The Reaction of Trifluoromethyl Radicals with Neopentane. An S_H2 Reaction at a Saturated Aliphatic Carbon Atom[1]

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When hexafluoroacetone is photolysed in the presence of neopentane at 300°, isobutane is formed as a primary product, and 1,1,1-trifluoroethane is formed in amounts much greater than would be expected from combination of methyl and trifluoromethyl radicals. These results strongly support the occurrence of a homolytic bimolecular substitution reaction (S_H2) by a trifluoromethyl radical at a methyl carbon atom, with the displacement of a t-butyl radical.

DESPITE the efforts of many investigators, the establishment of an unequivocal example of a homolytic bimolecular substitution (S_H2) by a thermally equilibrated radical at a saturated aliphatic carbon centre has proved to be very difficult,[2,3] though such S_H2 reactions are well established for reactions involving strained alicyclic rings[4] and attack at polyvalent atoms other than carbon.[2,5,6] In a preliminary communication,[1] we reported that the reaction of trifluoromethyl radicals with neopentane at 300° takes place to a small extent by an S_H2 reaction at one of the methyl groups; in this paper we provide further details. Since this study, it has been reported that cobalt-centred radicals can be displaced from organocobalt compounds in solution by an S_H2 reaction at a saturated carbon atom, either by organocobalt radicals (with inversion of configuration at the carbon atom)[7a] or by trichloromethyl radicals.[7b]

RESULTS AND DISCUSSION

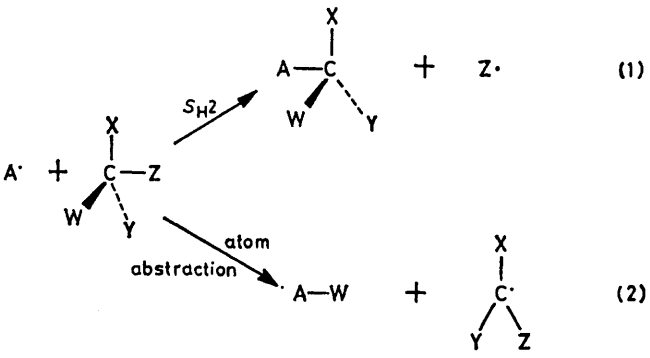
Design of a Suitable Experiment to show the Occurrence of an S_H2 *Reaction.*—Since the establishment of an example of an S_H2 reaction at a saturated aliphatic carbon centre has proved so difficult, it is likely that such reactions have high activation energies. All radical–molecule reactions have to compete with combination and disproportionation reactions: if A factors for S_H2 reactions are normal (see later) such reactions will not occur even to the extent of say 1% if their activation energies are above *ca.* 13 kcal mol^{-1} at 25°, or 21 kcal mol^{-1} at 200° (ref. 8).

Even if the S_H2 reaction (1) can compete successfully with the radical destruction reactions (3), atom abstraction reactions (2) are likely to be important. Most compounds of potential S_H2 interest will have C_{sp^3}–H bonds somewhere in the molecule: activation energies for abstraction of hydrogen atoms by reasonably reactive radicals will have activation energies which are typically <12 kcal mol^{-1}.

These difficulties suggest that in designing an experiment to establish S_H2 reactions of type (1), the following factors should be considered.†

(1) The S_H2 reaction should be as exothermic as possible. In a series of similar reactions the more exothermic ones usually have the lower activation energies. The bond C–Z should be weak either ' intrinsically ' or because stabilization by delocalization of the electron on Z is possible, for example in the benzyl radical.

Conversely, the bond A–C should be as strong as possible. This implies a reactive radical A; which may react rather indiscriminately with the molecule, including the unwanted atom abstraction reactions (2). However, if one is trying to establish the occurrence of an S_H2 reaction, such indiscriminate reactions can be tolerated provided that some reaction is taking place at the saturated carbon centre.



$2\,A\cdot \longrightarrow$ non-radical products (3)

(2) The S_H2 reaction goes through a transition state in which five groups surround a central carbon atom. The S_H2 reaction will be favoured if these groups are kept as small as possible. S_H2 Attack at the carbon atom of a methyl group will for example be favoured on these grounds.

(3) The molecule should if possible be unreactive to alternative radical–molecule reactions, such as addition to double bonds or abstraction of allylic or tertiary hydrogen atoms.

(4) The temperature should be as high as possible. Reactions with activation energies too high to allow their observation at 25° may be feasible at 200 or 300°.

