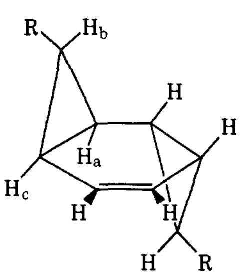
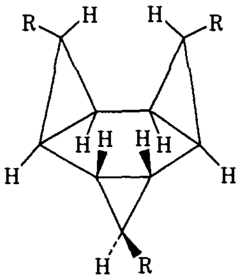
New Bis- and Trishomobenzene Derivatives

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

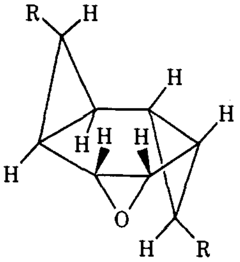


2

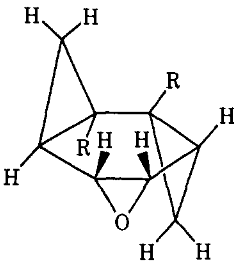
R = CO_2CH_3

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.

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

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[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).

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servations reported here indicate that individual rotational states within a given vibronic level may show irregular variations of lifetime, the variation being linked to "accidental" singlet–triplet degeneracies. In order to observe these variations, the half-width of the excitation source should be $<0.1\ \mathrm{cm}^{-1}$, a range that may soon be realized for tunable lasers.

The measurements described below are not time resolved; instead, they represent an analysis of mild perturbations observed in the 3260-Å ($2\nu_2 + \nu_4$) vibronic band of the ${}^1A_2 \leftarrow {}^1A_1[{}^1(n\pi^*)]$ band system of CH_2O vapor,[6,7] a band also known to give rise to a magnetic rotation spectrum.[8] This band was therefore recorded in an external magnetic field (13 kg) and a Zeeman effect observed for about 25 out of a total 800 lines present in the band. Every Zeeman-sensitive line corresponds to a transition found to be perturbed in the field-free absorption spectrum. Thus the perturbation is not induced by the Zeeman field; rather, the perturbation present at zero external field develops a magnetic moment which is observed through a shift or broadening of the line when the Zeeman field is switched on.

The rotational perturbations in the 3260-Å band occur in each subband for $K' = 0$–7, the point of resonance shifting progressively from $J' = 12$ at $K' = 0$ to $J' = 17$ at $K' = 7$. A number of otherwise unassigned extra lines associated with the perturbation are observed, and the available information is sufficient to obtain approximate values of the constants of the *perturbing* state from the analysis of the perturbation. The constants obtained in this way, $A = 8.5_8$, $B = 1.16_6$, and $C = 1.04_2\ \mathrm{cm}^{-1}$, resemble closely those of the zero-point 0^+ level of the triplet state ($A = 8.67$, $B = 1.156$, $C = 1.042\ \mathrm{cm}^{-1}$)[9] and so establish that the perturbing state must be a vibronic level of ${}^3A_2$, a fact which provides a natural explanation for the appearance of magnetically sensitive lines. It also emerges that the perturbation is not satisfactorily explained unless (a) the perturbing triplet state has the same vibronic symmetry, ${}^{ev}B_2$, as the ($2\nu_2 + \nu_4$) vibronic state of ${}^1A_2$,[10] (b) the interaction matrix elements have appreciable N,K dependence, and (c) the perturbing triplet state lies 5455.6 cm^{-1} higher in energy than the vibrationless ${}^3A_2$ state so that the perturbation is probably $2\nu_2 + \nu_4({}^1A_2) \leftrightarrow \nu_1 + 2\nu_2 + \nu_4({}^3A_2)$. Since the coupled states have the same vibronic symmetry, the interaction must be rotational in character.

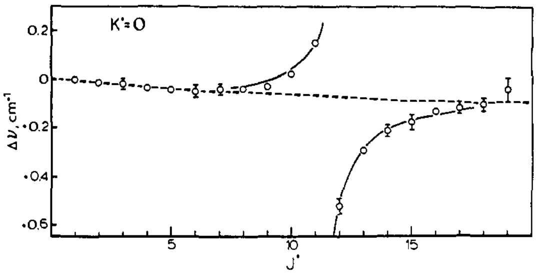

Figure 1. Calculated and observed perturbations in the $K' = 0$ submanifold (3260-Å band of CH_2O). The solid line shows the course of the perturbation calculated from the constants of the ${}^1A_2$ and ${}^3A_2$ states[7,9] with the coefficient $a_{xx} + a_{yy} = 0.043\ \mathrm{cm}^{-1}$ (see eq 1). The points represent "observed" values, obtained by subtracting the calculated *unperturbed* energy from the rotational term value. Owing to small errors in the rotational constants, the unperturbed term values (broken line) do not coincide exactly with $\Delta\nu = 0$.

Vibronic B_2 states of the electronic ${}^1A_2$ and ${}^3A_2$ states of CH_2O cannot interact by spin–orbit coupling (the spatial part of H_{SO} has no totally symmetric component) or by vibronic spin–orbit coupling, so that a third mechanism of interaction must be considered. An indirect second-order mechanism involving electronic orbital–rotation and spin–orbit coupling, analogous to the interactions that account for spin–rotation coupling in multiplet states,[11] does have the requisite properties and leads to the interaction matrix element

$$W({}^1A_2;\ {}^3A_2) = (a_{xx} + a_{yy})[N(N+1)]^{1/2} + (a_{zz} - a_{xx} - a_{yy})K/[N(N+1)]^{1/2} \quad (1)$$

in which the coefficients a_{qq}, $q = x, y, z$, are integrals over the electronic, vibrational, and spin coordinates. Figure 1 illustrates the analysis of the $K' = 0$ perturbation on the basis of eq 1. The interaction is weak, but leads to observable singlet–triplet mixing between nearly degenerate levels. This mechanism has recently been discussed theoretically[12] but has not previously been identified for polyatomic molecules.

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Catalytic Hydrogenolysis of Molecular Oxygen by Transition Metal Complexes in Nonaqueous Solution

Sir:

We wish to report some observations on what appears to be a homogeneous catalytic combination of molecular hydrogen and oxygen to form water (eq 1) in the

$$H_2 + 0.5O_2 \longrightarrow H_2O \quad (1)$$

presence of some triphenylphosphine complexes of platinum, iridium, rhodium, and ruthenium in toluene solutions under ambient conditions (Table I). Although the heterogeneous catalysis of this reaction (eq 1) by metal surfaces is among the first recognized catalytic reactions at large, for the corresponding homogeneous catalysis we find references only to systems involving copper ion in aqueous solution at elevated temperatures and under high pressures of the gases (eq 1).[1]

Our discovery originates from the observation that a volumetric uptake of a mixture of H_2 and O_2 by a

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