Polyfluorobicyclo[2.2.1]heptanes. Part 11.† Bridgehead Radicals: their Generation, Reactions, and CIDNP Effects

By **Paul L. Coe,* John H. Sleigh,** and **John Colin Tatlow,** Chemistry Department, The University of Birmingham, P.O. Box 363, Birmingham B15 2TT

Decomposition of bis-(4*H*-decafluorobicyclo[2.2.1]heptane-1-carbonyl) peroxide (I) alone affords 4*H*-decafluorobicyclo[2.2.1]heptan-1-yl 4*H*-decafluorobicyclo[2.2.1]heptane-1-carboxylate (III) and 4*H*,4*H*'-eicosafluoro-1,1'-bis(bicyclo[2.2.1]heptyl) (IV). In hexachloroacetone the peroxide (I) yields (IV) and 4*H*-1-chlorodecafluorobicyclo[2.2.1]heptane (V). Decomposition of (I) at 185° in hexachloroacetone in an n.m.r. probe showed large CIDNP effects. The decarbonylation of 4*H*-decafluorobicyclo[2.2.1]heptane-1-carbaldehyde (VI) by di-t-butyl peroxide yielded 1*H*,4*H*-decafluorobicyclo[2.2.1]heptane (VII). Electrolysis of 4*H*-decafluorobicyclo[2.2.1]heptane-1-carboxylic acid in the presence of methyl propenoate gave (*E*)-1-(4*H*-decafluorobicyclo[2.2.1]heptan-1-yl)-2-methoxycarbonylethylene (VIII), 1-(4*H*-decafluorobicyclo[2.2.1]heptan-1-yl)-2-methoxycarbonylethane (IX), and (±)- and *meso*-1,4-bis-(4*H*-decafluorobicyclo[2.2.1]heptan-1-yl)-2,3-bismethoxycarbonylbutanes (X) and (XI).

In hydrocarbon chemistry bridgehead carbonium ions,[1] carbanions,[1] and radicals [1,2] have been described, but in the fluorocarbon field the only reactive intermediates so far postulated have been the carbanion and the derived 'anti-Bredt' bridgehead olefin.[3]

We now report results which demonstrate the formation of polyfluoronorbornyl radicals by thermal decomposition of peroxides, by decarbonylation of an aldehyde, and by electrolysis of a carboxylic acid. The formation of radicals is indicated by some of their reactions and by the observation of a CIDNP effect.

The decomposition of apocamphoyl peroxide in CCl_4 reported by Kharasch [4] to yield biapocamphoyl and apocamphoyl chloride, the decarbonylation of an aldehyde described by Doering,[5] and our own previously described [6] method for the generation of fluoroalkyl radicals by the electrolysis of the corresponding carboxylic acids all suggested routes to the bridgehead radicals in our well characterised norbornyl series.

The starting materials for these routes, the bridgehead carboxylic acids, were readily available by carbonation of the corresponding lithio derivatives [3] and the aldehydes and peroxides were made from them by standard routes.

Thus, reaction of 4*H*-decafluorobicyclo[2.2.1]heptane-1-carbonyl chloride with lithium aluminium tri-t-butoxyhydride in diglyme afforded the corresponding aldehyde (VI) together with some 4*H*-(1-hydroxymethyl)-decafluorobicyclo[2.2.1]heptane. The aldehyde which was characterised as its 2,4-dinitrophenylhydrazone, formed a monohydrate on exposure to moist air, characteristic of many polyfluorocarbon aldehydes and ketones.

The carbonyl chloride above, in acetone, was treated with aqueous sodium peroxide at 0° to give bis-(4*H*-decafluorobicyclo[2.2.1]heptane-1-carbonyl) peroxide (I). In the same way, using undecafluorobicyclo-[2.2.1]heptane-1-carbonyl chloride, bis(undecafluorobicyclo[2.2.1]heptane-1-carbonyl) peroxide (II) was prepared.

