groups will occur in the course of these thermal rearrangements.

Table I. Structures for Photoadducts and Their Thermal Rearrangement Products

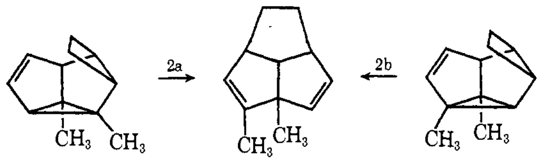
		Photoadduct I nmr spectrum		Pyroproduct II nmr spectrum		Possible CH_3 positions		
Aromatic compd	No. of adducts obsd	No. of olefinic protons obsd	Methyl group at δ	No. of olefinic protons obsd	Methyl group at δ	Photoadduct[a] I	Pyroproduct[b] II	Final[d] structure for photoadduct I
o-Xylene	1	2	1.08, 1.23	3	1.12, 1.58	7,1; 1,2; 2,10	3,4	1,2
m-Xylene	2	2	1.20, 1.30	3	1.12, 1.58	7,2; 1,10	3,4	1,10
		1	1.40, 1.80	3	1.12, 1.58	1,8; 7,9; 8,10; 9,2		1,8[c]
p-Xylene	1	1	1.36, 1.86	3	1.13, 1.60	1,9; 2,8	2,4; 3,10	1,9[c]
Toluene	1	2	1.27	4	1.09	1; 2; 10; 7	4; 10	1[c]

[a] Only structures consistent with the number of olefinic protons are given. [b] Only structures consistent with the number of olefinic protons and condition a are given. [c] Final structure based on absence of nmr absorption due to proton at C_1 position in photoadduct (see text). [d] All new compounds gave satisfactory elemental analyses.

It suggested that one substituent position was common to all of these adducts. This corresponded to the C_1 position in the two adducts for which unique structures were assignable. The final structures for the other three were selected on this basis (Table I).[8]

A fortuitous extra check of the assignments came out of the observation that the dimethyltricyclo-[5.2.1.0^{7,10}]deca-2,5-diene derived from the adduct of *o*-xylene to cyclobutene was identical with the one from one of the adducts of *m*-xylene to cyclobutene.

This was interpreted according to reactions 2a and 2b.



Pyrolysis of the second adduct from *m*-xylene (one olefinic proton) gave exactly the same dimethyltricyclodecadiene as the first adduct. A possible explanation is that this compound first undergoes the vinylcyclopropane rearrangement to yield the first adduct which then rearranges as in reaction 2b. Hence the second adduct is most likely to be the 1,8-dimethyl derivative. The absence of the nmr absorption at δ 3.1 as described before supports this.[9]

The most remarkable feature of these reactions is the limited number of adducts that are actually formed compared to the number that are theoretically possible. The selectivity seems to depend on the requirement that position 1 in the adduct must be substituted. Since no major adduct was unexamined, there are no negative exceptions to this statement, and the only positive exception (*i.e.*, a possible product that is not formed in significant quantity) is the 1,9-dimethyl derivative of I when the reactants are *o*-xylene and cyclobutene. The explanation may be simply that in a rigid structure such as I, it is impractical, on steric grounds, to have methyl groups at both positions 1 and 7.[10]

The preferential orientation of a methyl group at the C_1 position may be viewed as being due to either a strong directive influence from the CH_3 group or the intermediacy of an excited state in which one substituent will always be in this position. The latter hypothesis suggests that the excited state may have a high order of symmetry.[11] It is at present obscure whether or not a unique structure would satisfy this and the other observations (concertedness; constant ratio of 1,2, 1,3, 1,4 addition) concerning the 1,3-addition reaction.

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(8) A complication that can exist in all but one of these systems is that a vinylcyclopropane rearrangement in structure I may precede the (2′-vinylcyclopropyl)cyclobutane rearrangement. The exception is the adduct from *p*-xylene for which the photoadduct is degenerate with respect to the first transformation. In the other cases, the complication will arise only if the photoadduct can give one dimethyltricyclo[5.2.-1.0^{4,10}]deca-2,5-diene while its valence isomer (formed by a vinylcyclopropane rearrangement) can give a different dimethyltricyclo[5.2.1.0^{4,10}]-deca-2,5-diene with the same number of olefinic protons. Fortunately, this complication did not come up although evidence for the occurrence of the vinylcyclopropane rearrangement was uncovered in one instance.

(9) It is possible that the methyl group at the C_8 position impedes the pyrolytic rearrangement to the expected 1,7-dimethyltricyclo[5.2.1.0^{4,10}]-deca-2,5-diene.

(10) Molecular models show that the 1,2-dimethyl derivative of I is not similarly crowded.

(11) It may at first sight seem as if an excited prismane structure would be an appropriate choice as the reactive state. In addition to possessing a high symmetry it can account for the formation of 1,2, 1,3, and 1,4 adducts from a single intermediate. But on closer scrutiny it can be realized that it would have no better chance (on a statistical basis) of giving a limited number of products in the 1,3 addition than the substituted Kekulé benzene structure.

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The Stereochemistry of [2,3]-Sigmatropic Reactions. The Wittig Rearrangement

Sir:

The [2,3]-sigmatropic rearrangement of ylides and related anionic species, **1** to **2**, is now recognized as a process of great facility and widespread occurrence.[1] This reaction is accompanied by a second pathway of higher activation energy, shown to be a radical dissociation–recombination route, **1** to **3**, whose importance depends on the structural environment and temperature.[1c,i,j,2]

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(1) (a) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 538 (1968); (b) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *J. Amer. Chem. Soc.*, **90**, 4758 (1968); (c) J. E. Baldwin and R. E. Hackler, *ibid.*, **91**, 3646 (1969); (d) R. W. Jemison and W. D. Ollis, *Chem. Commun.*, 294 (1969); (e) J. E. Baldwin, J. E. Brown, and R. W. Cordell, *ibid.*, 32 (1970); (f) J. E. Baldwin and F. J. Urban, *ibid.*, 165 (1970); (g) J. E. Baldwin and C. H. Armstrong, *ibid.*, 659 (1970); (h) J. E. Baldwin J. E. Brown, and G. Höfle, *J. Amer. Chem. Soc.*, **93**, 788 (1971); (i) V. Rautenstrauch, *Chem. Commun.*, 4 (1970); (j) U. Schollkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

(2) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).