Free Radical Addition of Iodoperfluoroalkanes to Bicyclic Olefins

NEAL O. BRACE

Contribution No. 314, Research and Development Division, Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware

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The reaction of 1-iodoperfluoropropane with strained bicyclic olefins was carried out in order to study the effect of variation in structure of the olefin on the mode of addition. Norbornene gave a *trans* adduct, *endo*-2-iodo-*exo*-3-perfluoropropylnorbornane, in 95% yield which was unusually stable to hydrolysis. With norbornadiene rearrangement of the intermediate adduct radical occurred. As a result only one mole of 1-iodoperfluoropropane was added and two isomeric 5-perfluoropropyl-7-iodonortricyclenes were obtained in nearly equal amounts. Reduction of both isomers gave 5-perfluoropropylnortricyclene. β-Pinene (a bicyclic *exo*-olefin) gave, *via* ring opening, extremely light and air-sensitive 7-perfluoropropyl-8-iodo-Δ^1-*p*-menthene; co-pyrolysis with β-pinene *in vacuo* cleaved hydrogen iodide and the resulting diene disproportionated to the corresponding cyclohexane and benzene derivatives. In these addition reactions, the strongly polar and bulky iodo and perfluoroalkyl groups take positions in the adduct as far as possible from each other.

Free radical addition of halogen-containing compounds such as bromotrichloromethane, chloroform, and arenesulfonyl chlorides to cyclic olefins is well known.[1-4] The stereochemistry of addition to norbornene has been recently demonstrated,[5-7] while in the earlier work relative reactivities of olefins were emphasized. The mode of addition depends importantly on the size of the adding groups; *trans* addition occurs when both fragments are bulky polar groups,[6,7] but with chloroform[5,6] or ethyl bromoacetate[1] *cis* addition results. Size is not the only important factor since addition of thiols is generally not stereoselective,[8] whereas hydrogen bromide gives most often only *trans* adducts.[1,8] In chain reactions of this type addition occurs in two stages, with the intermediate radical adduct capable of undergoing dissociation, a change in configuration by rotation about a single bond in some cases or isomerization to an entirely different radical in other cases, before transfer occurs giving the final product. The relative rates of these various transformations are of critical importance in determining the nature of the over-all process.

Iodoperfluoroalkanes have even larger adding groups than does bromotrichloromethane, but the fluorinated compounds would be expected to react at a slower rate.[1] The effect of structure of some bicyclic olefins on the mode of reaction with 1-iodoperfluoropropane was therefore investigated. The results of an analogous study with some simple cyclic olefins are being reported separately.

Azonitrile-induced reaction with norbornene, aldrin, and norbornadiene occurred with exceptional ease. For example, norbornene and 1-iodoperfluoropropane with 1% of azonitrile initiator gave in 95% yield *endo*-2-iodo-*exo*-3-perfluoropropylnorbornane (Ia), a single isomer according to gas-liquid phase chromatography (g.l.c.). The perfluoropropyl radical adds first to the less-hindered *exo* side of the ring[1,6,7]; the iodine atom is abstracted from 1-iodoperfluoropropane by the adduct radical, and takes a position imposing the least strain on the already strained ring,[4] at a point farthest removed from the bulky and strongly negative perfluoroalkyl group. This position is *trans*.[7] It is possible that an intermediate adduct radical which is *cis*-like in configuration can dissociate, and the *trans*-like radical obtained by recombination then undergoes transfer. This concept[8b] cannot be distinguished experimentally at present from a planar radical intermediate.

The n.m.r. spectrum of Ia (Fig. 1) shows the proton on C-2 as a triplet shifted down to −258 c.p.s. (relative to tetramethylsilane), with $J = 4$ to 6 c.p.s. This splitting is attributed to coupling with protons on C-1 and C-3; the spacing is that anticipated[9] for protons at a 30 or 120° dihedral angle. Had the proton on C-2 been *endo* and at an angle of 90° to the proton on the adjacent bridgehead, splitting with C-1 would not occur.[9] The unsymmetrical splitting pattern may be understood as the result of unequal coupling of the proton on C-2 with two non-equivalent protons. The triplet observed under more favorable conditions could presumably be resolved into a four-line pattern, as was observed for the aldrin adduct II (see below).

The product Ia was unusually resistant to alkaline hydrolysis; refluxing in an ethanol solution of potassium hydroxide or steam distilling from 10% aqueous alkali did not affect the compound, nor did heating to 215° with an excess of tri-*n*-butylamine.

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[1] C. H. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, p. 247.

[2] A. Roedig in Houben-Weyl, "Methoden der organischen Chemie," 4th ed., Vol. V., Georg Thieme Verlag, Stuttgart, 1960, pp. 653–657.

[3] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, 1959, p. 743.

[4] F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **82**, 890 (1960).

[5] V. A. Rolleri, thesis, University of Delaware (1958), *Dissertation Abstr.*, **19**, 960 (1958).