Decarbonylation of the aldehyde (VI) occurred on treatment with di-t-butyl peroxide at 145—150°; two products were obtained as shown by g.l.c. The first was shown to be t-butyl alcohol and the second 1*H*,4*H*-decafluorobicyclo[2.2.1]heptane (VII). Although the latter could have arisen from hydrogen abstraction from the solvent by the desired radical, we could find no other evidence of radical species from this experiment. We therefore turned our attention to the decomposition of the peroxides (I) and (II). Although our attempted m.p. determination of the peroxide (I) showed that it decomposed at *ca.* 175°, we tried thermolysis of a thin film of the peroxide on the walls of a sealed Carius tube at 200° for 3 h. The two products obtained were identified as 4*H*-decafluorobicyclo[2.2.1]heptan-1-yl 4*H*-decafluorobicyclo[2.2.1]heptane-1-carboxylate (III) and the dimer 4*H*,4*H*'-eicosafluoro-1,1'-bis(bicyclo[2.2.1]heptyl) (IV). The ester gave an accurate mass measurement, and strong absorptions at 3 050 (=CH) and 1 822 cm^{-1} (=CO) in its i.r. spectrum. The dimer showed a correct molecular ion peak in its mass spectrum, had a correct elemental analysis, and consistent ^1H and ^{19}F n.m.r. spectra. The i.r. spectrum showed the absence of any carbonyl group. Whilst the formation of these products is good evidence for the involvement of radicals (*cf.* the decomposition of acyl peroxides [7]) their formation could be accounted for in different ways.

There is much evidence that radicals formed in perchlorocarbon solvents [4] readily abstract chlorine to give, amongst other products of decomposition, the corresponding halide. We thus studied the decomposition of the peroxide (I) in hexachloroacetone. Our choice of solvent was limited by the high decomposition temperature of the peroxide. Heating (I) in hexachloroacetone in a sealed Carius tube at 180° for 2 h afforded a mixture of three products, one in very minor amount which we believe to be the ester (III). The major component was shown by the usual spectroscopic and analytical techniques to be 4*H*-1-chlorodecafluorobicyclo[2.2.1]heptane (V), the other product was shown to be the dimer (IV). This result we take to be good evidence for the presence of the bridgehead radical. Probably the best physical method now available to indicate the presence of radicals in a reaction is the CIDNP effect [8] and having found a

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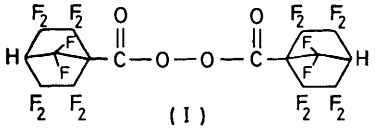
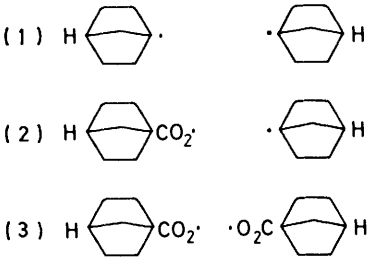
solvent system in which we could generate radicals we subjected our peroxides to CIDNP measurements. Examples of the spectra obtained from the decomposition of (I) have been treated as a Supplementary publication (No. SUP 22604, 3 pp.).* It is clear from the spectra



(I)

that significant emission–absorption effects occur, *i.e.* there is a CIDNP effect in the decomposition and that radicals are involved. Similar spectra were obtained for peroxide (II).

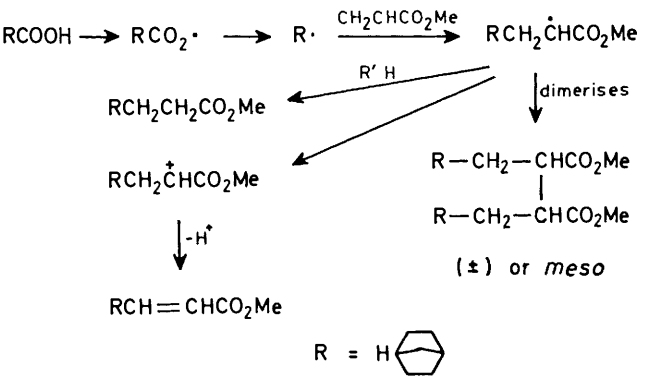
Although we at present have no quantitative results from these spectra (additional e.s.r. data are being sought) a brief qualitative discussion is of value. To obtain a CIDNP effect radical pairs must be involved and the possible combinations we can obtain in our decomposition are (1)—(3). A predominant feature of our spectra is



