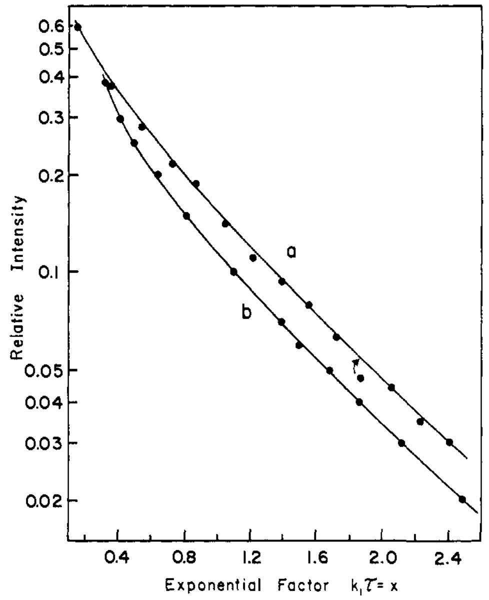

Figure 1. Best fit of data points to function (solid line) $f(x)$: curve a, 1.0 M benzophenone, $k_1 = 3.34 \times 10^5$ sec^{-1}, $\Delta = 6.0$; curve b, 0.5 M benzophenone, $k_1 = 2.40 \times 10^5$ sec^{-1}, $\Delta = 5.0$.

Table I. Derived Deactivation Parameters of the Benzophenone Triplet by the "Head-on" Experiment

[Benzophenone], M	k_1, sec^{-1}	Δ	O.d., cm^{-1}	$I(0,0)$,[a] einstein/(cm^2 pulse)	k_2, M^{-1} sec^{-1}
0.5	2.40×10^5	5.0	60	2.24×10^{-6} [a]	0.89×10^{10} (1.06×10^{10})[b]
1.0	3.34×10^5	6.0	120	2.24×10^{-6} [a]	0.74×10^{10} (1.10×10^{10})[b]

[a] Determined by ferrioxalate actinometry. [b] Corrected for viscosity. The viscosities of the benzophenone solutions relative to pure benzene are 0.5 M, 1.19:1; 1.0 M, 1.48:1.

Freon at room temperature to be $19 \pm 7 \times 10^9$ M^{-1} sec^{-1}. Calvert and coworkers[2b] determined k_2 for biacetyl vapor at 25° using a curve matching procedure that took into account the nonuniformity in the cross-section of the exciting laser pulse.

Further studies are in progress in our laboratory on triplet–triplet annihilation using the "head-on" monitoring and curve simulation procedures.

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Proton Coupling Constants in Methylcyclopentadienes

Sir:

Until very recently, the study of the fluxional behavior of metal cyclopentadienyls also containing methyl groups in the ring was rather qualitative. The results of all studies in this field[1] show that the main difficulty is the absence of an adequate method for analyzing the complex pmr spectra.[2] Methylcyclopentadiene ($CH_3C_5H_5$) can be considered as the simplest and most unique model for receiving all information concerning the following questions: how does a methyl group affect the ring proton chemical shifts and how do methyl protons couple with the ring protons?

Methylcyclopentadiene is also a classical model for a study of hydrogen migration. Under equilibrated conditions it consists of a mixture of all three isomers (A_1 or 5, A_2 or 1, and A_3 or 2 isomers; see Table I).

Based on ir,[3] uv,[4] and pmr[5] data, it has been shown that vinylic (A_2,A_3) isomers predominate in the equilibrium at ambient temperatures while the ratio of A_2 and A_3 isomers is close to 1:1 (see data in ref 3–5). Isomer A_1 is thermodynamically unstable and its content does not exceed a few per cent (*ca.* 3%, see ref 3).

