symmetric biphenyl chromophore. We are therefore confident that enantiomerically homogeneous material displays a Cotton effect of high amplitude, centered near 261 mμ, the $\lambda_{\max}$ of the conjugation band, and that the sign of that Cotton effect is positive for the configuration of (−)-Ia. A combination of circumstances unfortunately prevented the polarimetric exploration of this spectral region: the high extinction at the maximum (ε 16,800) appeared in this instance to be accompanied by relatively low rotations, the result of partial racemization. In the previous work[16] it had been found that Cotton effects could not be measured reliably under conditions of optical density much greater than unity. The concentration of the optically active component in our sample was apparently not sufficient to compensate for the intense absorption by a high enough optical rotation.

Experimental Part[17]

(−)-9,10-Dihydro-4,5-dimethylphenanthrene (Ia).—A filtered (under nitrogen) solution of phenyllithium (from 0.32 g. of lithium and 3.7 g. of bromobenzene) in 35 ml. of ether was added dropwise to a solution of (−)-2,2′-bis-(bromomethyl)-6,6′-dimethylbiphenyl (5.5 g., $[\alpha]^{24.5}\mathrm{D}$ −49.8° (c 1.2, C_6H_6)) in 130 ml. of ether at ice-bath temperatures. The reaction mixture was stirred at 0–5° for 1 hour and hydrolyzed by addition of ice-cold dilute sulfuric acid. The ether layer was washed with ice-cold sodium bicarbonate solution and water, and the ether was removed under reduced pressure at 0–5°. The residue was stirred for 30 minutes at ice-bath temperatures with a solution of 5.0 g. of silver nitrate in 10 ml. of water and 30 ml. of acetone. The mixture was filtered, the filtrate was concentrated at 0–5° and extracted with ether, and the ether was removed at 0–5°. The residue, dissolved in hexane, was chromatographed on 100 g. of silica gel (100–200 mesh) which was kept at 0–5° through use of a jacketed column. Bromobenzene was eluted first, followed by Ia. The material obtained on evaporation of the solvent at 0–5° was a solid, m.p. 50–52°, $\lambda_{\max}^{\mathrm{EtOH}}$ 261 mμ (ε 14,500), $\lambda_{\max}^{\mathrm{isooctane}}$ 261 mμ (ε 16,800); lit.[4,15] (estimated from the published graphs) $\lambda_{\max}^{\mathrm{EtOH}}$ 260 mμ (ε, 16,000); O.R.D. in isoöctane (0–1°, c 1.1–0.006): $[\alpha]_{589}$ −242°, $[\alpha]_{340}$ −726°, $[\alpha]_{296}$ +774°, $[\alpha]_{293}$ +290°; see Fig. 1. The cyclization and isolation steps described above took about 7 hours altogether.

The product, as eluted off the column and used in subsequent rate studies, was at least 90% homogeneous by gas chromatography at 200° on a 6′ × 0.25″ column packed with Apiezon L, helium carrier at 30 p.s.i., retention time 15.3 min. Bromobenzene (amounting to a few per cent.) was identified among the small forerun of contaminants (retention times 2.3 min. or less). No biphenyl was detected.

For purposes of comparison, a sample of racemic Ia was prepared by the older procedure.[15] On scratching the oil, crystallization was induced. The solid melted at 51–53° after recrystallization from ethanol. The infrared spectra of (−)-Ia and of authentic (±)-Ia were identical.

A sample of (−)-Ia was distilled (with concomitant racemization) under high vacuum at 70° (bath temperature) for elemental analysis.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.07; H, 7.92.

Racemization Experiments.—Thermostated 1% solutions of (−)-Ia in benzene were examined polarimetrically (2-dm. tube) over a period of at least 1 half-life. Readings were taken at 435 mμ and the results were plotted as log α_t *vs.* time. Excellent straight-line relationships resulted from the twelve or more readings which were obtained for each run. The values of k (and half-lives) obtained from the slopes of the curves are listed in Table I, as are the rotations observed at t_0. After a little less than 1 hour at 54.4°, or after heating 3 minutes near 100°, the rotation had become, and remained, zero.

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[17] Microanalysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The rotatory dispersion was measured with an automatic recording Rudolph spectropolarimeter.