(5) Ideally, the products of the S_H2 reaction should not be formed in other competing non-S_H2 processes.

Preliminary Experiments.—We first tried the reaction of methyl and t-butoxyl radicals (generated by homolysis of di-t-butyl peroxide) on bibenzyl at 140°. Although

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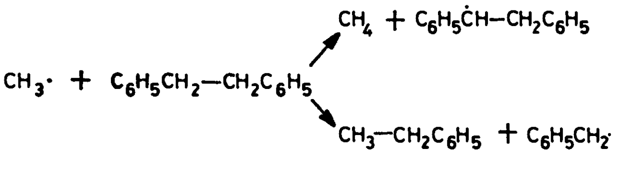
† Some of these factors have been discussed in ref. 2.

the major reaction will be abstraction of hydrogen from the benzylic positions, we hoped that some of the methyl radicals would react by S_H2 reactions at the saturated carbon atoms, since the resonance stabilization of the leaving benzyl radical should make the S_H2 reaction (5) more exothermic and therefore have a lower activation energy. No toluene or ethylbenzene was detected, showing that reaction (5) did not compete with (4) to an appreciable extent at 140°.

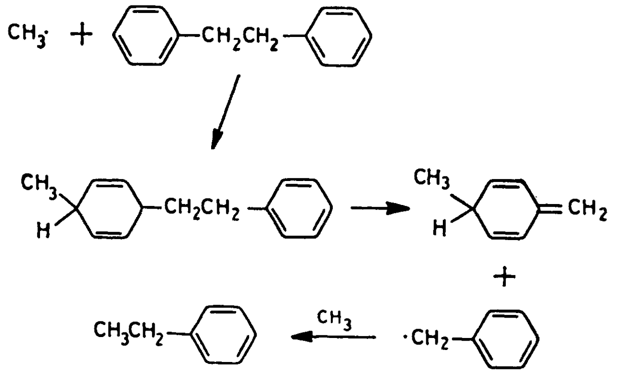
To rule out the possibility that our failure to observe the S_H2 reaction here is due to the great facility of the hydrogen abstraction reaction (4), we repeated the experiments using bicumyl (αα'α'-tetramethylbibenzyl) and αα'α'-tetrafluorobibenzyl as substrates; these two compounds contain no readily abstractable α-hydrogen atoms. Bicumyl gave no t-butylbenzene or cumene, and αα'α'-tetrafluorobibenzyl gave no αα'-difluoroethylbenzene or αα'-difluorotoluene, indicating that neither of these compounds was subject to S_H2 attack, possibly for steric reasons. An experiment with phenyl t-butyl ether, in which the phenoxyl radical rather than the benzyl radical was the potential leaving group, also failed to give evidence for an S_H2 reaction.



(4)

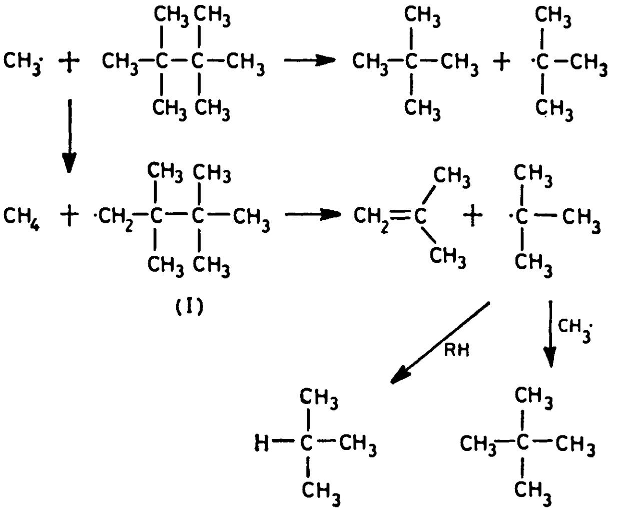
(5)

Although the resonance stabilization of the benzyl radical should make it a good leaving radical in S_H2 reactions, even if positive results had been obtained from the above experiments, an uncertainty would have remained. In principle methyl radicals could have attacked an aromatic ring in bibenzyl, and reaction sequence (6) could have led to the production of benzyl radicals, and hence ethylbenzene without the necessity to invoke the S_H2 reaction (5). In view of this we turned our attention to purely aliphatic compounds, where complications of this sort are impossible.