the occurrence of so-called multiplet effects. In particular the fluorine atoms at C-7 in the bridgehead chloro-compounds show quite distinctly an *E/A* multiplet. Since it has been reported [9] that in high magnetic fields only equivalent radicals give multiplet effects we must assume only (1) and (3) above are possible combinations. Further, since it has been reported [10] that acyloxyl radicals, particularly when α-branched, rapidly decarboxylate and that the ester (III) is only a minor product in the decomposition, we may reasonably assume that the multiplet effects in the spectra arise from the bridgehead radicals (1) above which either dimerise or more likely abstract chlorine from the solvent to give the observed product. Interestingly there appears to be the large *E/A* effect on 4-H and 4-F in the decomposition of (I) and (II). It is tempting to attribute this to a through-space effect in line with the suggestion of a similar phenomenon being concerned with the marked acidity changes found in various 4-substituted 1*H*-decafluorobicyclo[2.2.1]heptanes.[11] However, we have no quantitative evidence to support such a view which at this time can only remain a possibility.

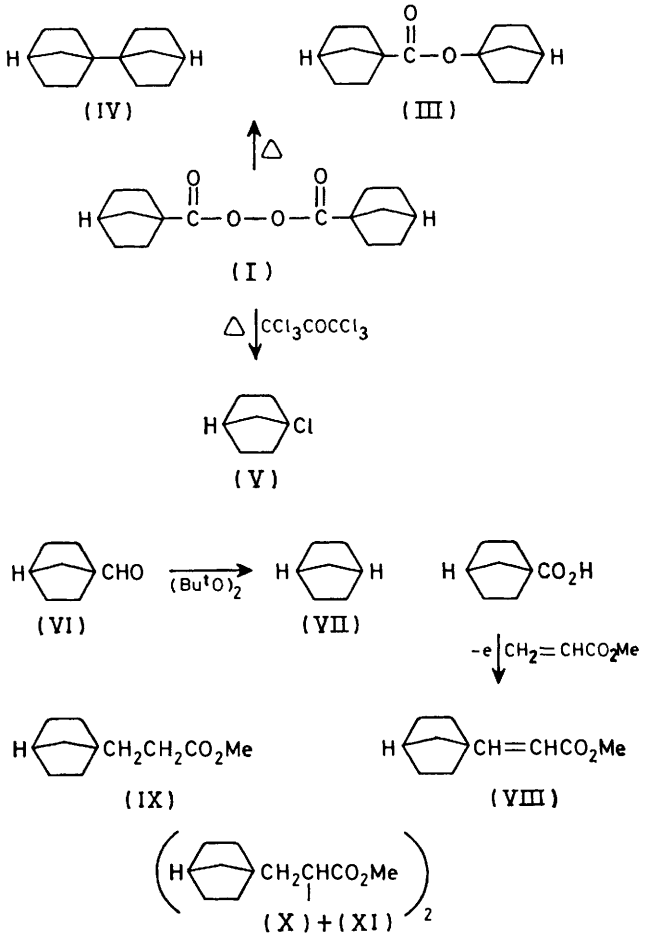
Having reasonably demonstrated the existence of bridgehead radicals in this area we have now investigated the use of the electrochemical method of generation of radicals we have recently used in acyclic systems.[6] Electrolysis of 4*H*-decafluorobicyclo[2.2.1]heptane-1-carboxylic acid was carried out in the presence of methyl propenoate in acetonitrile–water until the current fell to a low value (from 0.9 to 0.2 A).

