sodium pieces. After stirring the reaction mixture for 1 hr., the product was isolated and purified in the usual manner. The yield of VII was 0.350 g. (35%), m.p. 80–81°. The infrared and near infrared absorption spectra of this VII were identical to those of the specimens of VII obtained by the previous two reduction procedures.

Anal. Found: C, 78.87; H, 13.37; mol. wt., 201.

Samples of the alcohol VII obtained from chemical and catalytic reductions were mixed and sublimed together. No depression of melting point was observed.

4,4,8,8-Tetramethylcyclononanol 3-Nitro Acid Phthalate. —The alcohol VII (11 g., 0.056 mole) and 11.6 g. (0.06 mole) of 3-nitrophthalic anhydride were heated in 110 ml. of anhydrous toluene until all the anhydride dissolved, then refluxed for 0.5 hr. On cooling, 15 g. of solid was precipitated which, after crystallization from benzene, gave 10.2 g. of the pure 3-nitro acid phthalate derivative of VII which had m.p. 198° dec., and 2.65 g. which showed m.p. 188–192° dec. (58% total).

Anal. Calcd. for $C_{21}H_{29}NO_6$: C, 64.42; H, 7.47; N, 3.58; mol. wt., 391. Found: C, 64.68; H, 7.41; N, 3.85; mol. wt., 379.

The **methyl ester derivative of the above acid phthalate** was prepared using the diazomethane method[19]; m.p. 129–134° from hexane.

Anal. Calcd. for $C_{22}H_{31}NO_6$: C, 65.15; H, 7.71; N, 3.46; mol. wt., 405. Found: C, 65.27; H, 7.57; N, 3.73; mol. wt., 385.

Resolution of the 3-Nitro Acid Phthalate Derivative of VII.[2a]—In 1700 ml. of acetone there was dissolved, by gentle refluxing, 10.15 g. (0.026 mole) of the nitro acid phthalate of VII and 7.65 g. (0.026 mole) of cinchonidine. On cooling and evaporation of the solvent 16.69 g. of salt was obtained. The residue was hydrolyzed with 5% hydrochloric acid solution to yield after three recrystallizations from benzene 0.54 g. of solid, m.p. 188–189° dec., with softening at 175°, $[\alpha]^{25}D$ + 23.5 ± 1° (c 5, in acetone).

Fractional crystallization of the salt from acetone until the least soluble fractions showed no further change in m.p. or optical rotation gave 6.11 g. of (−)-acid-(−)-base salt, m.p. 199° (sl. dec.), $[\alpha]^{25}D$ −90.8 ± 1° (c 2.5, in chloroform).

Anal. Calcd. for $C_{40}H_{51}N_3O_7$: C, 70.05; H, 7.50; N, 6.13. Found: C, 70.10; H, 7.74; N, 6.14.

A solution of 6.11 g. of (−)-acid-(−)-base salt in 50 ml. of chloroform was shaken three times in succession with 50-ml. portions of 5% hydrochloric acid solution. On evaporation of the chloroform 2.44 g. (48%) of the (−)-3-nitro acid phthalate of VII was obtained; m.p. 187–188° dec. with softening at 180°, $[\alpha]^{25}D$ −23.4 ± 1° (c 5, in acetone), constant rotation on recrystallization from benzene.

Anal. Calcd. for $C_{21}H_{29}NO_6$: C, 64.42; H, 7.47; N, 3.58; mol. wt., 391. Found: C, 64.69; H, 7.38; N, 3.86; mol. wt., 390.

The more soluble salt (5.10 g.), m.p. 165–168°, $[\alpha]^{25}D$− 108.8 ± 1° (c 2.5, in chloroform), was obtained in a reasonably pure state on further fractional crystallization. This salt was decomposed as described above to give the crude

(+)-3-nitro acid phthalate of VII, m.p. 180–187°, $[\alpha]^{25}D$ + 16.8° (c 5, in acetone). On recrystallization of this crude phthalate from benzene–hexane the racemate, m.p. 198–199° dec., was obtained as insoluble material. The benzene–hexane solution deposited, on cooling, 1.1 g. of optically pure (+)-3-nitro acid phthalate; m.p. 191–192° dec., $[\alpha]^{25}D$ + 22.2 ± 1° (c 5, in acetone). The total yield of (+)-3-nitro acid phthalate of VII was 1.64 g. (32%).

Anal. Calcd. for $C_{21}H_{29}NO_6$: C, 64.42; H, 7.47; N, 3.58. Found: C, 64.61; H, 7.71; N, 3.67.

(+)- and (−)-Alcohol VII.—The (+)-3-nitro acid phthalate of VII (1.1 g., 2.82 mmoles) was hydrolyzed following a procedure described previously[2a] to yield 0.55 g. (90%) of (+)-VII, which after sublimation at 35° (0.07 mm.), showed constant m.p. 98.5–99.5° and $[\alpha]^{25}D$ + 12.6 ± 1° (c 5, in chloroform). After 3 weeks at room temperature, the material was unchanged; m.p. 99–100°, $[\alpha]^{25}D$ +12.0 ± 1° (c 5, in chloroform).

