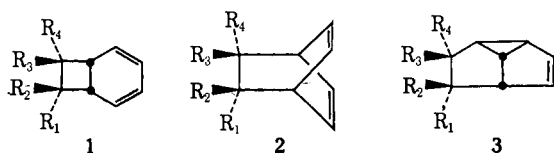


Photoaddition of Benzene to Olefins. II. Stereospecific 1,2 and 1,4 Cycloadditions^{1,2}

Sir:

We wish to report that bicyclo[4.2.0]octa-2,4-dienes **1** and bicyclo[2.2.2]octa-2,5-dienes **2** are formed by 1,2 and 1,4 cycloaddition of benzene to olefins upon irradiation of their solutions at 2537 Å. In products from *cis*-2-butene (a) and *trans*-2-butene (b) configuration is retained, as it is^{2,3} in the tricyclo[3.3.0.0^{2,5}]oct-3-enes **3** resulting from 1,3 cycloaddition,²⁻⁵ and indeed all three types of products appear to be derived from a common precursor. Heretofore, as pointed out by Bryce-Smith,⁶ 1,2 photoaddition has been observed only where the ethylenic compound is excited or where one of the reactants has marked acceptor properties, as with benzene-acrylonitrile⁷ or benzonitrile-trimethylethylene.⁸ The 1,4 addition of benzene to cyclobutene has been reported⁹ by Srinivasan, but provides no stereochemical information.



a, $R_1 = R_4 = \text{CH}_3$; $R_2 = R_3 = \text{H}$
b, $R_2 = R_4 = \text{CH}_3$; $R_1 = R_3 = \text{H}$

The cycloadducts are best prepared by 2537-Å irradiation of 5–10% solutions of benzene in olefin as solvent (at -15° for butenes) since quantum yields⁹ increase with olefin concentration. It is preferable to limit the irradiation when the desired product is a 1,2 adduct since these adducts are photolabile⁸ and soon reach a steady state, whereas the 1,3 and 1,4 adducts continue to grow.⁹ The 1,2 and 1,4 adducts are conveniently located on gas chromatograms by mass scanning, since they have characteristic spectra in which the parent peak is small and those for the aromatic and olefinic components are intense. The isolated adducts are readily distinguished by uv; *vide infra*. Utilizing this approach, we have isolated and characterized 1,2 adducts of benzene with tetramethylethylene and the but-2-enes and of toluene with *cis*-butene. The formation of 1,2 adducts with several other cyclic and noncyclic olefins has been inferred from the early appearance of characteristic absorption (280 nm, $\log \epsilon \sim 3.5$). The 1,4 adducts of benzene with six C_3 - C_5 olefins and of toluene and *o*-xylene

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Paper I: K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2066 (1966).

(3) A. Morikawa, S. Brownstein, and R. J. Cvetanovic, *ibid.*, **92**, 1471 (1970).

(4) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966).

(5) R. Srinivasan, *IBM J. Res. Develop.*, **15**, 34 (1971). We are indebted to the author for a preprint prior to publication.

(6) D. Bryce-Smith, *Chem. Commun.*, 806 (1969).

(7) B. E. Job and J. D. Littlehailes, *J. Chem. Soc. C*, 886 (1968).

(8) J. G. Atkinson, D. E. Ayer, G. Buchi, and E. W. Robb, *J. Amer. Chem. Soc.*, **85**, 2257 (1963).

(9) Quantum yields for formation of 1,2 adducts of benzene in neat olefin range from 0.1 for *trans*-butene (0.3 times that of 1,3 addition) to ~ 0.5 for tetramethylethylene (7 times that of 1,3 addition). Those for 1,4 addition to the but-2-enes are lower, 0.01–0.02. In a 20 min irradiation of 3 ml of benzene and 30 ml of *cis*-butene at -15° with a General Electric G8T5 lamp, yields of **1**, **2**, and **3** were 12, 2, and 80 mg, respectively. Yields after 6 hr were 14, 40, and ~ 1000 mg.

with *cis*-butene have also been isolated and characterized.