The first product obtained was shown by elemental analysis and mass spectrometry to be $C_{11}H_6F_{10}O_2$, *i.e.* the incorporation of one polyfluorobicyclo[2.2.1]heptane



SCHEME 1

residue. ^{1}H N.m.r. showed the presence of an AB quartet at τ 3.37 with J_{AB} 16.5 Hz; these data are consistent with a *trans*-CH=CH system, and a sharp singlet attributable to a methoxy-group at τ 6.18. Thus,



SCHEME 2 All unmarked bonds joined to fluorine

* See Notice to Authors No. 7, in *J.C.S. Perkin I*, 1978, Index issue, for details of the Supplementary Publications Scheme.

we assign the structure as (*E*)-1-(4*H*-decafluorobicyclo-[2.2.1]heptan-1-yl)-2-methoxycarbonylethylene (VIII). The second product isolated was indicated again to be an ester by i.r. spectroscopy, but the ^{1}H n.m.r. spectrum of this compound showed that the double bond signal had disappeared and had been replaced by a complex signal due to two CH_2 groups; the methoxy-signal was present at τ 6.28. Elemental analysis and mass spectrometry confirmed the structure as 1-(4*H*-decafluorobicyclo-[2.2.1]heptan-1-yl)-2-methoxycarbonylethane (IX). The third product, a high melting solid, was shown by elemental analysis and mass spectrometry to be $C_{22}H_4F_{20}O_4$, corresponding to a dimer. ^{1}H N.m.r. showed signals at τ 6.27 (OCH_3) and 6.3—8.8 ($\geqslant$CH and CH_2) in the integral ratio 3 : 4. These data suggest the compound to be 1,4-bis-(4*H*-decafluorobicyclo[2.2.1]heptan-1-yl)-2,3-bismethoxycarbonylbutane (X). A fourth product in small amounts was obtained which was shown to be a stereoisomer of (X) but we cannot at this point distinguish between $\pm$ and *meso*-structures.

We suggest that these products arise from the generation of bridgehead radicals which then added to the methyl propenoate as a first step and then follow a reaction pathway as outlined in Scheme 1. This is in keeping with the proposed reaction pathway for the addition of trifluoromethyl radicals, generated electrochemically, to olefins.[6]

Thus by the routes outlined above we demonstrated the existence of fluorocarbon bridgehead radicals. The reactions we have described above are outlined in Scheme 2.

EXPERIMENTAL

Preparation of 4H-*Decafluorobicyclo*[2.2.1]*heptane*-1-*carbonyl Chloride*.—4*H*-Decafluorobicyclo[2.2.1]heptane-1-carboxylic acid (16.0 g) and phosphorus pentachloride (10.4 g) were stirred together at 18° until the initial reaction had subsided and the mixture was then heated at 100° for 1 h. Phosphorus oxychloride formed in the reaction was distilled off through a Vigreux column (8.5 cm) and the residue sublimed at 14 mmHg to give 4*H*-decafluorobicyclo-[2.2.1]heptane-1-carbonyl chloride [12] (12.2 g).