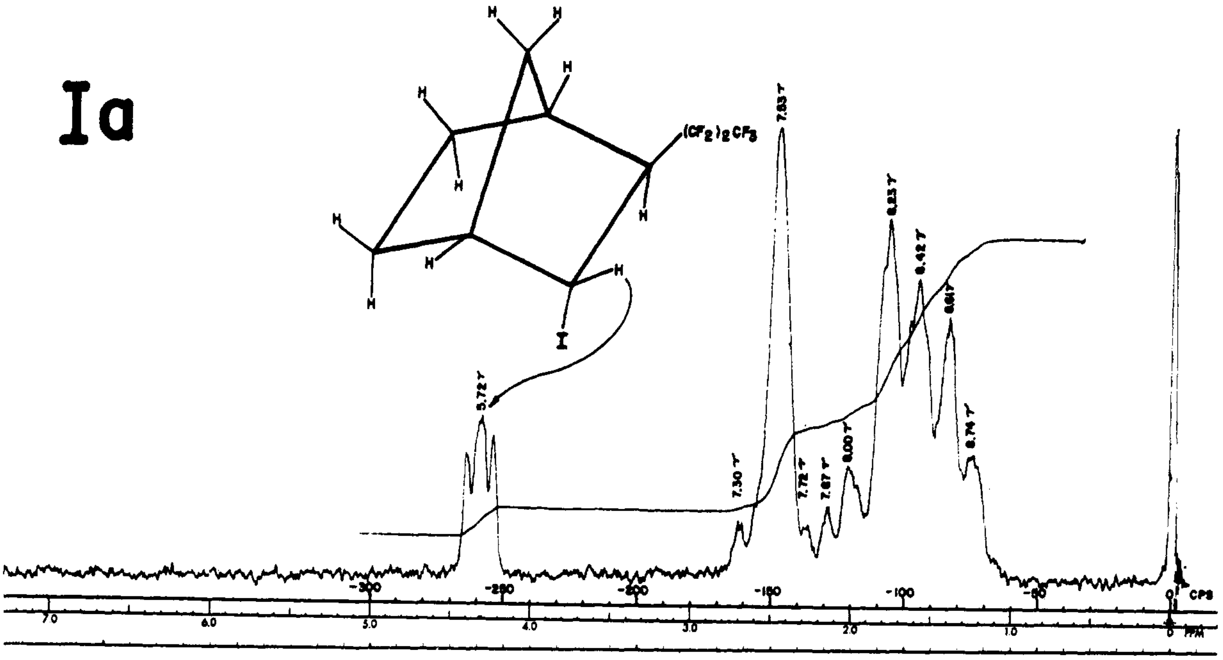
[6] D. I. Davies, *J. Chem. Soc.*, 3669 (1960); see references cited.

[7] (a) S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961); (b) S. J. Cristol and E. F. Hoegger, *J. Am. Chem. Soc.*, **79**, 3438 (1957).

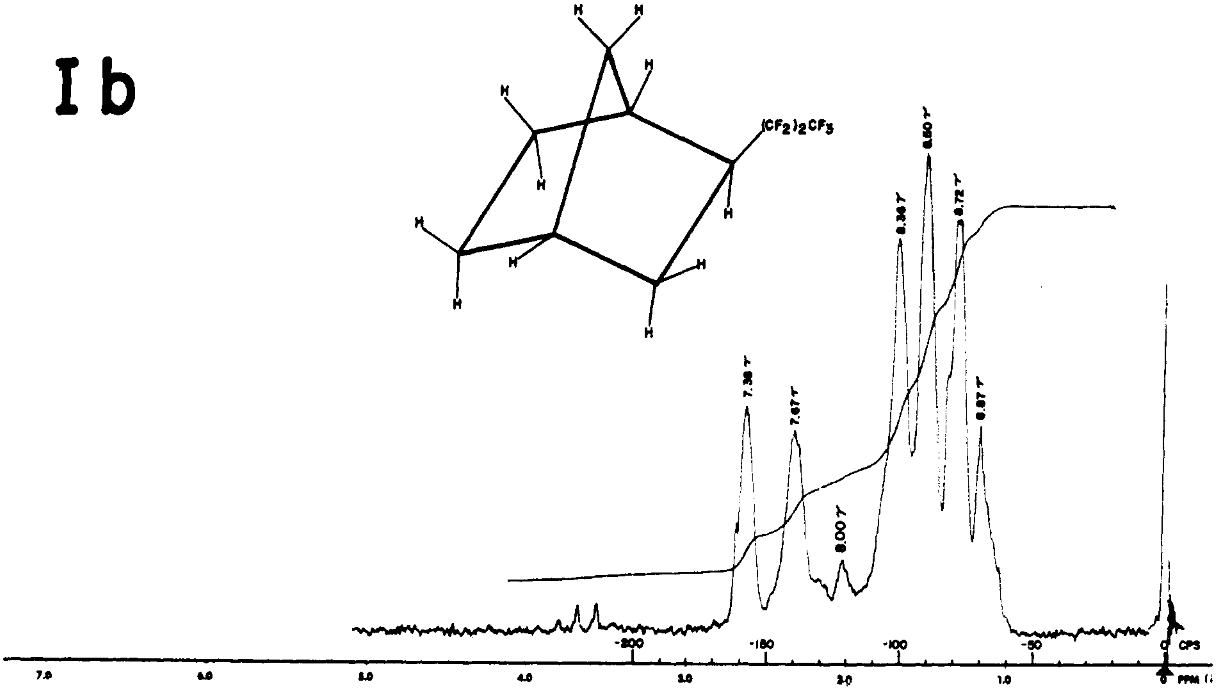
[8] (a) P. S. Skell and R. G. Allan, *ibid.*, **82**, 1511 (1960); (b) F. G. Bordwell and W. A. Hewett, *ibid.*, **79**, 3493 (1957).

[9] (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) F. A. L. Anet., *Can. J. Chem.*, **39**, 789 (1961); (c) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3347 (1961); (d) W. D. Kumler, J. N. Shoolery, and F. V. Brutcher, Jr., *ibid.*, **80**, 2533 (1958).