(6)

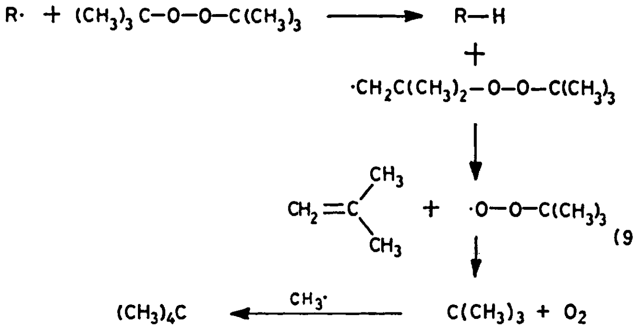
We treated di-t-butyl peroxide with 2,2,3,3-tetramethylbutane at 140°, hoping that the S_H2 reaction (7) would occur, giving rise to neopentane. The reaction mixture did indeed contain traces of neopentane, isobutene, and isobutane, but these compounds could also have been produced by the alternative route (8), or even by radical attack on di-t-butyl peroxide (9). Di-t-butyl peroxide decomposes in octane at 140°. In addition to the well known major products, we identified traces of neopentane, isobutene, and isobutane. Although it is possible that the neopentane arises by the S_H2 reaction of a methyl radical on t-butyl peroxide, the sequence of reactions (9) cannot be ruled out.



(7)

(8)

These preliminary experiments indicated therefore that di-t-butyl peroxide was an unsuitable source of radicals to demonstrate S_H2 reactions in neopentane-like systems, and also that higher temperatures would be needed if S_H2 reactions were to compete with hydrogen transfer reactions of lower activation energies. Accordingly we turned our attention to the reactions of CD_3· and CF_3·, generated photochemically from the corresponding ketones, with neopentane.



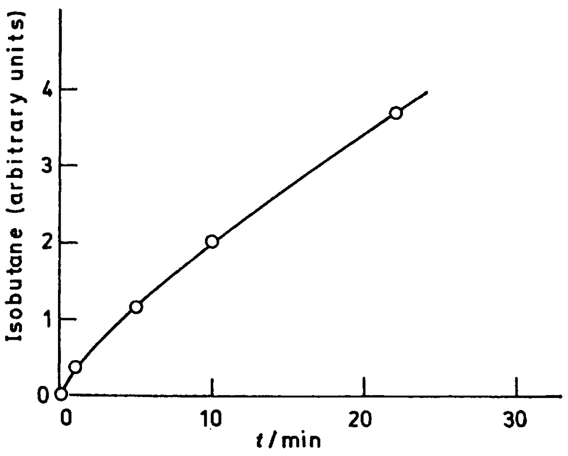
Reaction of Trifluoromethyl Radicals with Neopentane.—Trifluoromethyl radicals were generated in the presence of neopentane by irradiating a mixture of hexafluoroacetone and neopentane at 300° in a quartz vessel. The reaction mixture was analysed by g.l.c.–m.s. and the following products were identified by retention time and their mass spectra: methane, fluoroform, ethane, 1,1,1-trifluoroethane, isobutane, and isobutene. Hexafluoroethane was not present in sufficient quantity to permit identification by its mass spectrum, and was therefore identified on the basis of its retention time only. No reaction took place when hexafluoroacetone and neopentane were heated together in the dark at 300°. The reaction scheme (10)—(20) is proposed to account for the products.

$$\begin{array}{rcll}
(CF_3)_2CO & \xrightarrow{h\nu} & 2\,CF_3\cdot + CO & (10)\\
CF_3\cdot + (CH_3)_4C & \longrightarrow & CF_3H + \cdot CH_2C(CH_3)_3 & (11)\\
CF_3\cdot + (CH_3)_4C & \longrightarrow & CF_3CH_3 + (CH_3)_3C\cdot & (12)\\
(CH_3)_3C\cdot + (CH_3)_4C & \longrightarrow & (CH_3)_3CH + \cdot CH_2C(CH_3)_3 & (13)\\
\cdot CH_2C(CH_3)_3 & \longrightarrow & CH_2{=}C(CH_3)_2 + CH_3\cdot & (14)\\
CH_3\cdot + (CH_3)_4C & \longrightarrow & CH_4 + \cdot CH_2C(CH_3)_3 & (15)\\
2(CH_3)_3C\cdot & \longrightarrow & (CH_3)_3CH + CH_2{=}C(CH_3)_2 & (16)\\
CH_3\cdot + (CH_3)_3C\cdot & \longrightarrow & CH_4 + CH_2{=}C(CH_3)_2 & (17)\\
2\,CH_3\cdot & \longrightarrow & C_2H_6 & (18)\\
CF_3\cdot + CH_3\cdot & \longrightarrow & CF_3CH_3 & (19)\\
2\,CF_3\cdot & \longrightarrow & C_2F_6 & (20)
\end{array}$$

