COMMUNICATIONS TO THE EDITOR

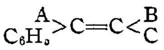
FLUORINE NUCLEAR SPIN-SPIN COUPLING IN *cis* AND *trans* PHENYL PERFLUOROALKENES

Sir:

The use of nuclear spin coupling constants as a diagnostic tool for the determination of isomer identity, particularly from the F^{19} n.m.r. spectra of appropriate *cis* and *trans* olefins, has received little attention because of the paucity of suitable examples. Some studies[1] with fluorine-containing olefins have been especially helpful, but, in certain cases, the possibility of incorrect assignments of coupling constants to specific pairs of nuclei remained because there was no unambiguous way of assigning a given multiplet.[1a] We wish to report F^{19} nuclear spin coupling constants[2] (Table I) for the pure *cis* and *trans* systems I along with independent ultraviolet spectral evidence for the isomer assignments.

TABLE I

NUCLEAR SPIN COUPLING CONSTANTS (J_{XY} c.p.s.) AND ULTRAVIOLET SPECTRAL DATA FOR THE FLUOROÖLEFINS Ia-Id



$$\overset{A}{\underset{C_6H_5}{}}>C=C<{}^{B}_{C}$$

	A	B	C	J_{AC}	J_{AB}	J_{BC}	λ_{max}, mμ	ε
Ia	F	CF_3	F	131	23	10	246	16,860
Ib	F	F	CF_3	13	9	9	232	8,800
Ic	CF_3	F	CF_3	1.5	28	7	226	2,840
Id	CF_3	CF_3	F	12	12	7	238	4,360

The data in Table I not only confirm earlier conclusions[1] but, in addition, it is noted that *cis*-trifluoromethyl fluorine nuclei are coupled (at long range) more strongly (Id, $|J_{AB}|$) than are the *trans*-trifluoromethyl groups (Ic, $|J_{AC}|$). It is apparent from Table I that *trans* coupling between vinyl fluorine nuclei (Ia, $|J_{AC}|$) is much greater than the corresponding *cis* coupling (Ib, $|J_{AB}|$); and *trans* coupling between CF_3 and F (Ib, $|J_{AC}|$, or Id, $|J_{AC}|$) is smaller than the corresponding *cis* coupling (Ia, $|J_{AB}|$, or Ic, $|J_{AB}|$). The coupling constant $|J_{BC}|$, between CF_3 and F on a methylene carbon atom is seen to be relatively invariant in the four compounds.[3]

Integrated intensity and chemical shift measurements made it possible to assign unambiguously CF_3 multiplets as opposed to F multiplets, in order to define $J_{CF_3-CF_3}$ and J_{F-F}. To obtain the various values of J_{CF_3-F}, assignments of each F multiplet in Ia and Ib, and of each CF_3 multiplet in Ic and Id were based in part on chemical shift comparisons with related compounds. Unqualified generalizations concerning the couplings should await studies of additional examples.

Shielding parameters[5] (not shown in Table I) were determined for each type of fluorine in an effort to detect increased shielding of the CF_3 or F groups (which are *cis* to the aromatic ring) due to intramolecular ring current effects of the type noted for certain hydrogen nuclei in 1,4-polymethylenebenzenes[6] or in *cis* and *trans* stilbenes.[7] Stuart–Briegleb models of Ic, in particular, indicate that the β-CF_3 group occupies a region near the 6-fold axis of the benzene ring where the induced magnetic lines of force would be opposed to the applied magnetic field H_0. However, diamagnetic shielding by a *cis*-CF_3 group apparently predominates since the β-CF_3 signal in Id appears at 0.4 p.p.m. higher field than the β-CF_3 multiplet in Ic. On the other hand, the α-CF_3 in Ic appears at 3.4 p.p.m. higher field than the α-CF_3 in Id. In general, attempts to distinguish ring current effects in these systems were greatly complicated by the large chemical shifts (normally encountered with F^{19} spectra) arising from other effects.