Only a qualitative analysis of the pmr spectra of methylcyclopentadiene ($CH_3C_5H_5$) had been performed previously.[5] The difficulties which hindered the complete analysis were due to the fact that: (i) separation of isomers from the mixture is a very laborious task to perform, (ii) slow isomer interconversion takes place due to prototropic rearrangement, (iii) the analysis of the simplest cyclopentadienyl derivatives (including cyclopentadiene itself) has become possible only recently.[6]

We now report the results of complete analysis of the 100-MHz proton magnetic resonance spectra of the equilibrated mixture of methylcyclopentadienes obtained by the distillation of a commercial methylcyclopentadiene. The spectra were obtained on a Varian HA-100 spectrometer for neat liquid; chemical shifts are given in δ scale from internal TMS. The sample was degassed by the usual procedure, and the tubes were sealed before recording the spectra.

The analysis of the pmr spectra of both the vinylic isomers has been performed directly for the mixture using a YaMR-1 simulating program[7] and the indor technique. The indor response has been analyzed with a special INDOR program which finds the true relative signs version starting from the results of the indor experiment. The employment of the indor program is necessary because the spectra include *all possible proton couplings* for isomers A_2 and A_3 (ten constants for each isomer), and we have to choose one of the 2^9 possible sign versions.[8]

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(1) See, *e.g.*, (a) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **1**, 323 (1964) (tin); (b) A. Davison and P. E. Rakita, *J. Amer. Chem. Soc.*, **90**, 4479 (1968) (silicon); (c) A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 313 (1970) (silicon, germanium, tin); (d) C. H. Campbell and M. L. H. Green, *J. Chem. Soc, A*, 1318 (1970) (ruthenium); (e) B. Floris, G. Illuminati, and G. Ortaggi, *J. Chem. Soc. D*, 492, (1969); C. H. Campbell and M. L. H. Green, *J. Chem. Soc. A*, 3282 (1971) (mercury); (f) H. P. Fritz and K. E. Schwarzhans, *Chem. Ber.*, **97**, 1390 (1964) (lead and tin, both two and four coordinated).

(2) Carbon-13 magnetic resonance has been demonstrated to be much more promising in this respect (see Yu. K. Grishin, N. M. Sergeyev, and Yu. A. Ustynyuk, *Org. Magn. Resonance*, 4, 377 (1972)). However, it is limited in sensitivity.

(3) S. M. Csicsery, *J. Org. Chem.*, **25**, 518 (1960).

(4) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

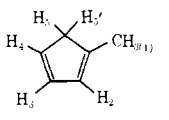
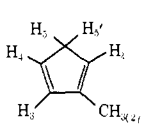
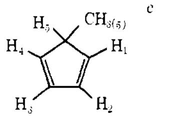
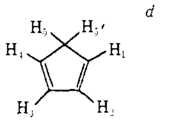
(5) S. McLean and P. Haynes, *ibid.*, **21**, 2329 (1965).

(6) N. M. Sergeyev, G. I. Avramenko, A. V. Kisin, V. A. Korenevsky, and Yu. A. Ustynyuk, *J. Organometal. Chem.*, **32**, 55 (1971).

(7) A. A. Fomichev, *Zh. Strukt. Khim.*, **9**, 700 (1968).

(8) The INDOR program has been written by M. I. Mstislavsky of this laboratory. The full procedure to analyze the pmr spectra of $CH_3C_5H_5$, as well as $(CH_3)_2C_5H_4$, will be given elsewhere.

Table I. Proton Nmr Parameters for Methylcyclopentadienes

Molecule	Nmr parameters					
 A$_2$	Chemical shifts^a					
	1	2	3	4	5	
	1.978	5.996	6.246	6.066	2.695	
	Methyl proton coupling constants^b					
	J_{12}	J_{13}	J_{14}	J_{15}		
	−1.6	+0.4	−0.4	−0.2		
	Other coupling constants^b					
	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}
	+1.9	+1.4	−1.3	+5.4	−1.5	+1.4
 A$_3$	Chemical shifts^a					
	1	2	3	4	5	
	5.834	1.911	6.230	6.230	2.788	
	Methyl proton coupling constants^b					
	J_{12}	J_{23}	J_{24}	J_{25}		
	−1.5	−0.4	+0.4	+2.0		
	Other coupling constants^b					
	J_{13}	J_{14}	J_{15}	J_{34}	J_{35}	J_{45}
	+1.4	+1.8	+1.8	+5.4	−1.4	+1.4
 A$_1$ ^{c}	Chemical shifts^a					
	Olefinic protons	5	(CH$_3$)$_5$			
	~6.35	3.03	1.08			
	Coupling constants^b					
	$J_{CH_3,H_5} \simeq 7.8$					
 ^{d}	Chemical shifts^a					
	1	2	3	4	5	
	6.27	6.43	6.43	6.27	2.80	
	Coupling constants^b					
	J_{12}	J_{13}	J_{14}	J_{23}	J_{15}	J_{25}
	5.05	1.09	1.98	1.93	1.33	−1.51