Preparation of 4H-*Decafluorobicyclo*[2.2.1]*heptane*-1-*carbaldehyde*.— 4*H*-Decafluorobicyclo[2.2.1]heptane-1-carbonyl chloride (3.38g, 10 mmol) in dry diglyme (5 cm^3) was stirred at −78° under nitrogen and a slurry of lithium aluminium tri-t-butoxyhydride (2.54 g, 10 mmol) in diglyme (15 cm^3) was added over 1 h. The mixture was allowed to warm to room temperature and then poured onto crushed ice and acidified with 1M-H_2SO_4 (30 cm^3). The aqueous layer was extracted with ether (3 × 30 cm^3), the combined extracts were dried ($MgSO_4$), and the ether distilled to low bulk (10.75 g). A portion of the residue (6.4 g) was distilled through a Vigreux column (8.6 cm) *in vacuo* at 18 mmHg to give (i) a mixture (3.9 g), b.p. 21—64°, shown to be ether–t-butyl alcohol–diglyme, starting material, and a new product. G.l.c. separation of the mixture afforded 4H-*decafluorobicyclo*[2.2.1]*heptane*-1-*carbaldehyde* (0.4 g), m.p. 133—134° (sealed tube) [Found: C, 31.6; H, 1.0; F, 62.7%; *M* (mass spectrometry), 304. $C_8H_2F_{10}O$ requires C, 31.6; H, 0.7; F, 62.5%; *M*, 304]; $\nu_{max.}$ 1 755 cm^{-1} ($\geqslant$C=O); τ ($CDCl_3$) 0.24 (CHO) and 6.4 ($\geqslant$CH) in the integral ratio 1 : 1. (ii) A second mixture, b.p. 64—102°, which deposited crystals of 4*H*-1-(hydroxymethyl) decafluorobicyclo[2.2.1]heptane [13] was obtained.

The aldehyde and 2,4-dinitrophenylhydrazine in the usual way gave 4H-*decafluorobicyclo*[2.2.1]*heptane*-1-*carbaldehyde* 2,4-*dinitrophenylhydrazone*, m.p. 203° (Found: C, 34.4; H, 1.2; F, 39.5; N, 11.5. $C_{14}H_6F_{10}N_4O_4$ requires C, 34.7; H, 1.2; F, 39.3; N, 11.6%). Exposure of the aldehyde to a moist atmosphere for 48 h at room temperature afforded 4H-*decafluorobicyclo*[2.2.1]*heptane*-1-*carbaldehyde monohydrate* (Found: C, 30.1; H, 1.4; F, 59.4. $C_8H_4F_{10}O_2$ requires C, 29.8; H, 1.2; F, 59.0%), *m/e* 304 (*M* − 18); $\nu_{max.}$ 3 420 cm^{-1} (OH); τ [$^2H_6$](DMSO) 3.05 [d, CH(O*H*)$_2$], 4.4 [t, C*H*(OH)$_2$], and 5.05 (s, $\geqslant$CH) in the ratio 2 : 1 : 1. Addition of CF_3COOH resulted in the collapse of the triplet to a singlet at τ 4.4, and the disappearance of the doublet.

Preparation of Bis-(4H-*decafluorobicyclo*[2.2.1]*heptane*-1-*carbonyl*) *Peroxide*.—4*H*-Decafluorobicyclo[2.2.1]heptane-1-carbonyl chloride (1.35 g) in acetone (2.5 cm^3) was added dropwise to a well stirred solution of sodium peroxide (0.15 g, 2 mmol) in water (2.5 cm^3) at 0°. After addition was complete stirring was continued at 0° for a further 30 min. The solution was poured into water, the precipitate filtered off, washed with cold water, and dried *in vacuo*. Recrystallisation from chloroform afforded *bis*-(4H-*decafluorobicyclo*[2.2.1]*heptane*-1-*carbonyl*) *peroxide* (0.36 g), decomposes at *ca.* 175° (Found: C, 30.4; H, 0.6; F, 59.1. $C_{16}H_2F_{20}O_4$ requires C, 30.1; H, 0.3; F, 59.6%); $\nu_{max.}$ 3 030 (C–H), 1 835, and 1 810 cm^{-1} (C=O).

In the same way as above undecafluorobicyclo[2.2.1]-heptane-1-carbonyl chloride (3.56 g) gave *bis*(*undecafluorobicyclo*[2.2.1]*heptane*-1-*carbonyl*) *peroxide* (0.68 g) (Found: C, 28.3; F, 62.2. $C_{16}F_{22}O_4$ requires C, 28.5; F, 62.0%); $\nu_{max.}$ 1 840 and 1 816 cm^{-1} (C=O).