Ia



Ib



Attack of base on the carbon atom beta to the iodine is therefore highly hindered. This would be the case where the bulky iodine and the adjacent hydrogen are both on the *endo* side of the ring. It is surprising that facile *cis* elimination *via* carbanion formation, which was observed by Cristol and Hoegger[7b] for *exo*-2-*p*-toluenesulfonyl-*endo*-3-chloronorbornane, did not occur in the case of Ia.

Reaction of Ia with magnesium in ether gave coupling to bi(3-perfluoropropylnorborn-2-yl), instead of a Grignard compound. The coupled product consisted of two stereoisomeric materials formed by coupling the planar radicals from Ia *cis* and *trans* to each other. Reduction of Ia by zinc and hydrogen iodide in ethanol gave 2-perfluoropropylnorbornane (Ib), a single isomer according to g.l.c., in 75% yield.

1-Iodoperfluoropropane and aldrin gave a crystalline adduct of probable *trans* structure II in analogy to norbornene. This is the mode of addition observed by Davies,[6] using bromotrichloromethane and aldrin. The n.m.r. spectrum supports this conclusion.

Norbornadiene and 1-iodoperfluoropropane gave two adducts in 95% combined yield which could not be readily separated by fractional distillation

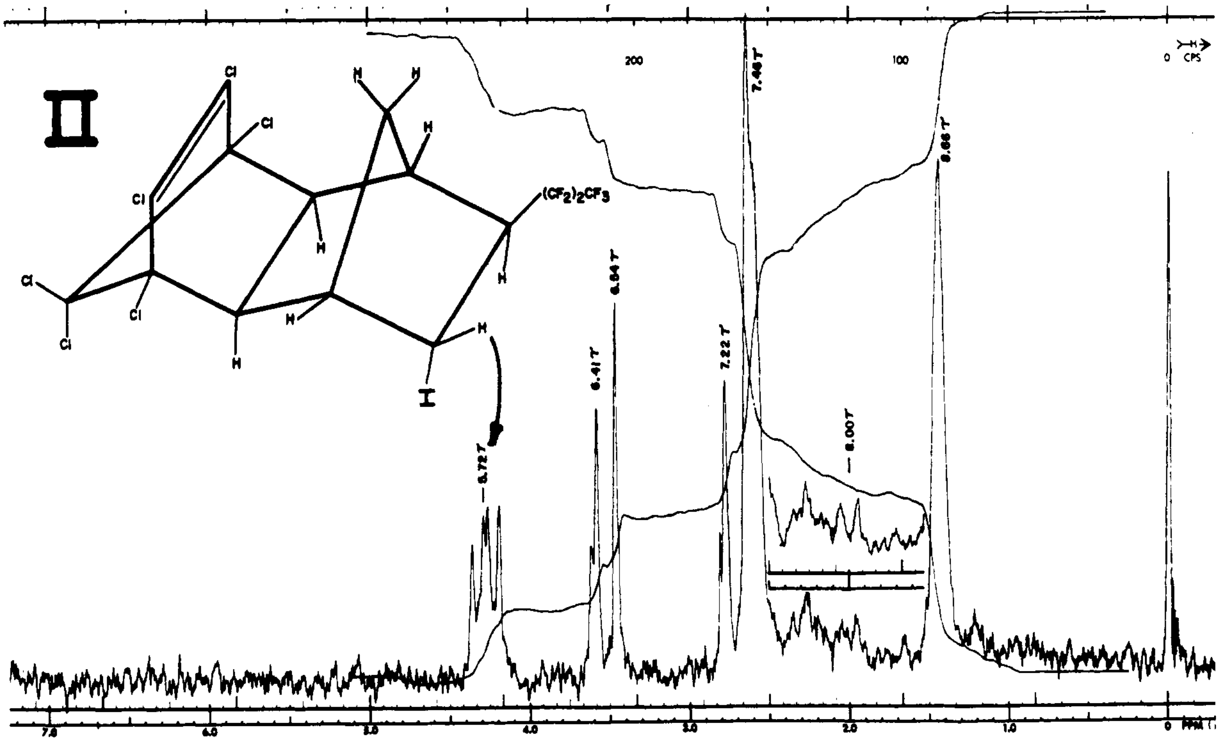
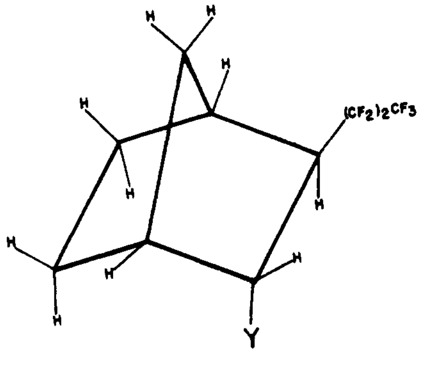
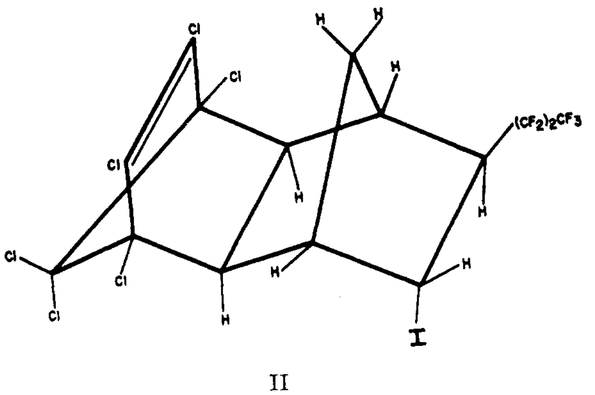


Fig. 1.—Proton n.m.r. spectra of *endo*-2-iodo-*exo*-3-perfluoropropylnorbornane (Ia), *exo*-2-perfluoropropylnorbornane (Ib), and *endo*-6-iodo-6,7-dihyro-*exo*-7-perfluoropropylaldrin (II) at 60 Mc. (relative to tetramethylsilane as internal standard). τ values are calculated in p.p.m. taking tetramethylsilane as 10.00. Electronic integration of the area under the curves is shown.