In this preliminary report, however, we will characterize only the 1,2 and 1,4 cycloadducts of benzene with *cis*- and *trans*-butene. Only one 1,2 cycloadduct and one 1,4 cycloadduct were detected with each olefin. The 1,2 adduct of *trans*-butene¹⁰ was identified as *trans*-7,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**1b**) by comparison of its properties with those of the known¹¹ compound: λ_{max} 276 nm (lit. 274,^{11a} 278^{11b}); nmr¹² δ (area, multiplicity) 1.02 (3, d, $J = 6$ Hz), 1.07 (3, d, $J = 6$ Hz), 2.25–2.55 (3), 3.05 (1, m), 5.4–5.7 (3), 5.75 (1, m) (lit.^{11a} 1.01 (3, d, $J = 6.5$ Hz), 1.09 (3, d, $J = 6.5$ Hz) or^{11b} 1.02, 1.07), 2.1–2.6 (3), 2.8–3.2 (1), 5.3–6.0 (4). The 1,4 adduct, which showed only end absorption, was identified as *trans*-7,8-dimethylbicyclo[2.2.2]octa-2,5-diene (**2b**) from its nmr spectrum: 0.85 (6, d, $J = 5$ Hz), ~ 1.0 (2, m), 3.15 (2, m), 6.07 (2, m), 6.36 (2, m). The olefinic protons at δ 6.07 and 6.36 were observed to be coupled to each other, $J = 7$ Hz, with each being additionally coupled to the bridgehead protons at δ 3.15 with $J = 6$ and 1.5 Hz. The shifts and coupling constants correspond to those¹³ of bicyclo[2.2.2]octadiene, which has resonances at δ 1.25, 3.59, and 6.27, with $J_{2,3} = 7.3$, $J_{1,2} = 6.5$, and $J_{1,3} = 1.3$ Hz. Since the protons at C-2 and C-3 in the photoproduct have different chemical shifts, it must have the *trans* configuration.

The 1,2 adduct of *cis*-butene was characterized as *cis,endo*-7,8-dimethylbicyclo[4.2.0]octa-2,4-diene on the basis of its uv and nmr spectra: λ_{max} 277 nm; nmr δ 1.03 (6, d, $J = 7$ Hz), 2.80 (2, m), 3.20 (2, d, $J = 6$ Hz), 5.34 (2, m), 5.69 (2, m). A known¹¹ *cis* isomer, formed by thermal cyclization of *cis,cis,cis,trans*-decatetraene,^{11b} has a somewhat different nmr spectrum:^{11b} δ 1.03 (6, d, $J = 6.4$ Hz), 2.56 (2, s, br), 2.75 (2, m), 5.72 (4, s). The fact that the bridgehead protons (δ 3.20) in the photoproduct appear as a doublet, whereas they are evidently¹⁴ a singlet in the thermal product, suggests that the methyl groups are *exo* in the latter and *endo* in the photoproduct. Upon irradiation of the 1,2 adduct at 2537 Å uv absorptions indistinguishable from those of the aforementioned tetraene appear. The 1,4 adduct of *cis*-butene, which again showed only end absorption, was identified as *cis*-7,8-dimethylbicyclo[2.2.2]octa-2,5-diene on the basis of shifts and coupling constants in its nmr spectrum: δ 0.76 (6, d, $J = 7$ Hz), 1.69 (2, m), 3.25 (2, m), 6.1–6.3 (4). An AA'BB' analysis¹⁵ of the olefinic region indicated that each of the olefinic protons at δ 6.20 and 6.22 was coupled to a like proton, $J = 7$ Hz, as well as to a distant (δ 3.25) proton, $J \sim 6$ Hz. In this case, like olefinic protons are coupled to each other and the product must have the *cis* configuration.

(10) This adduct is inseparable from the major 1,3 adduct **3b** on many gc columns, but elutes at one-sixth its distance on an AgNO_3 -glycerol column at 40° .

(11) (a) E. N. Marvell and J. Seubert, *J. Amer. Chem. Soc.*, **89**, 3377 (1967); (b) R. Huisgen, A. Dahmen, and H. Huber, *ibid.*, **89**, 7130 (1967).

(12) 100-MHz spectra in CCl_4 with TMS as internal lock. We thank Mrs. Geraldine McDonald for these measurements.

(13) K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2802 (1964).

(14) The reported multiplicities suggest that the assignments of protons 1 and 7 in ref 11b should be reversed.