Propane, propene, ethylene, 1,1,1-trifluoro-3-methyl-3-trifluoromethylbutane, and 1,1,1-trifluoro-3,3-dimethylbutane were also detected and identified by g.l.c.–m.s These are thought to be secondary products.

The occurrence of step (12), which is an S_H2 reaction at a saturated carbon atom, is supported by two lines of evidence.

(1) A plot of isobutane in the reaction mixture against time gives a curve (see Figure) which indicates a finite rate of reaction at t 0. This indicates that isobutane is formed as a primary product. This accords with the production of t-butyl radicals immediately the reaction commences, indicating occurrence of reaction (12) followed by (13). Other sources of isobutane, *e.g.* from isobutene, would have to wait until a sufficient concentration of the appropriate precursor had built up.



Photolysis of hexafluoroacetone and neopentane at 300°: rate of formation of isobutane

(2) The amount of 1,1,1-trifluoroethane produced is much greater, relative to ethane and hexafluoroethane, than can be accounted for by reaction (19). If these three products are only being formed by reactions (18)—(20), the product ratio $[CF_3CH_3]^2/[C_2H_6][C_2F_6]$ would be expected to have approximately the statistical value of 4. In four experiments at 300°, values of 31—61 for this ratio were obtained. At 200°, small amounts of hexafluoroethane were formed, but ethane and 1,1,1-trifluoroethane were absent from the products, in agreement with the observations of Bell and Platt.[9] This indicates that at 300° (but not at 200°), the S_H2 reaction (12) is producing 1,1,1-trifluoroethane.

The amounts of isobutane and trifluoroethane formed are approximately equal. When hexafluoroacetone and neopentane were photolysed at 300° for 40 min, corresponding to *ca.* 50% reaction, the isobutane formed corresponded to 1.4% of the trifluoromethyl radicals produced, and the 1,1,1-trifluoroethane corresponded to 1.5%. On the argument on cross product ratios presented above, at least two-thirds of the trifluoroethane comes from the S_H2 reaction, corresponding to *ca.* 1% of the total reaction taking place this way. The amount of isobutane produced also accords with approximately this proportion of reaction going *via* the S_H2 path. It seems likely that Arrhenius A factors for S_H2 reactions will not differ too much from the 'normal' range[10] of $10^{8.5\pm0.5}$ l mol^{-1} s^{-1} found for radical transfer reactions: A factors for S_H2 reactions at boron have been found to vary[6] in the range of 6×10^6—5×10^9 l mol^{-1} s^{-1}, though the analogy here may not be very close since substitution reactions at boron almost certainly go through a relatively stable intermediate adduct. If the difference in rate between the S_H2 reaction (12) and the dominant hydrogen transfer reaction (11) is due to the activation energy difference, this corresponds to $E_{12} - E_{11}$ 5.2 kcal mol^{-1} and E_{12} 13.6 kcal mol^{-1}, using a literature value[9] for E_{11}. That an activation energy difference of this amount can make an energetically favourable S_H2 reaction of only minor importance at 300° highlights the difficulty which will be found in identifying such reactions in organic systems at lower temperatures. Apart from the cyclopropyl systems referred to earlier, where the strong C–H bonds will disfavour the competing hydrogen abstraction reactions, and the release of the ring strain energy will favour ring-opening S_H2 reactions, the most promising field for identifying S_H2 reactions at saturated carbon atoms would appear to be the use of organometallic radicals. For some metallic or metalloid elements at least, the ratio of bond dissociation energy to carbon compared with hydrogen is more favourable than for organic molecules, which will favour S_H2 reactions over hydrogen abstraction. This factor may explain the occurrence of S_H2 reactions of organocobalt-centred radicals in solution.[7]

Other Experiments.—Photolysis of mixtures of hexafluoroacetone and ethane at 300° gave inconclusive results: CH_3CF_3 was formed but could not be estimated quantitatively because of the large amount of ethane present. Methane was formed, but the rate of production indicated that it was mainly at least a secondary product. No ring-opened products were obtained when a mixture of perfluorocyclobutane and hexafluoroacetone was photolysed at 300°: we had hoped that the ring strain present, and the absence of abstractable hydrogen atoms might favour the S_H2 reaction. Attempts to detect an S_H2 reaction in the reaction of trideuteriomethyl radicals with neopentane or butane at 250° failed because of difficulties of quantitative analysis of the ethane fraction for C_6D_6, $C_6H_3D_3$, and C_2H_6 by mass spectrometry.