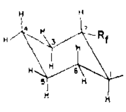
COMMUNICATIONS TO THE EDITOR

trans AND *cis* CONFORMATION ISOMERS OF 1-IODO-2-PERFLUOROALKYLCYCLOHEXANES AND THEIR NUCLEAR MAGNETIC RESONANCE SPECTRA

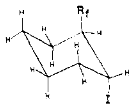
Sir:

Trans and *cis* isomers of 1-iodo-2-perfluoroisopropylcyclohexane and of 1-iodo-2-perfluoropropylcyclohexane have been prepared and characterized.[1] Evidence obtained to date strongly indicates that these products have chair structures Ia (R_f = $(CF_3)_2CF$–), Ib (R_f = $CF_3CF_2CF_2$–) and IIb (R_f = $(CF_3)_2CF$– and $CF_3CF_2CF_2$–).[2,3]

Free radical addition of heptafluoro-2-iodopropane to cyclohexene gave two adducts (*trans*, A and *cis*, B) which were separated by gas liquid phase chromatography.[4] Heptafluoro-1-iodopropane and cyclohexene gave two adducts[5] also, but



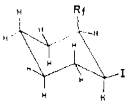
Ia



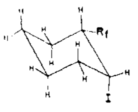
Ib

trans

A C



IIa



IIb

cis

B, D

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[1] N. O. Brace, to be submitted to the *Journal of the American Chemical Society*.

[2] A full exposition of the evidence will be given with an appropriate discussion in a later publication; space permits here only a summary of the salient points.

[3] For a review of the stereochemistry of cyclohexanes, see W. G. Dauben and K. S. Pitzer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

[4] Tricresyl phosphate on a firebrick column at 124°, 1.5 p.s.i. helium pressure, 6.0 flow rate with a Perkin–Elmer Vapor Fractometer was used in all cases. Preparative scale separation of adducts was done by John Robson. A [R_f = $(CF_3)_2CF$–] gave a retention time (R.T.) of 9.2 minutes; $n^{25}\mathrm{D}$ 1.4373; $d^{25}{}_4$ 1.792. B [R_f = $(CF_3)_2CF$–] gave an R.T. of 12.6 min.; $n^{25}\mathrm{D}$ 1.4378; $d^{25}{}_4$ 1.804. *Anal.* Calcd. for $C_9H_{10}F_7I$: C, 28.6; H, 2.67; F, 35.3; I, 33.6. Found: (A) C, 28.7; H, 2.9; F, 35.8; I, 33.0. (B) C, 28.9; H, 2.8; F, 35.7; I, 33.3.

[5] C (R_f = $CF_3CF_2CF_2$–) gave 7.9 R.T.; $n^{25}\mathrm{D}$ 1.4310; $d^{25}{}_4$ 1.772. D (R_f = $CF_3CF_2CF_2$–) gave R.T. 15.5; $n^{25}\mathrm{D}$ 1.4325; $d^{25}{}_4$ 1.784. *Anal.* Calcd. for $C_9H_{10}F_7I$: C, 28.6; H, 2.67; F, 35.3; I, 33.6. Found: (C) C, 28.8; H, 2.7; F, 35.3; I, 33.8. (D) C, 28.8; H, 2.7; F, 35.4; I, 33.8.

trans isomer C has a proton n.m.r. spectrum[6] which differs considerably from *trans* isomer A, while that of *cis* isomer D is almost identica' to *cis* isomer B (Fig. 1). There is evidence in the spectrum of A for strong coupling of the proton on C.1 wi h two adjacent axial protons, while the spectra of B, C or D do not show coupling of this proton.[7] The chemical shift and presence or absence of noticeable coupling[8-13] of the protons on C.1 and C.2, and the width[10,11,13] of the resonance peaks in A to D were consistent with the previously known n.m.r. behavior of chair conformations of substituted cyclohexanes. The two chair conformers of iodocyclohexane equilibrate rapidly at 25°, but at −80° to −105° interconversion becomes very slow and n.m.r. spectra[14] show resonances for an equatorial hydrogen on C.1 at 4.83 p.p.m. (7 cps. peak width) as in B, C or D and for an axial hydrogen on C.1 at 4.06 p.p.m. (a multiplet 20 cps. wide) as in A. *Heating* A to D (diluted with 25% of carbon disulfide) *to +75° or cooling to −88° did not affect their spectra.* Unless the rate of interconversion is greater than it is for iodocyclohexane, which seems rather improbable, A to *D* exist *predominantly* in a single conformation over this temperature range. The unusual preference of *trans* isomer C for conformation Ib also extends to analogs having perfluorobutyl and perfluoroheptyl groups. A perfluoroisopropyl group, however, must occupy only an equatorial position.[15] Normally rapid chair to chair interconversion in both

