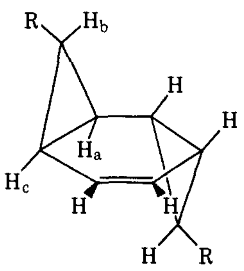
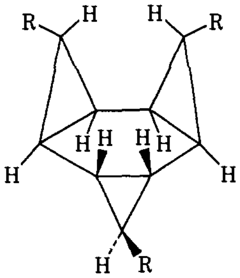
New Bis- and Trishomobenzene Derivatives

Sir:

Considering the amount of work which has been reported on norcaradiene–cycloheptatriene equilibria in general,[1] and specifically on the structures of Buchner's esters,[2] we were surprised to find two new adducts of carbomethoxycarbene and benzene, *i.e.*, the 2:1 and 3:1 adducts, **1** and **2**. We are prompted to report their preparation and stereochemistry now by recent reports of other bis- and trishomobenzene derivatives.[3]



1

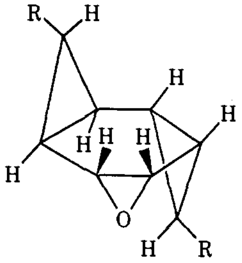


2

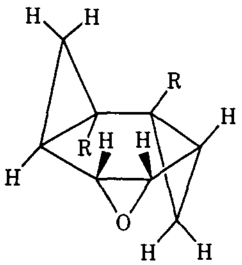
R = CO_2CH_3

The synthetic procedure consists of slowly adding (24 hr) a solution of 20 g of methyl diazoacetate in 50 ml of benzene to 50 ml of refluxing benzene containing 0.5–1.0 g of finely powdered copper–bronze. After evaporation under vacuum of the volatile components of the reaction mixture (benzene, dimethyl fumarate, dimethyl maleate, and methyl cycloheptatriene-7-carboxylate), the 2:1 and 3:1 adducts were isolated by column chromatography of the residual oil (Silica gel, CCl_4–$CHCl_3$).

The 2:1 adduct, dimethyl tricyclo[5.1.0.0^{2,4}]oct-5-ene-3,8-dicarboxylate (**1**), mp 130–132°, was isolated in 3% yield and was shown to have the structure and stereochemistry indicated by the following observations.[4] The nmr spectrum ($CDCl_3$) showed two olefinic protons as an apparent triplet at δ 5.70, six methoxy protons as a singlet at 3.65, and a complicated multiplet of six protons at 1.5–2.2. The proton ratios indicate a tricyclic skeleton, and the magnetic equivalence of the olefinic protons and the methoxy protons suggested a symmetrically substituted (*exo,exo*- or *endo,endo*-) tricyclo[5.1.0.0^{2,4}]oct-5-ene. Double irradiation at δ 1.6 caused the olefinic triplet to collapse to a singlet, and, conversely, irradiation at 5.7 simplified the high-field signals allowing analysis of the region as two identical ABC systems: H_a, δ 2.12; H_b, 1.78; H_c, 1.63; J_{ab} = 3.9 Hz, J_{ac} = 8.6 Hz, J_{bc} = 4.0 Hz.[5] Based on the small values of the coupling constants J_{ab} and J_{bc},[6] proton B was trans to protons A and C, and therefore the carbomethoxy substituents must be exo,exo. The syn or anti nature of the ring fusions was determined by converting **1** to its epoxide (**3**),[4] mp 163–164°, with *m*-chloroperbenzoic acid. After decoupling from the adjacent protons, the protons on the epoxide ring in **3** appeared as an AB pattern: H_A, δ 3.33; H_B, δ 3.13; J_{AB} = 4.0 Hz. Their nonidentity and the similarity of their chemical shifts and coupling constant to those reported for compound **4**[3a] confirm the anti ring fusion in **1**.



3



4

R = CO_2CH_3

The 3:1 adduct, trimethyl tetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane-3,6,9-tricarboxylate (**2**),[4] mp 139–140°, was isolated in 4% yield and was characterized by its nmr spectrum ($CDCl_3$) which showed, in addition to a complex pattern at δ 1.2–2.0 (9 H) for the skeletal protons, two methoxy proton signals at 3.69 and 3.70 (9 H) in an approximate ratio of 2:1. The complete stereochemistry shown was assigned on the basis of the (presumed) formation of **2** from **1** and the apparent equivalence of two methoxy groups.

The unexpected formation of compounds **1** and **2** raises several questions regarding the norcaradiene–cycloheptatriene equilibrium in Buchner's esters. We have found no evidence of the expected adducts (bicyclo[5.1.0]octadienes). The following explanations have been considered. The norcaradiene tautomer, though unfavored at equilibrium, is either more reactive than the cycloheptatriene or reacts with a second carbene faster than it tautomerizes. Neither situation seems likely unless the rate and perhaps even the position of the tautomeric equilibrium are affected by the heterogeneous catalyst surface. Experiments to test these possibilities are in progress and will be reported in a full paper.

David L. Dalrymple,* Stephan P. B. Taylor
Department of Chemistry, University of Delaware
Newark, Delaware 19711

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[1] G. Maier, *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967).

[2] W. Braren and E. Buchner, *Ber.*, 34, 982 (1901); C. Grundmann and G. Ottman, *Justus Liebigs Ann. Chem.*, **582**, 163 (1953); W. von E. Doering, *et al.*, *J. Amer. Chem. Soc.*, **78**, 5448 (1956).

[3] (a) H. Prinzbach and D. Stusche, *Angew. Chem.*, **82**, 836 (1970); (b) H. Prinzbach and D. Stusche, *Helv. Chim. Acta*, **54**, 755 (1971); (c) H. W. Whitlock, Jr., and P. F. Schatz, *J. Amer. Chem. Soc.*, **93**, 3837 (1971).

[4] Satisfactory elemental analyses and mass spectral molecular weights have been obtained for all new compounds reported. The nmr spectra reported were recorded on a Varian A-60.

[5] Parameters refined by LAOCN3 spectral analysis program of A. A. Bothner-By and S. M. Castellano, "Computer Programs for Chemistry," Vol. I, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, pp 10–53.

[6] L. M. Jackman and S. Sternhell, "Applications of Nulcear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 286.

Singlet–Triplet Resonance Interaction in the A_2 States of Formaldehyde[1]

Sir:

Narrow-band excitation has recently been developed as an important method for investigating radiative and nonradiative processes in excited states.[2–5] The ob-

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[1] Work supported by the National Research Council of Canada.

[2] B. K. Selinger and W. R. Ware, *J. Chem. Phys.*, **53**, 3160 (1970).

[3] L. S. Anderson, C. S. Parmenter, H. M. Poland, and J. D. Rau, *Chem. Phys. Lett.*, **6**, 345 (1970).

[4] W. M. Gelbart, K. G. Spears, K. F. Freed, J. Jortner, and S. A. Rice, *ibid.*, **6**, 345 (1970).