EXPERIMENTAL

Gas-phase experiments were carried out in a cylindrical quartz vessel of volume 97.4 ml, closed at one end and tapering at the other to a Pyrex 'Rotaflo' high vacuum tap *via* a graded seal. The outside of the vessel was wound with heating wire, and the temperature was controlled by a 0—400° Eurotherm temperature controller and an iron–constantan thermocouple. An outside quartz tube plugged with glass wool at the ends prevented heat losses by convection. The unheated part of the vessel was wrapped with aluminium foil to prevent irradiation of the cool gases.

Reagents.—With the exception of acetone and hexadeuterioacetone all the reagents were supplied in a state of high purity in lecture bottles and used without further purification.

Procedure.—Reagent pressures were measured in a manifold before condensing into the reaction vessel. A pressure of 1 mmHg in the manifold = a concentration of 1.55×10^{-4} M in the reaction vessel. The vessel was degassed twice, then wrapped in aluminium foil, and allowed to warm up to room temperature. The foil was removed, the vessel was fitted with the thermocouple and the quartz jacket, and clamped vertically in front of the mercury lamp. For the preliminary work a G.E.C. 250 W ME/D lamp was used 10 cm from the vessel, for later work a 500 W Hanovia U.V.S. 500/A lamp was used 5 cm from the vessel, and finally a 125 W water-cooled Hanovia medium pressure mercury lamp with a Vycor sheath was used 2.5 cm from the vessel. A period of 30 min was allowed before experiments for the vessel to warm up to the required temperature and the u.v. light output to stabilize.

After reaction, the vessel was allowed to cool to room temperature. The products were transferred to a vacuum system and analysed by g.l.c. (5 ft Poropak P column at 25, 50, or 100°). In experiments where residual ketones were present, a pre-column of phosphoric acid and 2,4-dinitrophenylhydrazine on Chromosorb G was used. Each pre-column (20 cm length, 2 mm i.d.) was used only once.

Reaction of Methyl Radicals with Neopentane at 250°.—Acetone (10 mmHg) and neopentane (100 mmHg) were condensed into the reaction vessel from the vacuum system. The mixture was irradiated for 2 h at 250° using the 250 W mercury vapour lamp. G.l.c.–m.s. showed the presence of methane, ethane, isobutane, and isobutene in relative proportions (area) of 25.9 : 2.7 : 0.36 : 0.91.

Reaction of Trideuteriomethyl Radicals with Neopentane and Butane.—Hexadeuterioacetone (10 mmHg) and neopentane (100 mmHg) were condensed into the reaction vessel. The mixture was irradiated for 2 h at 250° using the 250 W lamp, followed by analysis by g.l.c.–m.s. The procedure was repeated using a mixture of hexadeuterioacetone (10 mmHg) and butane (100 mmHg). In each case the mass spectrum of the ethane component was studied but could not be analysed quantitatively because of the large quantities of ethane and trideuterioethane presumably arising from methyl radicals formed in radical fragmentation reactions.

Reaction of Trifluoromethyl Radicals with Neopentane. Identification of Products.—Hexafluoroacetone (10 mmHg) and neopentane (100 mmHg) were condensed into the reaction vessel and irradiated for 2 h at 300° using the 250 W u.v. lamp. The following compounds were identified by their mass spectra and retention times on a 5 ft Poropak P column at 25, 50, or 100° (in increasing order of retention time): methane, fluoroform, ethylene, ethane, 1,1,1-trifluoroethane, propane, propene, isobutane, isobutene, neopentane. Hexafluoroethane was not identified in this reaction mixture, but was found in subsequent reactions.