Ultraviolet spectra of Ia–Id in pure ethanol (Table I) provide evidence for the isomer assignments. In Ib and Ic, the *cis*-CF_3 group restricts the phenyl ring to an orientation which is almost perpendicular to the plane of the double bond as indicated by Stuart–Briegleb models. In Ia and Id, on the other hand, rotation of the phenyl group is much less restricted and coplanarity with the double bond may be approached. This situation is reflected in the bathochromic shift (and a concomitant increase in the extinction coefficient) exhibited by Ia and Id (Table I) relative to their respective isomers. Ia, in which rotation of the phenyl group is the least restricted, shows the highest values of ε and λ_{max}. Spectra obtained in isoöctane changed only slightly.

Isomer mixtures of Ia–Ib and of Ic–Id were prepared by the reaction of phenyllithium in ether with hexafluoropropylene[8] and octafluoro-2-butene respectively, at −80°. Each isomer was separated and purified by vapor phase chromatography on a 2 meter × 63 mm. o.d. copper column packed with 20% w./w. tetrakis-(1H,1H,5H-octafluoropentyl and 1H,1H,7H-dodecafluoroheptyl) pyromellitate supported on a 40–60 mesh firebrick maintained at 118° with the vaporizer at 160° and a helium flow rate of 26 cc./min. Since bromo-

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[1] (a) H. M. McConnell, C. A. Reilly and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956); (b) J. D. Swalen and C. A. Reilly, *ibid.*, **34**, 2122 (1961); (c) H. M. McConnell, C. A. Reilly and A. D. McLean, *ibid.*, **23**, 1152 (1955); (d) H. M. McConnell and C. A. Reilly, *ibid.*, **25**, 184 (1956).

[2] These data were determined with a Varian Associates high resolution n.m.r. spectrometer operated at 56.4 Mc./sec. with a magnetic field of 14.1 kgauss. For the purposes of this discussion, the coupling constants with one exception are given to the nearest c.p.s.

[3] The fact that the *cis* couplings involving CF_3 groups are greater than the corresponding *trans* couplings is consistent with recent proposals[4] involving direct through-space coupling when the interacting fluorine atoms are less than 2.73 Å. apart.

[4] L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961).

[5] G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[6] J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

[7] D. Y. Curtin, H. Gruen and B. A. Shoulders, *Chem. and Ind.*, 1205 (1958).

[8] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956); Canadian Patent No. 557,946, May 27, 1958.

benzene (an impurity in the phenyllithium reagent) eluted with Ib under these conditions, Ib was rechromatographed on a similar column packed with 20% w./w. of the diglyceride of ω-trifluorohexanoic acid supported on 40–60 mesh Columpak (Fisher Scientific Co.) maintained at 82° with the vaporizer at 140° and a helium flow rate of 92 cc./min.

Additional studies of these and related systems will be published at a later date.

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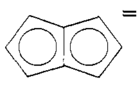
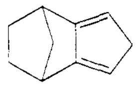
THE PENTALENYL DIANION

Sir:

We wish to report the synthesis of dilithium pentalenide, the first derivative of the pentalenyl dianion (I), the pure reduction product of the unknown pentalene and the lower homolog of naphthalene. Since the pentalenyl dianion and the cyclopentadienyl anion are related in the same way as naphthalene and benzene, the preparation of this dianion seemed a natural entry into the elusive pentalene series.[1] Previous success in the preparation of salts of the cycloöctatetraenyl dianion[2] strengthened our faith in this supposition.


I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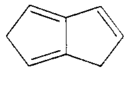
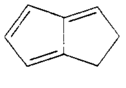

III


IV

Dilithium pentalenide forms readily on treatment of dihydropentalene in tetrahydrofuran solution with somewhat more than two moles of *n*-butyllithium in *n*-heptane. The salt, which is white, crystallizes beautifully from solution on cooling, or precipitates on addition of *n*-pentane. Solutions in tetrahydrofuran are slightly yellow but appear to be perfectly stable at room temperature. The presence of the dianion in these solutions and in the crude reaction mixtures is signalled in the nuclear magnetic resonance spectrum (Fig. 1) by the replacement of the intricate dihydropentalene spectrum by one consisting of two bands, a triplet centered at $\tau = 4.27$ and a doublet centered at $\tau = 5.02$. The spin-spin splittings are identical ($J = 3.0$ cps.), and the ratio of intensities is exactly 1:2.