Anal. Found: C, 78.75; H, 13.21; mol. wt., 218.

The (−)-3-nitro acid phthalate of VII (1.52 g., 3.89 mmoles) was hydrolyzed in a similar manner to yield 0.72 g. (94%) of (−)-VII, which after sublimation at 35° (0.07 mm.) showed constant m.p. 97.5–98.5° and $[\alpha]^{25}D$ −13.0 ± 1° (c 5, in chloroform).

Anal. Found: C, 78.87; H, 13.40; mol. wt., 199.

(−)-VII 3-Nitro Acid Phthalate from (−)-VII.—Compound (−)-VII (0.2 g., 1.01 mmoles) and 3-nitrophthalic anhydride (0.2 g., 1.04 mmoles) were dissolved in 5 ml. of anhydrous toluene and refluxed for 20 min. On cooling, 0.09 g. of unreacted anhydride was obtained. The solvent was removed and the residue sublimed to yield trace amounts of unreacted alcohol. The sublimation residue was crystallized from hexane to give 0.055 g. (14%) of the (−)-3-nitro acid phthalate of VII, m.p. 188.5–189° dec. with softening at 178°, $[\alpha]^{25}D$ −23.0 ± 1° (c 5, in acetone). A high melting material (m.p. > 220°) interfered with the hexane crystallization and caused the poor yield.

Chromic Acid Oxidation of (+) and (−)-VII.—The chromic acid oxidation procedure described in an earlier article in this series,[2a] but done at 0°, was followed. Thus, from 0.140 g. (0.715 mmoles) of (+)-VII there was obtained 0.134 g. (97%) of VI, $[\alpha]^{25}D$ 0° (c 13, in chloroform), $[\alpha]^{25}D$ 0° (c 13, in hexane), $[\alpha]^{25}_{4358}$ 0° (c 13, in chloroform) and $[\alpha]^{25}_{4358}$ 0° (c 13, in hexane). After molecular distillation the ketone VI showed $n^{20}D$ 1.4686. The infrared absorption spectrum of this VI was identical to that of the original ketone VI.

Anal. Found: C, 79.20; H, 12.58.

Similarly, from 0.50 g. (2.52 mmoles) of (−)-VII there was obtained 0.48 g. (96%) of VI, $[\alpha]^{25}D$ 0° (neat), $[\alpha]^{25}D$ 0° (c 3, in hexane), $[\alpha]^{25}D$ 0° (c 2.4, in chloroform), $[\alpha]^{25}_{4358}$ 0° (c 2.4, in chloroform). This ketone VI showed b.p. 46–47° (0.075 mm.) and $n^{20}D$ 1.4700. The infrared absorption spectrum of this VI was identical to that of the original ketone VI, as well as to that of the ketone VI obtained from (+)-VII.

Anal. Found: C, 79.43; H, 12.55.

COMMUNICATIONS TO THE EDITOR

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. LONG-RANGE SPIN-SPIN COUPLINGS IN SATURATED MOLECULES[1]

Sir:

It is usually assumed that spin–spin couplings except those involving fluorine–fluorine interactions[2] are negligibly small over more than three

bonds in saturated systems.[3] At this time, we should like to report four examples of H–H and H–F spin–spin couplings that involve more than three consecutive single bonds. Each of these systems is characterized by having either fixed or at least reasonably favored geometrical conformations.

(1) Supported in part by the Office of Naval Research.

(2) See, for example, (a) A. Saika and H. S. Gutowsky, *J. Am. Chem. Soc.*, **78**, 4818 (1956); (b) N. Muller, P. C. Lauterbur and G. F. Svatos, *ibid.*, **79**, 1807 (1957).
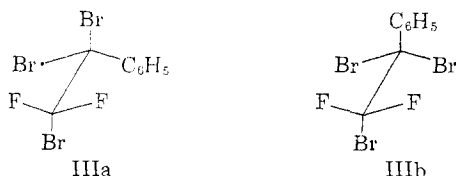
(3) (a) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, Chap. 3; (b) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chap. 6; (c) M. Karplus, *J. Am. Chem. Soc.*, **82**, 4431 (1960).