Reduction of Bis-(4H-*decafluorobicyclo*[2.2.1]*heptane*-1-*carbonyl*) *Peroxide*.—The peroxide (1.27 g) in dry benzene (5 cm^3) under nitrogen was treated by dropwise addition of a solution of triphenylphosphine (0.52 g) in dry benzene (15 cm^3) at room temperature. After the mixture had been stirred for 20 min the residual solid was filtered off and recrystallised from light petroleum to yield 4H-*decafluorobicyclo*[2.2.1]*heptane*-1-*carboxylic anhydride* (0.93 g), m.p. 114—116° (Found: C, 30.9; H, 0.5; F, 61.6. $C_{16}H_2F_{20}O_3$ requires C, 30.9; H, 0.3; F, 61.1%); $\nu_{max.}$ 3 030 (C–H), 1 855, and 1 790 cm^{-1} (C=O).

Decarbonylation of 4H-*Decafluorobicyclo*[2.2.1]*heptane*-1-*carbaldehyde*.—The aldehyde (0.25 g) in di-t-butyl peroxide (1.5 cm^3) under oxygen-free nitrogen was heated at 145—150° for 2 h. Separation of the mixture (1.35 g) by preparative g.l.c. gave (i) a mixture of di-t-butyl peroxide and t-butyl alcohol (0.9 g) and (ii) 1*H*,4*H*-decafluorobicyclo-[2.2.1]heptane (0.06 g), identical with an authentic sample.

Thermolysis of Bis-(4H-*decafluorobicylo*[2.2.1]*heptane*-1-*carbonyl*) *Peroxide*.—(a) *Alone*. The peroxide (1.27 g) was heated in a Carius tube at 200° for 3 h. The tube was cooled in liquid air, opened, and allowed to warm to room temperature. The gaseous product (0.14 g) evolved was shown by i.r. spectroscopy to be pure carbon dioxide. The residue was washed with ether (3 cm^3) to leave an intractable brown solid (0.22 g). The ether solution (3.15 g) was separated by preparative g.l.c. to give (i) ether (1.86 g), (ii) 4H-*decafluorobicylo*[2.2.1]*heptan*-1-*yl* 4H-*decafluorobicyclo*[2.2.1]*heptane*-1-*carboxylate* (0.02 g), *m/e* 575 (*M* − F) and 303 ($C_8HF_{10}O^+$) (Found: M^+, 574.973 970. $C_{15}H_2F_{19}O_2$ requires *M*, 574.975 131); $\nu_{max.}$ 3 050 (C–H) and 1 822 cm^{-1}

(C=O), and (iii) 4H,4'H-*eicosafluoro*-1,1'-*bis*(*bicyclo*[2.2.1]-*heptyl*) (0.13 g), m.p. 87—88° (sealed tube) [Found: C, 30.7; H, 0.5; F, 69.5%; *M* (mass spectrometry), 550. $C_{14}H_2F_{20}$ requires C, 30.5; H, 0.4; F, 69.1%; *M*, 550]; $\nu_{max.}$ 3 035 cm^{-1} (C–H); τ 6.42br (s, CH).

(b) *In hexachloroacetone.* The peroxide (1.27 g) and hexachloroacetone (15 cm^3) were heated together in a Carius tube at 180° for 2 h. A portion (10.1 g) of the product mixture was separated by preparative g.l.c. to give (i) 4H-1-*chlorodecafluorobicyclo*[2.2.1]*heptane* (0.24 g), m.p. 108—109° (sealed tube) [Found: C, 27.2; H, 0.4; Cl, 11.2; F, 61.7%; *M*, 310, 312 (ratio 3 : 1). C_7HClF_{10} requires C, 27.1; H, 0.3; Cl, 11.4; F, 61.2%; *M*, 310, 312], (ii) 4*H*, 4'*H*-eicosafluoro-1,1'-bis(bicyclo[2.2.1]heptyl) (0.03 g), identical with an authentic sample, and (iii) hexachloroacetone (7.35 g).