[a] Chemical shifts in ppm downfield from TMS. [b] Coupling constants in Hz. [c] Data from ref 5 for nonequilibrated conditions. [d] Data from ref 9.

The results of the complete analysis are given in Table I. In accordance with the previously reported data no A$_1$ isomer has been detected. The ratio of vinylic isomers is equal to almost 1:1 (accuracy ± 1%). For the sake of comparison, the values are given in Table I for C_5H_6 and the A$_1$ isomer of $C_5H_5CH_3$ calculated through the full[9] and partial[5] analyses, respectively.

We can now make the following conclusions: (a) introduction of methyl in each of the isomers results in a displacement of all signals to the higher fields (compare with the cyclopentadiene's data, Table I); the displacement is especially pronounced for the ortho-positioned protons (proton 2 in isomer A$_2$, proton 1 in isomer A$_3$), where it is ~0.4 ppm for both of the isomers; (b) olefinic proton couplings are very close to the values previously reported[6,9] in both their moduli and their relative signs; (c) allylic proton couplings, $^4J_{\text{trans}}$, are all negative (*ca.* −1.5 Hz); (d) the coupling constants of methyl protons with protons H$_3$ and H$_4$ for both the isomers are equal to 0.4 Hz, while their signs are alternating (see Table I); (e) finally, it is interesting to note that the coupling constant J_{CH_3,CH_2} across four bonds in isomer A$_2$ is equal to −0.2 Hz, while the respective coupling constant J_{CH_3,CH_2} across five bonds in isomer A$_3$ is equal to +2.0 Hz. The latter constant may serve as a good criterion for identifying methyl position in the cyclopentadienyl ring.

It is also noteworthy that the signs of coupling constants of methyl protons with olefinic ones strongly support the idea that π-electron contribution is almost completely responsible for the spin coupling in such conjugated systems as *cis*-dienes.[10]

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(9) M. A. Cooper, D. D. Elleman, C. D. Pearce, and S. L. Manatt, *J. Chem. Phys.*, **53**, 2343 (1970).

(10) (a) R. A. Hoffman, *Mol. Phys.*, **1**, 326 (1958); (b) P. Albriktson, A. V. Cunliffe, and R. K. Harris, *J. Magn. Resonance*, **2**, 150 (1970).

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An Unusually Strong Intramolecular Interaction between the Sulfone or Sulfoxide and the Alkoxide Functions

Sir:

In further pursuit of the study[1] of conformational equilibria in 1,3-dioxanes bearing polar substituents at C-5 we have examined the equilibria of the 5-methylthio- (**1a** ⇌ **1b**), 5-methylsulfinyl- (**2a** ⇌ **2b**) and 5-methylsulfonyl-2-isopropyl-1,3-dioxanes (**3a** ⇌ **3b**) (eq 1), the 2-isopropyl group acting as an effective holding group for the 1,3-dioxane ring.[2] The results for the 5-methylthio series **1** in several solvents are summarized in Table I; in parentheses, for comparison, are given the corresponding[3] values for the 5-methoxy compounds. The results are on the whole unexceptional in that the equatorial (trans) isomer is favored throughout and in that there is a marked solvent effect such

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(2) F. W. Nader and E. L. Eliel, *J. Amer. Chem. Soc.*, **92**, 3050 (1970).

(3) R. J. Abraham, H. D. Banks, E. L. Eliel, O. Hofer, and M. K. Kaloustian, *J. Amer. Chem. Soc.*, **94**, 1913 (1972); E. L. Eliel and O. Hofer, submitted to *J. Amer. Chem. Soc.*