Measurement of the Product Ratio $[CF_3CH_3]^2/[C_2H_6][C_2F_6]$.—A series of mixtures of neopentane (100 mmHg) and hexfluoroacetone (20—40 mmHg) were irradiated at 300° for 60 min using the 500 W lamp after which time no residual $(CF_3)_2CO$ could be detected. The mixtures were analysed by g.l.c. to give the area ratio $[CF_3CH_3]^2/[C_2F_6][C_2H_6]$. Since the C_2F_6 peaks were very small, to prevent underestimation of these peaks, thereby overestimating the above area ratio, the peak areas for C_2F_6 were deliberately overestimated by measuring the area enclosed by the top of the peak and the bottom of the noise of the baseline, rather than the middle of such noise. The procedure was repeated for experiments carried out at 200°. Calibration of the g.l.c. by known mixtures gave mol ratios $[CF_3CH_3]^2/[C_2F_6][C_2H_6]$ of 20, 60, and 59 at 300°, and 0.7 and 0.6 at 200° (C_2F_6 peaks at this temperature were large enough to be measured normally). In experiments carried out with a 125 W Vycor-sheathed lamp to minimize photosensitized decomposition of the neopentane, mixtures of neopentane (100 mmHg) and hexafluoroacetone (20—40 mmHg) irradiated for 60 min at 300° gave mol ratios $[CF_3CH_3]^2/[C_2F_6][C_2H_6]$ of 42, 31, and 61, calculated as above, and for one experiment where the C_2F_6 peak was large enough for 'normal' measurement of C_2F_6 (100 mmHg neopentane, 50 mmHg hexafluoroacetone) a value of 35 for the above ratio was calculated.

Photodecomposition of Neopentane.—Neopentane alone (100 mmHg) was irradiated at 300° for 60 min using the 500 W lamp. CH_4 and C_2H_6 were found to be present in quantities of the same order of magnitude as found in experiments with trifluoromethyl radicals. The procedure was repeated using the 125 W lamp which was fitted with a Vycor sheath to prevent mercury photosensitization. This time, methane and ethane were present, but only in barely detectable trace quantities.

Determination of the Product Ratio for the Combination of Methyl and Trifluoromethyl Radicals.—Mixtures of acetone (20, 30, and 40 mmHg) and hexafluoroacetone (80, 70, and 60 mmHg) were irradiated at 20° for 60 min with the 500 W lamp. Mol ratios $[CF_3CH_3]^2/[C_2F_6][C_2H_6]$ of 4.8, 4.6, and 3.1 were determined. To determine this ratio at 200 and 300°, mixtures of hexafluoroacetone (5—50 mmHg) and methane (100—150 mmHg) were used. At 200°, the mol ratio $[CF_3CH_3)^2/[C_2F_6][C_2H_6]$ was 3.7 and 3.9. Twelve experiments at 300° gave product ratio values of 3.7 ± 0.4.

Rate of Formation of Isobutane.—A series of identical mixtures of hexafluoroacetone (25 mmHg) and neopentane (100 mmHg) were irradiated for 0, 1, 5, 10, 22, 34, 45, and 63 min at 300° using the 125 W lamp. The isobutane produced (relative areas) was 0, 0.35, 1.14, 2.00, 3.68, 5.04, 6.94, and 7.90 respectively. A blank run of 100 mmHg neopentane irradiated at 300° for 74 min was found to contain only a trace of isobutane (relative peak area 0.26).

Homogeneity of the Reaction.—A modified reaction vessel (120 ml) was fitted with a ground glass joint so that the vessel could be used with or without packing. When packed, the vessel was filled with quartz tubing (O.D. 2 mm) which decreased the free volume to 66 ml and increased the surface : volume ratio by a factor of *ca.* 10 : 1. Irradiation of hexafluoroacetone (25 mmHg) in the unpacked vessel with the 125 W lamp for 30 min at 300° gave 21% decomposition. A pressure of 13.75 mmHg of hexafluoroacetone in the packed vessel (same molar concentration) gave 19% decomposition after 60 min irradiation. Hexafluoroacetone (25 mmHg) and neopentane (100 mmHg) were irradiated in the unpacked vessel for 30 min at 300°. Analysis of the mixture for CF_3CH_3 and isobutane gave peaks of area 23.5 and 25.2 (arbitrary units) respectively. A similar experiment carried out in the packed vessel at 300° for 60 min using hexafluoroacetone (13.75 mmHg) and neopentane (55 mmHg) (similar molar concentrations) gave CF_3CH_3 and isobutane peak areas of 18.1 and 25.8 arbitrary units under the same g.l.c. sampling conditions.