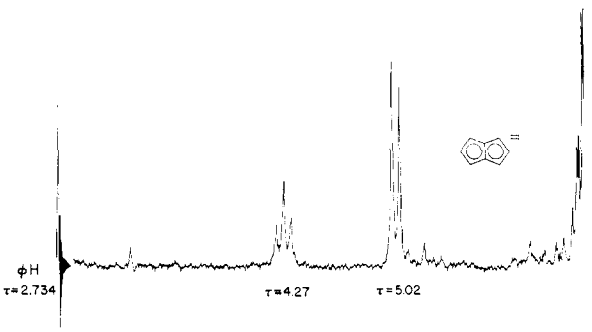
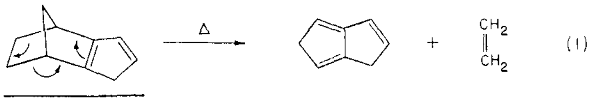


Fig. 1.—N.m.r. spectrum of dilithium pentalenide in tetrahydrofuran (containing pentane) with benzene and tetramethylsilane as internal reference standards. Spectra were determined on the Varian A-60 spectrometer.

Dihydropentalene was prepared pyrolytically from isodicyclopentadiene (II)[3] by passing the vapor in a nitrogen stream at 20 mm. pressure through a quartz tube packed with quartz chips at 575°.[4] Distillation of the pyrolysate resulted in a 30% yield of a yellow liquid, b.p. 52.5–53° at 18 mm., which was shown to be homogeneous by vapor phase chromatography. Addition of hydroquinone prevented its otherwise ready polymerization. That this was dihydropentalene was proven by analysis (Calcd. for C_8H_8: C, 92.26; H, 7.74. Found: C, 92.48; H, 7.81) and by hydrogenation over platinum in ether, a reaction which proceeded with the absorption of three moles of hydrogen and yielded a hydrocarbon shown to be *cis*-bicyclo[3.3.0]octane. The identity of the latter with an authentic sample[5] was demonstrated by comparison of the n.m.r. spectra, the infrared spectra, and the retention times characteristic of vapor phase chromatography on an Aerograph 5% SE-30 column. If dihydropentalene is not a mixture of double bond isomers, the location of the double bonds is indicated by the n.m.r. spectrum, which consists of four multiplets of equal intensity centered at τ = 3.67, 4.2, 6.77, and 7.02. Thus, two structures for dihydropentalene, of sufficient symmetry that only one methylene peak can be anticipated, are eliminated by the observation of two high field resonances, while of the remaining structures III and IV, only III seems consistent with the observed chemical shifts.[7,8]



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[1] The pentalene system has attracted considerable theoretical and experimental interest. References to the field may be found (a) in the chapters by E. D. Bergmann and D. Craig in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Editor, Interscience Publishers, Inc., New York, N. Y. 1959, and (b) in H. J. Dauben, Jr. and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1961).

[2] T. J. Katz, *ibid.*, **82**, 3784, 3785 (1960).

[3] K. Alder, F. H. Flock, and P. Janssen, *Chem. Ber.*, **89**, 2689 (1956).

[4] P. Janssen, Dissertation, Köln, 1959; R. Reimschneider and K. Heymans, *Monatsh.*, **92**, 1080 (1961).

[5] We are grateful to J. D. Roberts, W. F. Gorham, and M. Caserio for a gift of this compound.[6]

[6] J. D. Roberts and W. F. Gorham, *J. Am. Chem. Soc.*, **74**, 2278 (1952).

[7] This latter observation is that of Professor Ronald Breslow.

[8] The methylene protons in cyclopentadiene appear at τ = 7.10,[9] while the allylic methylenes of cyclopentadiene appear at τ = 7.7.[10]

[9] G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance (NMR) 'Shielding Values' (Spectral Positions) for Hydrogen in Organic Molecules," Central Research Lab., Minnesota Mining and Manufacturing Co., St. Paul, Minnesota, 1958.

[10] "A Catalogue of the Nuclear Magnetic Resonance Spectra of Hydrogen in Hydrocarbons and their Derivatives," Humble Oil and Refining Co., Research Division, Baytown, Texas, 1959.