Ia. Y = I; Ib, Y = H



II

but were obtained by g.l.c. on a preparative scale. Analysis, infrared and n.m.r. spectra[10] indicated the nortricyclene (tricyclo-[2.2.1.0^{2,6}]heptane) structures IVa, b. Which isomer has the *syn* and which the *anti* structure was not determined. They were obtained in almost equal amounts at a 1:1 to 2:1 reactant ratio. Two minor components (1–2% yield) were indicated only by g.l.c. analysis.

Evidence for structures (IVa, b) is as follows: (1) analyses of the original mixture and of the isolated compounds were identical and agreed with theory, (2) the infrared spectra of both have the CH stretching band of a cyclopropyl ring at 3.20 μ and the band at 12.25 μ reported[11,12] for nortricyclene compounds. There are no bands associated with the olefinic group as in norbornene (3.16, 6.10, 6.18, and 6.35 μ).[11] N.m.r. spectra show no olefinic proton resonance peak in either product; the CHI peak is at 6.14 τ[13] in both isomers; (3)

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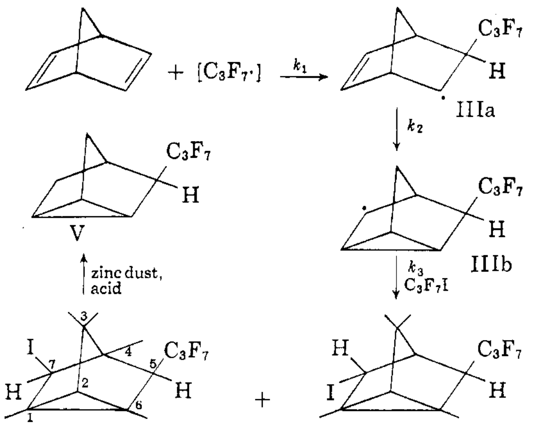
[10] I am indebted to W. D. Phillips for aid in obtaining and interpreting the n.m.r. data; τ values given are in p.p.m. with reference to tetramethylsilane at 10.00 as internal standard. A Varian Associates high resolution n.m.r. spectrometer operated at 60 Mc. (spinning) was used.

[11] E. R. Lippincott, *J. Am. Chem. Soc.*, **73**, 2001 (1951).

[12] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

[13] The absence of splitting of the resonance at 6.14 τ in either isomer is at first puzzling, as is the lack of change in chemical shift with change of position of the iodine atom. In the highly strained symmetrical nortricyclene structure, however, the protons on C-4 and C-1 are apparently at an unfavorable angle for coupling with the proton on C-7 in either the *syn* or *anti* position relative to C_3F_7. The molecular model drawn in ref. 11 shows clearly the threefold axis of symmetry.



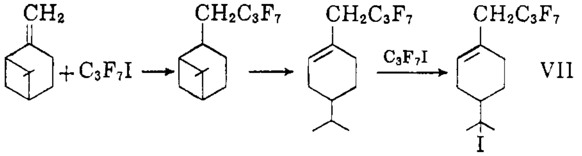
IVa,b

reduction by zinc of a 20/80 mixture of IVa and IVb gave a *single* compound (g.l.c.) in 80% yield which spectra and elemental analysis showed to be 5-perfluoropropylnortricyclene (V). The infrared spectrum of V has the cited[11,12] CH band at 3.22 μ and a new C—H deformation band at 6.79 μ not in IVa or IVb. The n.m.r. spectrum of V has no peak at 6.14 τ, since the CHI has been converted to CH_2. The two adducts differ in the relative positions of the iodine atom and the perfluoropropyl group, therefore, since in V positions 3, 5, and 7 become equivalent, because of symmetry of structure.[11]

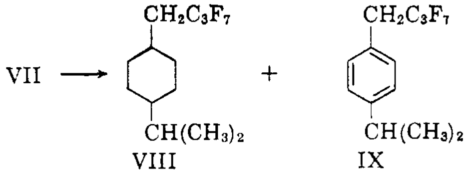
These results show that the intermediate perfluoropropylnorbornenyl radical IIIa rearranges to the nortricyclyl radical IIIb at a rate (k_2) considerably greater than the transfer step (k_3) on the iodoperfluoroalkane. This is in contrast to analogous reaction of thiols with norbornadiene,[14] which gave a mixture of substituted nortricyclenes having structures similar to IVa and IVb and also a substituted norbornene. The formation of a more stable radical which undergoes slow chain transfer and elimination of crowding of the *two* polar bulky groups on adjacent carbons could account for this behavior in the case of reaction with 1-iodoperfluoropropane. In the displacement step of the nortricyclyl radical IIIb on iodoperfluoroalkane, crowding by the attached perfluoropropyl group *across* the ring is not apparent, since about equal amounts of *syn* and *anti* isomers were formed. This is indirect evidence for the *trans* addition to norbornene where such crowding is probable, and would be consistent with the anticipated *exo* addition of the perfluoropropyl radical.

No report of the reaction of bromotrichloromethane and norbornadiene has been noted. We found that three principal products were formed. They were isomeric and not readily separated by fractional distillation. From the infrared spectra of several fractions taken, the components appear to have structures analogous to IVa and b. There were no bands (found in norbornene, for example) of the olefinic group at 3.16, 6.08, or 6.35 μ, but the C—H band at 3.22 μ was very strong. These data exclude a substituted norbornene, but further effort to separate the isomers or to define their structures more closely was not made.