(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 141.

The retention of olefin configuration in the 1,2, 1,3, and 1,4 additions suggests that these reactions are concerted. There is good evidence³ that 1,3 addition involves the singlet (B_{2u}) state of benzene. It is likely that this state is also involved in 1,2 and 1,4 addition, since the relative (initial) yields of the various adducts remain constant¹⁶ over a wide range of concentrations and proportions of reactants, such that the benzene singlet-triplet ratio would almost certainly vary. From orbital symmetry considerations, however, Bryce-Smith has concluded⁶ that concerted 1,2 and 1,4 cycloadditions in which configuration is retained are allowed from excited olefin plus ground-state benzene, or from B_{1u} benzene plus ground-state olefin, but *not* from B_{2u} benzene plus ground-state olefin. If all of these interpretations are correct, an apparently forbidden process does, in fact, occur with at least moderate quantum efficiency.⁹ This result can, perhaps, be rationalized by the intervention of an excited complex, formed from ${}^1B_{2u}$ benzene and ground-state olefin, in which mixing of states¹⁷ results in relaxation of orbital-symmetry restrictions. The formation of such benzene-olefin exciplexes has been previously suggested¹⁸ but not yet proven.

(16) R. Srinivasan (ref 5) has observed similar invariance in the relative yields of 1,3 and 1,4 cycloadducts of benzene and cyclobutene.

(17) M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *J. Amer. Chem. Soc.*, **92**, 6991 (1970).

(18) H. Morrison and W. I. Ferree, Jr., *Chem. Commun.*, 268 (1969).

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The Synthesis of Spiro Systems by the $\alpha\alpha'$ -Annellation Process

Sir:

The synthesis of spiro-fused ring systems has usually been accomplished by multistep techniques which often preclude the obtention of structures having diverse functionality.¹ The $\alpha\alpha'$ -annellation reaction,² which has been used for the synthesis of a variety of bridged bicyclic compounds,³ may be applied to enamines of certain ketones to afford, in essentially a single step, spiro frameworks having functionality usefully disposed for the conversion to other systems.

Condensation of the pyrrolidine enamine of acetyl-cyclopentane⁴ (**1**) (54% from ketone; bp 76–80° (0.1 mm); ν_{\max}^{neat} 2790, 1620, 1385 cm^{-1}) with methyl α -(1-bromomethyl)acrylate^{5,6} (**2**) (bp 68–74° (12 mm); $\nu_{\max}^{\text{CHCl}_3}$ 2940, 1715, 1630, 1175 cm^{-1}) in benzene⁷

(1) R. Baird and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 756 (1957); M. Mousseron, H. Christol, and F. Pleint, *C. R. Acad. Sci.*, **245**, 1281 (1957); H. deJongh, F. Gerharth, and H. Wynberg, *J. Org. Chem.*, **30**, 1409 (1965); M. Khuda and A. Ray, *J. Indian Chem. Soc.*, **16**, 525 (1939); M. Monsseron, R. Jacquier, and H. Christol, *Bull. Soc. Chim. Fr.*, 346 (1957); E. J. Corey and J. I. Shulman, *J. Amer. Chem. Soc.*, **92**, 5522 (1970).

(2) R. P. Nelson and R. G. Lawton, *ibid.*, **88**, 3884 (1966).

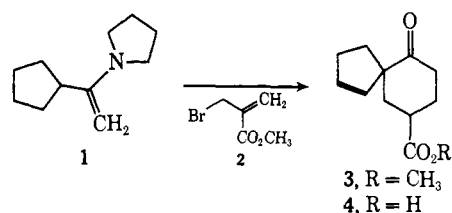
(3) (a) R. P. Nelson, J. M. McEwen, and R. G. Lawton, *J. Org. Chem.*, **34**, 1225 (1969); (b) **35**, 690 (1970).

(4) Prepared by Jones oxidation of 1-cyclopentylethanol, Aldrich Chemical Co.

(5) Prepared most easily by diisopropylethylamine dehydrohalogenation of methyl β,β' -dibromoisobutyrate.^{8b} See A. F. Ferris, *J. Org. Chem.*, **20**, 780 (1955), and ref 3. The compound has vesicant properties.