Electrolysis of 4H-*Decafluorobicyclo*[2.2.1]*heptane*-1-*yl carboxylic Acid in the Presence of Methyl Propenoate.*—The acid (9.6 g) in an acetonitrile (50 cm^3)–water (6 cm^3)–sodium hydroxide (0.25 g) mixture containing methyl propenoate (10.3 g) in the anode compartment was electrolysed as previously described [6] at an initial current of 0.9 A which fell to 0.2 A after 1.75 h. The dark yellow cell contents were poured into water (100 cm^3), the lower layer separated, and the aqueous layer extracted with ether (3 × 50 cm^3). The combined organic extracts were washed with sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and the ether distilled off to give a liquid residue (22.5 g) which was distilled through a Vigreux column (8.5 cm) to give (i) a mixture of ether, acetonitrile, and methyl propenoate (11.84 g), b.p. 34—80°, a mixture (1.15 g), b.p. 52—74° at 0.02 mmHg, which was separated by preparative g.l.c. to give (a) (E)-1-(4H-*decafluorobicyclo*-[2.2.1]*heptan*-1-*yl*)-2-*methoxycarbonylethylene* (0.4 g), m.p. 33—34° (sealed tube) (Found: C, 36.6; H, 1.7; F, 52.9%; *M*, 360. $C_{11}H_6F_{10}O_2$ requires C, 36.7; H, 1.7; F, 52.8%; *M*, 360); $\nu_{max.}$ 1 730 (C=O) and 1 667 cm^{-1} (CH=CH); τ 3.37 (ABq, $\Delta\nu_{AB}$ 16.16, J_{AB} 16.5 Hz, CH=CH), 6.18 (s, OCH_3), and 6.4br (s, CH) in the ratio 2 : 3 : 1. The ^{19}F spectrum was in accord with that expected for the bicycloheptane unit; (b) 1-(4H-*decafluorobicyclo*[2.2.1]*heptan*-1-*yl*)-2-*methoxycarbonylethane* (0.3 g), m.p. 38—39° (sealed tube) (Found: C, 36.5; H, 1.9; F, 52.3. $C_{11}H_8F_{10}O_2$ requires C, 36.5; H, 2.2; F, 52.5%); $\nu_{max.}$ 1 740 cm^{-1} (C=O); τ ($CDCl_3$) 6.28 (s, OCH_3), 6.48 (s, C–H), and 7.1—8.3 in the ratio 3 : 1 : 4; and (iii) a fraction (1.7 g), b.p. 140—145° at 0.05 mmHg, which crystallised on standing. Recrystallisation from carbon tetrachloride afforded 1,4-bis-(4*H*-decafluorobicyclo-[2.2.1]heptan-1-yl)-2,3-bismethoxycarbonylbutane (0.8 g), m.p. 149—152° (Found: C, 36.5; H, 1.8; F, 52.3%; *M*, 722. Calc. for $C_{22}H_{14}F_{20}O_4$: C, 36.6; H, 1.9; F, 52.6%; *M*, 722). Evaporation of the mother-liquors gave an oil which on treatment with methanol gave a different stereoisomer of the above (0.2 g), m.p. 125.5—126° (Found: C, 36.8; H, 1.8; F, 52.9%; *M*, 722).

Recording of CIDNP Effects.—The thermal decomposition of bis-(4H-*decafluorobicyclo*[2.2.1]*heptane*-1-*carbonyl*) *peroxide in hexachloroacetone.* The peroxide (0.042 5 g) and hexachloroacetone were placed in an n.m.r. sample tube. The sample in the probe of a Varian XL 100 spectrometer was heated to 105° and the ^{19}F spectrum recorded. The sample was then heated at 185° (the decomposition temperature of the peroxide) for 15 min and the resultant spectrum recorded. The spectrum was then divided into three regions and each was scanned individually during the decomposition of a sample. In a similar way the ^1H spectrum was recorded.

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