β-Pinene (an exocyclic olefin with fused 4 and 6 rings) and 1-iodoperfluoropropane gave a rearranged adduct also, but in this case isomerization was the result of ring opening as was previously reported[15] for the radical addition of carbon tetrachloride or related compounds.[1] 7-Perfluoropropyl 8-iodo-Δ^1-*p*-menthene (VII) was obtained in 90% yield (74% conversion) in five hours heating at 50–60°, using 2% of azo initiator.



When the heat and light sensitive crystalline adduct VII was exposed to air, it immediately darkened; but when it was heated in mixture with β-pinene above 100°, hydrogen iodide split out and disproportionation of the resulting diene occurred. The products isolated were the cyclohexane (VIII) and the aromatic compound (IX). Such rearrangements are commonly noted for terpenes such as dipentene. The hydrogen iodide which was formed was removed from the reaction mixture by addition to β-pinene *inter alia*, giving bornyl iodide. The mixture of VIII and IX was separated by g.l.c. on a preparative scale and their structures were ascertained by analysis, infrared and n.m.r. spectra; details are in the Experimental. Further study of these novel perfluoroalkyl-substituted cyclic compounds is being carried on.



Experimental

Azonitrile-Induced Reaction of Iodoperfluoropropane and Norbornene.—Norbornene (9.4 g.; 0.10 mole), 1-iodoperfluoropropane (29.6 g.; 0.10 mole), and azobis(α,γ-dimethyl)valeronitrile[(AVN) (the half-life of AVN is 1 hr. at 68°, as compared to a $t^1/_2$ of 1 hr. at 84° for azobisisobutyronitrile) 0.3 g.; 1.22 mmole] were heated under nitrogen at 60 to 80° for 5 hr. *endo*-2-Iodo-*exo*-3-perfluoropropylnorbornane (Ia) distilled in a 3-ft. platinum spinning band column (column A) at b.p. 105° (20 mm.); $n^{25}D$ 1.4401 to 1.4406; 35.2 g. (4 cuts). The trap contained 4.3 g. of a mixture of

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(14) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

(15) D. M. Oldroyd, G. S. Fisher, and L. A. Goldblatt, *ibid.*, **72**, 2407 (1950).

liquid and solid (n^{25}_{D} 1.4437). The residue was 0.1 g. The conversion to Ia was 90% and the yield quantitative. G.l.c. analysis showed 98.8% of the total area was under one peak.

Anal. Calcd. for $C_{10}H_{10}F_7I$: C, 30.8; H, 2.58; F, 34.1; I, 32.6. Found: C, 30.8; H, 2.3; F, 34.0; I, 32.4.

An n.m.r. spectrum (Fig. 1) taken at 60 Mc. with tetramethylsilane as internal reference gave proton resonances at 5.72 τ, a triplet (J = 4 to 6 c.p.s.; a single proton on C-2); at 7.30, 7.53, 7.72, 7.87, and 8.00 τ (3 protons on C-1 and C-4, and on C-3) and at 8.23, 8.42, 8.61, and 8.74 τ (6 protons of C-5, C-6, and C-7, not in order). The areas under the peaks corresponded to the number of hydrogens on the respective carbons. The resonances at 7.30 to 8.00 τ, however, were probably from a splitting pattern lying partly under the 7.53 and 8.23 τ peaks as obtained also with the reduced product (see below). The dipole moment measured in benzene solution by Mr. C. G. Wortz was 3.09 D.

2-Iodoperfluoropropane and norbornene gave a 92% yield of an adduct analogous to Ia under these conditions; b.p. 113° (36 mm.); n^{25}_{D} 1.4472. The proton n.m.r. spectrum was almost identical to that of Ia. The analysis of this adduct was identical to Ia.

Elimination of hydrogen iodide by bases which occurred very readily in the case of open-chain analogs did not occur with Ia. Refluxing for 8 hr. an $N/3$ alcoholic potassium hydroxide solution with 7.913 g. of Ia gave only 7.5% loss of alkali; 76.6% of Ia was recovered unchanged upon distillation. Heating 4.5 g. of Ia for 1 hr. at 100° with 20 ml. of 10% aqueous sodium hydroxide solution and distilling for 2 hr. at 100–143° gave 96% of unchanged Ia. Ia (6.5 g., 0.01 mole) and tri-*n*-butylamine (6.7 g., 0.036 mole) was heated in an oil bath at 200–215° for 1 hr. in column A. No olefin distilled out and, under reduced pressure, the unchanged materials were recovered by distillation as a mixture. After washing with dilute acid, Ia was obtained (95% recovery) having unchanged boiling point, refractive index, and retention time by g.l.c. analysis.

Coupling of Ia to 2,2'-Bis(3-perfluoropropyl)norbornyl.—A solution of 20.0 g. (0.05 mole) of Ia in 20 ml. of anhydrous ether was added during 0.5 hr. to 1.5 g. (0.062 g.-atom) of magnesium turnings and an iodine crystal in 50 ml. of refluxing ether, stirred by a magnetic stirrer. One hour later, ethyl bromide (0.5 ml.) was added, refluxing increased and a solid began to separate. After 2 hr., the suspension was poured onto crushed solid carbon dioxide and 18 hr. later, hydrolyzed with dilute hydrochloric acid, and extracted with ether. Acidification of a 5% aqueous sodium carbonate extract gave less than 2.0 g. of brown, acidic oil. The neutral ether solution was fractionated in a 16-in. platinum spinning band column (column B); b.p. 96° (0.7 mm.); n^{25}_{D} 1.4021 to 1.4026 (three fractions); 10.3 g. (76%); a low-melting solid and oil. The product was neutral, inert to alcoholic silver nitrate and to 1% permanganate solution. Part of the solid was filtered; melting range 93–99°. G.l.c. showed two isomers.