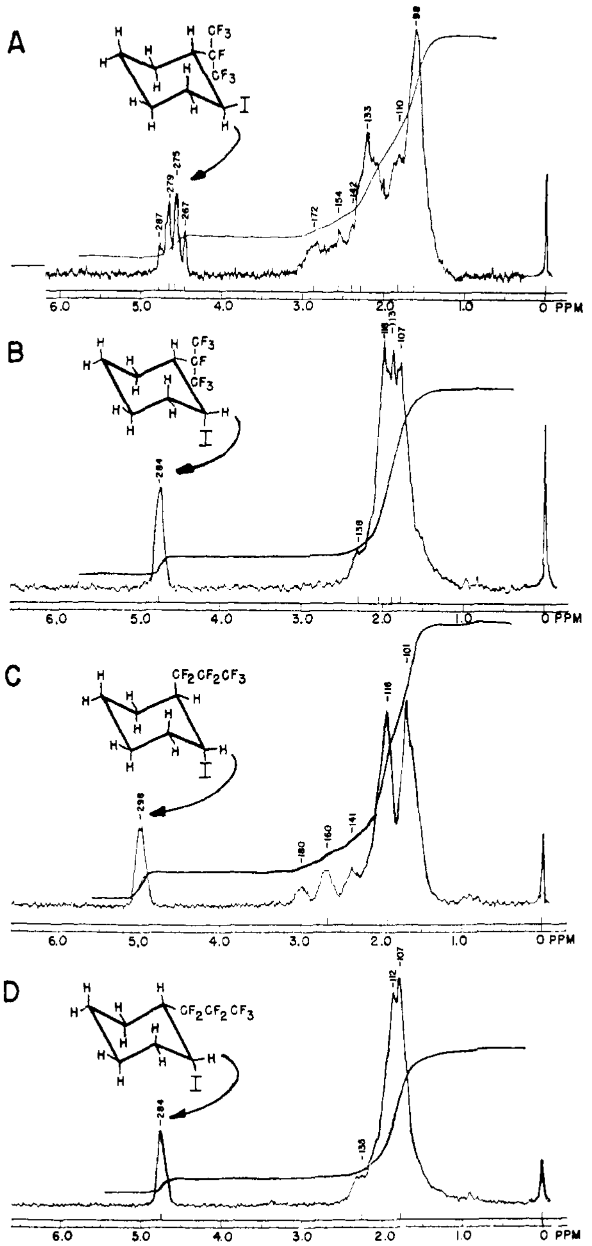

Fig. 1.—Proton n.m.r. spectra of 1-iodo-2-perfluoroalkylcyclohexanes at 60 Mc. (relative to tetramethylsilane internal standard) at −88 to +75°. Electronic integration of areas is shown. There was some loss in resolution, but no shift of peaks at −88°, of samples containing about 25% by weight of carbon disulfide. A mixture of C and D showed no change in positions of the two C.1 proton resonance peaks over this temperature range.

sets of isomers is apparently restrained by the close proximity of two bulky polar groups.[2]

D is slightly more stable at 180° than the *trans* conformer C, while the opposite is true for A and B. B and A isomerized at an initial rate several times that of D and C, which is consistent with the greater steric requirements of the isoperfluoropropyl group.[15] Heating A or B at 180° gave a mixture of only A and B; the same was true for C and D. That both sets of isomers are 1,2-substituted cyclo-

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(6) The spectra were obtained with the assistance of C. B. Matthews. Helpful discussions of the n.m.r. spectra with W. D. Phillips, W. S. Johnson, S. Andreades and J. D. Roberts are gratefully acknowledged.