Our first example of long-range proton–proton couplings in saturated systems is the 1.3 cps. splitting of the aldehyde proton in methacrolein dimer (I). The resonance involved is a doublet, the spacing of which is field-invariant.[3a] The coupling probably involves one of the ring protons located at the β-position relative to the aldehyde group. The vinyl hydrogen definitely is not implicated since the appearance of its resonance does not change when deuterium is substituted for the aldehyde hydrogen.
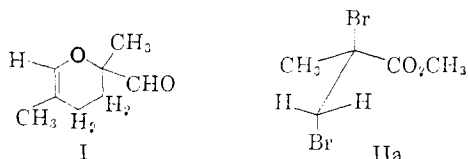
Another example involving proton–proton interactions is afforded by methyl α,β-dibromoisobutyrate (II), which exists in a preferred conformation,[3a,4] probably IIa, with the bromines *trans*. One of the non-equivalent[3a,4] methylene protons of II is coupled to the protons of the C-methyl group with $J = 0.75$ cps. (*cf.* Fig. 1A). It is not known whether the coupled proton is that which is *trans* or *gauche* to the methyl group. This point will be checked with appropriate stereospecifically deuterium-labeled compounds.

Our third example is 1,1-difluoro-1,2,2-tribromo-2-phenylethane (III), which below −60° displays the n.m.r. spectrum expected for the "locked-in" rotational conformers, with the "D,L" configura-

tions (IIIa) being particularly favored.[3a,4] At −85°, the fluorine spectrum shows unmistakable evidence of H–F coupling across at least five bonds, three of them in a row saturated. This coupling is stereospecific. As can be seen from Fig. 1B, only one of the fluorines of IIIa is involved, and this is coupled to two phenyl protons (presumably those at the 2,6 positions) with $J = 1.6$ cps.

At 25°, the fluorine resonance of III is several cycles broad; but, at 85°, it becomes a clean triplet with $J = 1.1$ cps. The fact that J does not drop to half of its low-temperature value for one fluorine may indicate that some contribution to the long-range H–F couplings arises from the conformation IIIb with both the fluorines *gauche* to the phenyl group. In agreement with this idea, the fluorine resonance of IIIb is seen in Fig. 1B to be broader than that of the apparently uncoupled fluorine of IIIa.

Long-range H–F couplings also have been seen with 1,1-difluoro-1,2-dibromo-2-phenylethane (IV), which is expected by analogy with III to exist principally as IVa. The n.m.r. spectrum of IV (Fig. 1C) at 25° shows the expected non-equiva-
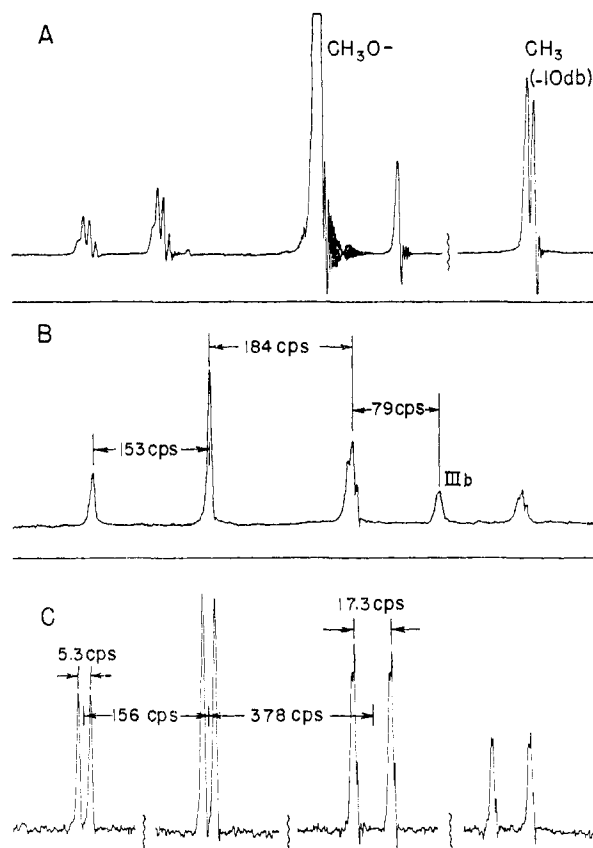
(4) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957).

Fig. 1.—Nuclear magnetic resonance spectra: A, protons of methyl α,β-dibromoisobutyrate (II) at 60 Mc. and 25° with discontinuous sweep, one of the resonances of the CH_3 quartet being hidden under the CH_3O resonance (compare the 40 Mc. spectrum[4]); B, fluorines of 1,1-difluoro-1,2,2-tribromo-2-phenylethane (IIIa) at 56.4 Mc. and −84°; C, fluorines of 1,1-difluoro-1,2-dibromo-2-phenylethane (IV) at 56.4 Mc. and 25° with discontinuous sweep. Increasing field in all cases from left to right.

lent fluorines[4] each split by three-bond coupling to the proton at the two position. The fluorine most strongly coupled to the proton is also coupled to two of the phenyl protons with $J = 1.0$ cps. This result is most interesting because if the strong
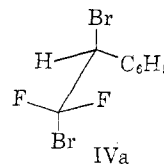
H–F three-bond coupling involves *trans* groups, then the five-bond couplings are *gauche* and possibly exerted through space instead of through the bonds.

Further discussion of these cases will be given later.

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