Anal. Calcd. for $C_{20}H_{20}F_{14}$: C, 45.6; H, 3.02; mol. wt. 526.4. Found: C, 46.4; H, 3.8; mol. wt. 515, 510 (freezing point in benzene).

Zinc Reduction of Ia to *exo*-2-Perfluoropropylnorbornane (Ib).—A slurry of 5.0 g. (0.08 g. atom) of zinc (20–40 mesh), 25 ml. of absolute alcohol, and 10 g. of Ia was heated on the steam table and 1 ml. of 55% aqueous hydriodic acid added, whereupon the slurry began to reflux and in 3 min. became cloudy. Two additions of 1 ml. of acid at 1-min. intervals gave clear liquid and vigorous reaction; after 1 hr., the process was repeated and heating continued for 1 hr. The product was isolated by pouring the liquid into 100 ml. of water and extracting with ether, which was dried over potassium carbonate and magnesium sulfate. Fractionation in column gave a forerun, b.p. 104–134°; n^{25}_{D} 1.3631; 0.74 g. (containing ether); and Ib, b.p. 146–148°; n^{25}_{D} 1.3631; 0.74 g. (containing ether); and Ib, b.p. 146–148°; n^{25}_{D} 1.3688; 5.03 g. (75%). G.l.c. analysis showed 99% of the total area was from Ib, and 1.0% was ether.

Anal. Calcd. for $C_{10}H_{11}F_7$: C, 45.46; H, 4.2; F, 50.34. Found: C, 45.9; H, 4.4; F, 50.1.

An n.m.r. spectrum (Fig. 1) at 60 Mc. gave single proton peaks at 7.38 and 7.67 τ (probably protons on C-1 and C-4, since the bridgehead protons are at 7.81 τ in norbornane); at 8.00 τ; and at 8.36, 8.50, 8.72, and 8.87 τ (protons attached to C-3, C-5, C-6, and C-7, not in order). The areas under the peaks were correct for the total number of hydrogens. The proton resonance at 5.72 τ in Ia (hydrogen on C-2) was not present.

Aldrin and 1-Iodoperfluoropropane.—Aldrin (1,2,3,4,10,-10-hexachlorohexahydro-*endo*,*exo*-dimethanonaphthalene) was recrystallized from methanol; m.p. 102°; reported[6] m.p. 103°. A solution of 35.3 g. (0.10 mole) of aldrin and 35.0 g. (0.11 mole) of 1-iodoperfluoropropane in 25 ml. of ethyl acetate was heated to reflux (67°) under a Dry Ice reflux condenser and 0.2 g. (1.2 mmoles) of azobisisobutyronitrile (ABN) was added. The mixture was heated for 7 hr. at 70–77°; the solvent and unchanged 1-iodoperfluoropropane were evaporated at 80°. Two fractions of II (24 g. and 17 g.), m.p. (sinter 100°) 111–120°, were collected at 25° and were recrystallized from methanol. The mother liquor yielded 7.8 g. of solid, m.p. 61–69°, and 4.1 g. of residual oil (95% recovery of unchanged aldrin and II). The solid (m.p. 61–69°) was a mixture of unchanged aldrin and II which crystallized from methanol as long needles (aldrin) and rosettes (II). Only small amounts of isomeric material could have been present in the residual oil. Twice recrystallized II (*endo*-6-iodo-6,7-dihydro-*exo*-7-perfluoropropylaldrin; 31.0 g.), m.p. 122–124°, was analyzed. The n.m.r. spectrum of II (Fig. 1) shows the proton on C-6 shifted to 5.72 τ and split by protons on C-5 and C-7 (J = 6 and 4 c.p.s.).

Anal. Calcd. for $C_{15}H_8Cl_6F_7I$: C, 27.2; H, 1.2; Cl, 32.3; I, 19.2. Found: C, 27.2; H, 1.1; Cl, 33.9; I, 19.6.

Norbornadiene and 1-Iodoperfluoropropane.—Norbornadiene (18.4 g.; 0.2 mole), 1-iodoperfluoropropane (30.0 g., 0.1 mole), and AVN (0.3 g.; 1.2 mmoles) gave in 5 hr. at 50–60° liquid product (IVa, b), b.p. 79–80° (5.0 mm.) to 43° (0.4 mm.); n^{25}_{D} 1.4474 to 1.4491 (column A); 37.0 g. (95% conversion on 1-iodoperfluoropropane). A residue of 1.9 g. remained. The trap contained 7.8 g. (85% recovery) of norbornadiene. The product mixture contained three components by g.l.c. analysis; 1.0% unknown; 52% of IVa, and 46% of IVb.

These reactants with ABN (0.5 g., 0.003 mole) in ethyl acetate (180 g.) at 70–80° for 7 hr. gave 37.5 g. (99% conversion) of residual oil after solvent was removed by distillation. G.l.c. analysis showed 4% of norbornadiene, 0.7% of an unknown, 50% of IVa, and 45% of IVb. The product was saturated to permanganate in acetone solution, but gave immediately a precipitate with 5% solution of silver nitrate in alcohol. An infrared spectrum had a CH stretching band at 3.21 μ, a shoulder at 3.32 μ, two CH bands at 3.35 and 3.42 μ, no vinyl absorption bands, but bands at 6.78, 10.08, 10.30, 10.50, 11.0, and 12.30 μ. The band at 6.78 μ is also present in nortricyclene.[11,12] Reactions using reactant ratios of 1:1.5 or 1:1 under these conditions gave the same yield of IVa and IVb according to g.l.c. analysis.