Reaction of Di-t-butyl Peroxide with Bibenzyl, Bicumyl, Tetrafluorobibenzyl, Phenyl t-Butyl Ether, and 2,2,3,3-*Tetramethylbutane.*—A mixture of di-t-butyl peroxide (0.015 g) and bibenzyl (0.012 5 g) was degassed five times, sealed in a Pyrex ampoule, and heated at 140° for 16 h. No evidence was found for the presence of either toluene or ethylbenzene at the 0.001% level. A mixture of di-t-butyl peroxide (0.009 g) and bicumyl (0.106 g) treated similarly showed no t-butylbenzene at the 0.001% level. A mixture of t-butyl peroxide (0.015 g) and αα α'α'-tetrafluorobibenzyl (0.163 g) treated similarly was found to contain only the decomposition products of the peroxide and unchanged tetrafluorobibenzyl. A mixture of di-t-butyl peroxide (0.011 5 g) and t-butyl phenyl ether (0.136 g) after being heated at 140° for 16 h showed the presence of *ca.* 0.01% each of neopentane, isobutane, and isobutene. Similar quantities of these products were found when a mixture of di-t-butyl peroxide (0.017 g) and 2,2,3,3-tetramethylbutane (0.14 g) was heated under the same conditions, but these products were also produced in approximately the same amounts when a mixture of t-butyl peroxide (0.025 g) and sodium-dried octane (0.162 g) was heated in the same way.

Hexafluoroethane was prepared by irradiating hexafluoroacetone (200 mmHg) in the reaction vessel for 4 h using the 500 W lamp. The reaction vessel was cooled in liquid nitrogen while CO was pumped off. Five bulb-to-bulb distillations (CO_2–acetone) gave hexafluoroethane with only 0.5% hexafluoroacetone as impurity. The residue from the distillation contained C_2F_6, $(CF_3)_2CO$, and $(CF_3)_3COCF_3$, presumably formed by addition of two CF_3 radicals across the C=O double bond,[11] identified by its mass spectrum. 1,1,1-Trifluoroethane was prepared from 1,1,1-trifluoroethanol by $LiAlH_4$ reduction of the toluene-*p*-sulphonate. Five bulb-to-bulb distillations (CO_2–acetone) gave trifluoroethane, identified by its mass spectrum, with only 0.3% trifluoroethanol as impurity.

Phenyl t-butyl ether [12] and ααα'α'-tetrafluorobibenzyl [13] were made by established methods and had physical properties in agreement with literature values.

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REFERENCES

[1] Preliminary communication, R. A. Jackson and M. Townson, *Tetrahedron Letters*, 1973, 193.

[2] K. U. Ingold and B. P. Roberts, 'Free-radical Substitution Reactions', Wiley-Interscience, New York, 1971.

[3] M. L. Poutsma in 'Free Radicals', ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol II, p. 113.

[4] C. J. Upton and J. H. Incremona, *J. Org. Chem.*, 1976, **41**, 523; G. G. Maynes and D. E. Applequist, *J. Amer. Chem. Soc.*, 1973, **95**, 856 and references cited therein.

[5] A. G. Davies and B. P. Roberts, *Accounts Chem. Res.*, 1972, **5**, 387.

[6] A. G. Davies and B. P. Roberts, in 'Free Radicals', ed. J. K. Kochi, Wiley, New York, 1973, vol. I, p. 547.

[7] (*a*) J. Z. Chrzastowski, C. J. Cooksey, M. D. Johnson, B. L. Lockman, and P. N. Steggles, *J. Amer. Chem. Soc.*, 1975, **97**, 932; (*b*) T. Funabiki, B. D. Gupta, and M. D. Johnson, *J.C.S. Chem. Comm.*, 1977, 653.

[8] R. A. Jackson, in 'Essays in Free Radical Chemistry', Chemical Society Special Publication No. 24, London, 1970, p. 295.

[9] T. N. Bell and A. E. Platt, *Internat. J. Chem. Kinetics*, 1970, **2**, 299.

[10] S. W. Benson, 'Thermochemical Kinetics', Wiley, New York, 1968, p. 100.

[11] P. J. Krusic, Kuang S. Chen, P. Meakin, and J. K. Kochi, *J. Phys. Chem.*, 1974, **78**, 2036, and references cited therein.

[12] M. R. V. Sahyun and D. J. Cram, *Org. Synth.*, 1973, Coll. vol. 5, 926.

[13] L. V. Johnson, F. Smith, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1952, 4710.