(7) Ia is the only chair conformation having two axial protons on C.2 and C.6 with which strong coupling of the C.1 proton can occur (ref. 8–11). One interpretation is that the C.1 proton in A is coupled to two adjacent protons almost equally ($J \approx 8$ cps.) and also to another proton with $J \approx 4$ cps. The individual multiplet components are somewhat broadened by additional weak I.I (nuclear spin) coupling so that complete resolution of all six resonances is not achieved. The broad envelope of $-(CH_2)_4-$ proton resonances (1.3 to 3.0 p.p.m.) also indicates this to be the *trans* (e,e) isomer (ref. 10, 11, 12). This broadening results from coupling with C.1 and C.2 protons. C has an equatorial hydrogen on C.1 at 5 p.p.m. (peak width of 7 cps.) and on C.2 (probably split into three peaks by adjacent CF_2. $J = ca.$ 20 cps.) at 2.65 p.p.m. The two large 4-proton peaks at 1.70 and 1.92 p.p.m. are of the axial and equatorial protons of $-(CH_2)_4-$, respectively (see ref. 11). In this conformation only, coupling between protons on C.1 and C.2 and other protons will be at a minimum. The *cis* conformers (B) or (D) have proton resonances of C.1 *and* C.2 both shifted to higher field as compared with C, and a narrower envelope (from 1.78 to 2.30 p.p.m.) of $-(CH_2)_4-$ proton resonances. The peak width of proton resonance on C.1 is 7 cps. in both B and D. This denotes an equatorial proton, which appears to be shielded somewhat more in B and D than in C.

(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(9) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(10) (a) R. U. Lemieux, P. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958); (b) R. U. Lemieux, P. K. Kullnig and R. Y. Moir, *ibid.*, **80**, 2237 (1958).

(11) J. I. Musher, *J. Chem. Phys.*, **34**, 594 (1961).

(12) A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958).

(13) S. Brownstein and R. Miller, *J. Org. Chem.*, **24**, 1886 (1959).

(14) Three molar in carbon disulfide at 60 Mc., relative to tetramethylsilane; at 25° the broad multiplet of the mixture of conformers is at 4.0 to 4.38 p.p.m. (a) E. L. Eliel, *Chem. and Ind.*, 558 (1959); (b) *J. Chem. Ed.*, **37**, 126 (1960); (c) A. J. Berlin and F. R. Jensen, *Chem. and Ind.*, 998 (1960); (d) L. M. Reeves and K. O. Stromme, *Can. J. Chem.*, **38**, 1241 (1960).

(15) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955), report group "A" values: *t*-butyl, > 5.4; isopropyl, > 3.3; *n*-propyl or ethyl, 2.1. Fluorine substitution would increase the steric effects further.

hexanes was likewise demonstrated by dehydrohalogenation to the same pair of Δ^1 and Δ^2 perfluoropropylcyclohexenes in each instance. C gave a 15/85 mixture and A gave a 60/40 mixture of Δ^1/Δ^2 olefins according to gas chromatography, n.m.r. vinyl proton resonance areas and infrared analysis. D gave pure Δ^1 olefin. A study of related chemistry of these substances is being carried on.

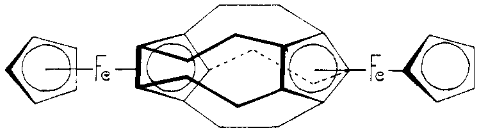
CONTRIBUTION NO. 325 FROM THE
PIONEERING RESEARCH SECTION
JACKSON LABORATORY NEAL O. BRACE
E. I. DU PONT DE NEMOURS AND CO.
WILMINGTON, DEL.

RECEIVED FEBRUARY 10, 1962

PENTAETHANODIFERROCENE

Sir:

Experimental results, obtained in this laboratory, provide evidence in serious contradiction to the recent assignment of Structure I to material obtained by prolonged treatment of ferrocene with aluminum chloride in the presence of ethylene dichloride.[1] The substance in question, whose formation is viewed as resulting from multi-alkylation of two ferrocene nuclei by five molecules of ethylene dichloride, possesses the name, "pentaethanodiferrocene";[1] and, the present experimental basis for rejection of I lies in the observation that material identical with "pentaethanodiferrocene" is produced by treatment of ferrocene with aluminum chloride *in the absence of ethylene dichloride.*



Structure I.