Anal. Calcd. for $C_{10}H_8F_7I$: C, 30.95; H, 2.07; F, 34.3; I, 32.8. Found: C, 31.0; H, 2.1; F, 33.8; I, 31.7.

A column of about 20 theoretical plates efficiency gave incomplete separation of IVa and IVb, but preparative g.l.c.[16] using a 6-ft. by 3/4-in. diameter column containing 25% silicone oil (Dow Corning 703) on firebrick operated at 150° with 875 ml./min. helium carrier gas gave nearly pure isomers. Fraction 1 (n^{25}_{D} 1.4459) contained 93% of IVa and 7% of IVb; fraction 2 (n^{25}_{D} 1.4488) contained 17% of IVa and 81% of IVb (and 2% of an unknown). Fractions 1 and 2 gave very similar infrared spectra, but bands at 11.05 and 12.70 μ in (1) were very weak in (2), and bands at 10.32,

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[16] Assistance by Mrs. Adah Richmond and John Robson is gratefully acknowledged.

10.70, and 10.90 μ in (2) were very weak in (1). The n.m.r. spectra of (1) and (2) showed, in comparison to norbornene, that no olefinic proton resonances were present (toluene and water reference liquids). Both isomers had proton resonance of CHI at 6.15 τ (at 60 Mc.). Both fractions had the same elemental analysis as the original mixture. The n.m.r. spectrum of IVa gave a single proton peak at 6.15 τ (C-5) and a triplet from $—CHCF_2CF_2CF_3$ centered at 6.93 τ ($\delta =$ 17 c.p.s.), at 7.60 τ (2 protons), and at 8.18, 8.35, 8.42, 8.47, 8.65, 8.70 τ (6 protons). The last two appeared to be a doublet (7 c.p.s. spacing). The spectrum of IVb had, besides the 6.15 τ peak, a 2 proton peak at 7.68 τ, complex multiplets at 8.00, 8.10, 8.23, 8.33, 8.42, 8.58, and 8.69 τ (area corresponding to that for 5 protons).

Zinc Reduction of IVa and IVb to V.—A mixture containing 61% of IVa and 38% of IVb (10.0 g., 0.025 mole), zinc dust (50 g., 0.77 g.-atom), magnesium powder (4 g., 0.16 g.-atom), and 20 ml. of 16% hydrochloric acid was heated at 100° under reflux for 3 hr. Extraction and distillation (column B) gave V; b.p. 151°; n^{25}D 1.3722; 5.35 g.; (80% of theory). G.l.c. analysis (same conditions as for IV above) showed it contained 3% of an unknown component and 97% of 5-(heptafluoropropyl)nortricyclene. An infrared spectrum showed the CH stretching band at 3.22 μ, CH bands at 3.37 and 3.40 μ as in Ia and IV; 2 CH deformation bands at 6.75 μ (present in Ia also) and at 6.83 μ (present in IVa and b), no bands at 10.32, 10.70, or 11.05 μ, but the strong 12.40-μ band found in nortricyclene. The n.m.r. spectrum (60 Mc.) showed no proton resonance at (or near) 6.15 τ as in IVa, IVb or I, but peaks at 7.65 and 7.77 τ (two protons), 8.22 and 8.27 τ (1 proton, doublet), and at 8.64, 8.73, and 8.88 τ (6 protons).

Anal. Calcd. for $C_{10}H_9F_7$: C, 45.8; H, 3.46. Found: C, 46.0; H, 3.8.

Addition of Bromotrichloromethane to Norbornadiene.—A mixture of 9.0 g. (0.1 mole) of norbornadiene, 19.8 g. (0.1 mole) of bromotrichloromethane (b.p. 104°, n^{25}D 1.5038, redistilled), and 0.1 g. (0.6 mmole) of ABN was stirred under nitrogen and heated to 80° in an oil bath. The temperature rose to 98° and was cooled to 85°; after 15 min., the temperature rose from 93 to 150° in 1 min. where it dropped to 71° on cooling. Further heating at 80–84° for 1.5 hr. gave no further exothermic reaction.

A sample (4.4 g.) removed for g.l.c. analysis showed bromotrichloromethane (20% of total area) and four new compounds: 2, 9, 24, and 45% relative areas.

Fractionation in column A of 24.1 g. gave bromotrichloromethane and norbornadiene (3.1 g.) and product fractions: (1), b.p. 132° (10 mm.); n^{25}D 1.5568; 2.2 g.; (2), b.p. 133–134° (9.0 mm.); n^{25}D 1.5606; 8.4 g.; and (3), b.p. 120–116° (2.4 mm.); n^{25}D 1.5619; 5.9 g. (a total of 67%). A tarry residue (2.4 g.) remained. Infrared spectra of the several fractions were very similar, having CH stretching bands at 3.22 (cyclopropyl CH), 3.32 (shoulder), 3.36, and 3.44 μ. There were *no* CH bands of the —CH=C vinyl hydrogen at 3.15 μ nor C=C stretching bands at 6.08, 6.18, or 6.35 μ as in norbornene. The CH deformation band at 6.78 μ in the isomeric adducts IVa, IVb, and bands at 10.20, 10.70, 10.90, 11.05, 11.45, 12.10, and 12.35 μ were present.

Anal. Calcd. for $C_8H_9Cl_3Br$: C, 33.1; H, 2.8; Cl, 36.6; Br, 27.5. Found (cuts 2 and 3): C, 33.5; H, 2.8; Cl, 35.7; Br, 27.7.