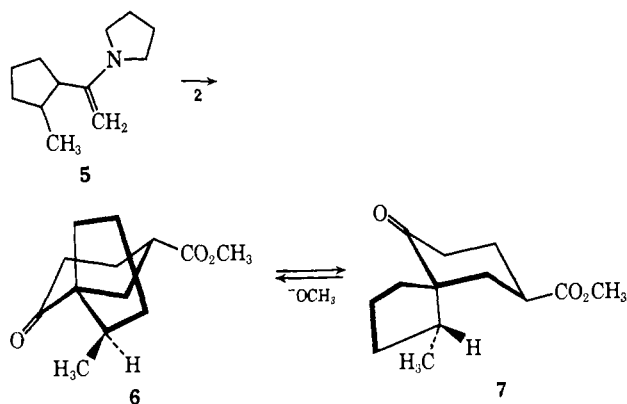
(6) Correct analytical figures have been obtained for all compounds for which physical and spectral data are given.

followed by addition of triethylamine, acetonitrile, and reflux afforded; after aqueous acetic acid hydrolysis, a

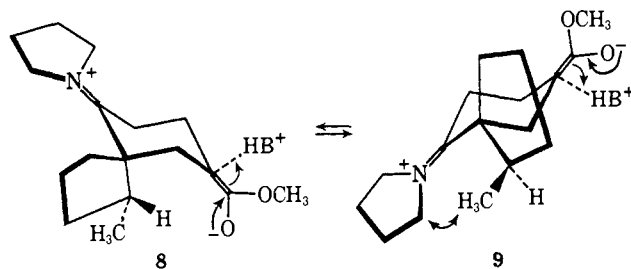


78% yield of methyl spiro[4:5]decan-1-one-4-carboxylate⁶ (**3**) (bp 130–135° (0.25 mm); ν_{CHCl_3} 2960, 1730, 1710, 1440, 1175 cm^{-1} ; $\tau_{\text{ppm}}^{\text{CDCl}_3}$ 6.32 (3 H, s), 7.0–8.50 (envelope)). The corresponding acid **4** (mp 102–103°; ν_{CDCl_3} 2960 (b), 1730 cm^{-1} ; τ 5.33 (2 H, s), 7.20–8.80 (envelope)) was produced by basic hydrolysis.

In a similar fashion, reaction of **2** with the pyrrolidine enamine of 1-acetyl-2-methylcyclopentane⁸ (**5**) produced a 78% yield of a *single isomer* of methyl 6-methyl-spiro[4:5]decan-1-one-4-carboxylate (bp 110–112° (0.2 mm); ν_{CHCl_3} 1735, 1710 cm^{-1} ; $\tau_{\text{ppm}}^{\text{CDCl}_3}$ 6.30 (3 H, s), 7.00–8.70 (envelope), 9.00 (3 H, bd)) shown to have



the configuration **6** by its sodium methoxide isomerization to isomer **7** (ν_{CHCl_3} 2960, 1735, 1710, cm^{-1} ; τ_{CDCl_3} 6.28 (3 H, s), 7.0–8.70, envelope with strong peaks at 7.65, 7.90, and 8.40, 9.15 (3 H, d, $J = 6.5$ Hz)) having a *shielded* methyl doublet. Interestingly, at equilibrium the ratio of **7** to **6** is 70:30. The production of **6** as a single isomer in the annellation suggests the intramolecular Michael is occurring from the least-hindered side, opposite the methyl, and that the protonation transition state has a configuration and idealized conformation approaching those of **8**. In the alternate transition state **9**, severe nonbonded interactions develop between the methyl and the α -methylene



(7) The intermediate methyl α -(3-keto-3-cyclopentyl-*n*-propyl)acrylate (bp 108–110° (0.2 mm): ν_{CHCl_3} 1715, 1630, 1450, 1155, 960 cm^{-1} ; $\tau_{\text{ppm}}^{\text{CDCl}_3}$ 3.92 (1 H, d), 4.48 (1 H, bd), 6.23 (3 H, s), 7.40 (4 H, s), 8.16–8.45 (envelope)) may be isolated.

(8) I. Tabushi, K. Fujita, and R. Oda, *Tetrahedron Lett.*, 4248 (1968).