Careful repetition of the procedure reported by the original workers[1] gave rise to a yellow-colored solid possessing properties [dec., near 130°; mol. wt., 527 (benzene); d^{22}_4 1.37 ± 0.14 (methanol)] strikingly close to those reported for pentaethanodiferrocene [dec., near 130°; mol. wt., 545, 568 (benzene); d^{20}_4 1.461 (methanol)].[1] A yellow-colored solid (dec., near 130°), then obtained from similar treatment of ferrocene—except that benzene was used in place of ethylene dichloride—was found to be identical with the material produced in ethylene dichloride. The identity was demonstrated by means of superimposable infrared spectra (chloroform) and, more definitively, by the congruence of X-ray powder patterns determined from the two purified solids.[2]

These results clearly show that the aliphatic carbons present in structural association with the two ferrocene nuclei of "pentaethanodiferrocene" must have as their source a third ferrocene nucleus or its equivalent; and, that the sequence of bonding for all of these units is different from that depicted by I. Since ferrocene is known to undergo oxidation to ferricinium cation in the presence of strong electrophile and air,[3,4,5] and decomposition of the unstable ferricinium species in the presence of a proton source[6] may be expected to result in generation of cyclopentadiene, it would appear likely that the aliphatic carbons exist as substituted cyclopentane rings either as such or in a modified form. Experiments designed to provide information to allow a choice among several structural possibilities are now in progress, and all results will be reported in a full account of this work.

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(1) A. N. Nesmeyanov and N. S. Kochetkova, *Doklady Akad. Nauk, S.S.S.R.*, **126**, 307 (1959).

(2) The author is indebted to Prof. Richard Layton of this Department for determination of these X-ray powder patterns.

(3) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(4) V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955).

(5) M. Rosenblum and J. O. Santer, *ibid.*, **81**, 5517 (1959).

(6) Under the experimental conditions used,[1] it is not unreasonable to expect appreciable amounts of hydrogen chloride formed by the action of atmospheric moisture on aluminum chloride.

DEPARTMENT OF CHEMISTRY STANLEY I. GOLDBERG
UNIVERSITY OF SOUTH CAROLINA
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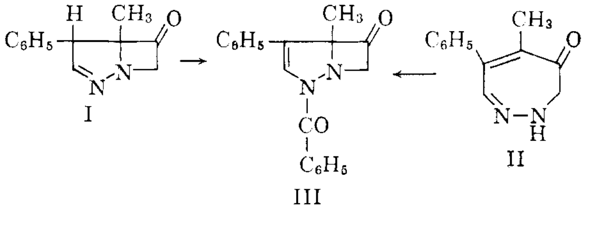
RECEIVED APRIL 25, 1962

HETEROCYCLIC STUDIES. IX. SOME TRANSFORMATIONS OF THE 1,2-DIAZABICYCLO[3.2.0]HEPTANE SYSTEM[1]

Sir:

Current interest in the chemistry of strained bicyclic systems prompts us to report very briefly the formation and some of the reactions of 2-benzoyl-5-methyl-4-phenyl-1,2-diazabicyclo[3.2.0]-3-hepten-6-one (III). This compound is produced by benzoylation of the bicyclic ketone (I)[2] with benzoyl chloride in pyridine; m.p. 126–127° (dec.), (Found: C, 75.07; H, 5.33; N, 9.15). The structure follows from the method of preparation and the physical properties (λ_{KBr} 5.56, 6.13 μ; n.m.r. (60Mc.): 3 proton CH_3 peak at 95 c.p.s., 2 proton quartet for CH_2 at 277 c.p.s., J_{AB} 17 c.p.s., 11 proton aryl and vinyl peak at 450 c.p.s. max.).

A more practical preparation of III is provided by a facile bridging reaction that occurs on treatment *of the diazepinone* II[3] with benzoyl chloride in pyridine or dimethylaniline; acetyl chloride furnishes the corresponding 2-acetylbicyclic ketone.



In contrast to the parent bicyclic ketone I, which is tautomeric with II and is rapidly converted to II or derivatives thereof under most reaction conditions, III displays a remarkably broad

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(1) Supported in part by a grant from the Geschickter Fund for Medical Research.

(2) J. A. Moore and R. W. Medeiros, *J. Am. Chem. Soc.*, **81**, 6026 (1959).

(3) J. A. Moore and J. Binkert, *ibid.*, **81**, 6029 (1959).