Reaction of 1-Iodoperfluoropropane and β-Pinene; 7-Perfluoropropyl-8-iodo-Δ¹-*p*-menthene (VII).—A mixture of 27.2 g. (0.20 mole) of β-pinene, 29.6 g. (0.10 mole) of 1-iodoperfluoropropane, and 0.5 g. (0.002 mole) of AVN was heated under nitrogen in an oil bath at 50°. After 0.5 hr. at 53°, exothermic heat carried the liquid temperature to 59°; when the temperature dropped to 55° (15 min.), external heating was resumed for 5 hr. The reaction liquid remained colorless throughout. Unchanged materials were pumped off at 1.0 mm. pressure (bath up to 70°) into a trap, leaving 31.8 g. (74% conversion; 90% yield) of light yellow liquid VII which solidified. It was possible to recrystallize VII from cold methylene chloride in the dark, but the white crystals quickly turned brown on exposure to light and air. The three-times crystallized VII, m.p. 35–36.5°, was analyzed the same day.

Anal. Calcd. for $C_{13}H_{16}F_7I$: C, 36.2; H, 3.7; F, 30.8; I, 29.4. Found: C, 36.1; H, 3.9; F, 30.2; I, 28.3.

An infrared spectrum showed no CH of the vinyl group at 3.20 μ, but CH stretching bands at 3.37, 3.42, and 3.50 μ, $CH_3—C$ at 7.25 μ, CF bands at 8.15, 8.50, and 8.95 μ (C_3F_7 group) and at 10.10, 10.50, 10.85, 13.05, 13.55, and 13.80 μ. The infrared spectrum of the crude reaction product was identical to the purified material. An n.m.r. spectrum (56.4-Mc. field spectrometer) showed an olefinic proton resonance at −53 c.p.s. relative to water, and five other proton resonance peaks. The olefinic proton resonance was also present at −67 c.p.s. in the spectrum of 7-trichloromethyl-8-chloro-Δ¹-*p*-menthene[15] of analogous structure.

Distillation of the trap liquid (25.2 g.) gave 17% of 1-iodoperfluoropropane charged and 66% of the pinene as a mixture of α- (about 10%) and β-pinene. There was probably that amount of α-pinene in the starting material.

Pyrolysis of VII to VIII and IX in the Presence of β-Pinene.—A mixture of 13.6 g. (0.10 mole) of β-pinene, 29.6 g. (0.10 mole) of 1-iodoperfluoropropane and 0.20 g. (0.0012 mole) of ABN was heated with the oil bath at 75° for 7.5 hr., and distilled in column A. There was no reflux up to 85° pot temperature (20 mm. pressure) but at 108° decomposition set in and a yellow distillate began to reflux. Heat was removed and the pressure reduced further. A series of fractions containing VIII and IX distilled: 1, 2, and 3, b.p. 40–46° (1.0 mm.); n^{25}D 1.412 to 1.408; 9.7 g.; and VIII and IX mixed with bornyl iodide (XI),[17] b.p. 45° (0.5 mm.); n^{25}D 1.5111; 9.0 g. A residual oil of 5.6 g. remained; n^{25}D 1.4621.

A shaker tube was charged with 40.8 g. (0.30 mole) of β-pinene, 100 g. (0.33 mole) of 1-iodoperfluoropropane, and 1.0 g. (0.0041 mole) of benzoyl peroxide and heated at 100° for 8 hr. The product mixture (134 g.) was distilled in column A. The products recovered were: 1-iodoperfluoropropane (75%); β-pinene (50%); VIII and IX (17%); and XI, 17.9 g. XI was refractionated, b.p. 53° (0.5 mm.; n^{25}D 1.5401 [lit.,[17] b.p. 108–109° (10 mm.)].

The mixture of VIII and IX was treated with 5% aqueous sodium carbonate solution for 0.5 hr. and with saturated sodium bisulfite solution for 2 hr. to remove iodine. After extracting into ether and drying, the mixture had b.p. 130–131° (80 mm.); n^{25}D 1.4011 to 1.4033. G.l.c. analysis showed that two components, VIII (36%) and IX (62%), were present. There were 0.5% or less of three other components. The two main components were concentrated into two fractions by preparative g.l.c. Fraction 1 contained 77% of VIII and 16% of IX (and 5% of an unknown material). Fraction 2 contained 5% of VIII and 94% of IX. It was distilled in a micro column, b.p. 118° (70 mm.); n^{25}D 1.4047. VIII (1) showed no olefinic proton resonance in an n.m.r. spectrum but did show the characteristic resonance of the isopropyl group hydrogens. IX (2) at 60 Mc. showed a single aromatic proton resonance peak of a symmetrical *para* substituted benzene at −427 c.p.s. relative to tetramethylsilane, the isopropyl group peaks (doublet at −66 and −73 c.p.s.) and a triplet at −190 c.p.s. ($\delta = 20$ c.p.s.) which are the resonances of the CH_2 group split by the adjacent CF_2^-. The infrared spectrum of IX showed overtone bands in the 5–6-μ region typical of *p*-substitution. These data, together with the elementary analysis, are consistent with the structures assigned.

Anal. Calcd. for $C_{13}H_{19}F_7$: C, 50.6; H, 6.24; F, 43.2. Found (1): C, 51.7; H, 5.2; F, 39.5.

Anal. Calcd. for $C_{13}H_{13}F_7$: C, 51.6; H, 4.34; F, 44.0. Found (2): C, 51.4; H, 4.6; F, 44.0.

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(17) Beilstein, **5**, p. 100; G. Wagner and W. Brickner, *Ber.*, **32**, 2302 (1899).