synthesized by treating the Grignard reagent obtained from *p*-bromophenyl vinyl ether,[31] prepared by eliminating hydrogen bromide from β-bromoethyl *p*-bromophenyl ether, with tritiated water. Ethyl vinyl ether was obtained commercially.

The physical properties of these vinyl ethers were in good agreement with literature values; their identity was further confirmed by their nmr spectra. Kinetic samples were purified usually by fractional distillation and occasionally by gas chromatography; purity was monitored by gas chromatography. All other reagents were the best available commercial grades.

Kinetics. Spectroscopic Methods. Reactions with half-lives greater than *ca.* 20 sec were conducted in 1-cm silica cells contained in the sample compartment of a Cary Model 11 spectrometer; thermostating was provided by water from a constant-temperature bath (25.0 ± 0.1°) circulating through a Cary thermostatable cell jacket. Both sample and reference cells were filled with buffer or perchloric acid solution, and sufficient time was allowed for the sample solution to come to temperature; reaction was then initiated by adding vinyl ether, in quantity sufficient to give a final concentration *ca.* 10^{-3} *M*, to the sample cell and shaking vigorously to effect solution. Absorbance at a fixed wavelength in the region 210–230 nm was recorded continuously in the case of faster reactions and at 5- to 10-min intervals in the case of slower runs. Readings were continued for 4–5 half-lives and infinity values were measured after 8–10 half-lives. In some of the slower runs, infinity readings were not made and the data were treated by the method of Guggenheim[32] and/or Swinbourne.[33] Rate constants were evaluated graphically.

For reactions with half-lives shorter than *ca.* 20 sec, a commercial Durrum–Gibson stopped-flow spectrometer was used. This machine has a mixing time of 2 msec; the fastest reactions measured here had half-lives of 70 msec. Thermostating was provided by constant-temperature water (25.0 ± 0.05°) circulating through the reservoir containing the driving syringes and through the mixing and observation block. Substrate solution and buffer or perchloric acid solution were allowed to remain in the driving syringes long enough to equilibrate with the constant temperature fluid; they were then mixed, and changes in transmittance at 220 nm were recorded on a storage oscilloscope. This record was then photographed with a Polaroid camera, and transmittance changes were read off the developed photograph. Transmittance was converted to absorbance, and first-order rate constants were evaluated graphically.

Radiochemical Method. Aqueous solutions of phenyl-*4-t* vinyl ether and buffer, whose combined volume totaled 100 ml, were allowed to equilibrate separately with a constant-temperature bath operating at 25.0 ± 0.02°. These solutions were then mixed, the reaction mixture was replaced in the bath, and 5-ml samples were removed by pipet at appropriate time intervals (all corresponding to less than 3% reaction). These samples were immediately quenched in 2.00-ml portions of 1 *M* aqueous sodium hydroxide, and the quenched aliquots were then extracted with three successive 25-ml portions of toluene; control experiments showed that each extraction removed 99% of the vinyl ether remaining in the aqueous phase. Aliquots (3 ml) of these thrice-washed aqueous solutions were then added to 10.0-ml portions of Bray's counting solution,[34] and radioassay was performed with a Packard Tri-Carb Model 314 EX liquid scintillation spectrometer. Infinite-time radioactivities were determined by adding 10.00 ml of 0.2 *M* perchloric acid to 10.00-ml portions of reaction mixture, allowing the resultant solutions to stand at 25° for at least 6 hr (10 half-lives at 0.1 *M* acid) and then treating 5.00-ml aliquots in the usual way.

Zero-order rate constants were evaluated as slopes of plots of counts per minute *vs.* time; these were converted to first-order rate constants by dividing by the average cpm of the infinite time samples times two (the correction for perchloric acid dilution).

---

(31) M. Julia, *Bull. Soc. Chim. Fr.*, 186 (1956).

(32) E. A. Guggenheim, *Phil. Mag.*, 2, 538 (1926).

(33) E. S. Swinbourne, *J. Chem. Soc.*, 2371 (1960).

(34) G. A. Bray, *Anal. Biochem.*, 1, 279 (1960).

Hexafluoroacetone Azine. Reaction with Cyclohexane by a Radical Double Chain Mechanism

William J. Middleton

Contribution No. 1729 from the Central Research Department,
E. I. du Pont de Nemours and Company, Experimental Station,
Wilmington, Delaware 19898. *Received July 23, 1970*

Abstract: The thermal reaction of hexafluoroacetone azine with cyclohexane gave three principal products: [2,2,2-trifluoro-1-(trifluoromethyl)ethyl]cyclohexane (**5**), the azo compound **7**, and the hydrazone **8**. Evidence is presented for a unique double radical chain mechanism that involves the intermediate formation of bis(trifluoromethyl)diazomethane (**4**) to account for these products.

We reported earlier that hexafluoroacetone azine (**1**) reacts thermally with cyclohexane to give the carbene insertion product, [2,2,2-trifluoro-1-(trifluoromethyl)ethyl]cyclohexane (**5**).[1] Since both bis(trifluoromethyl)diazomethane and bis(trifluoromethyl)diazirine react with cyclohexane to give primarily nitrogen-containing products, we concluded that the azine may be a better source of bis(trifluoromethyl)carbene than either the diazomethane or the diazirine in reactions with saturated hydrocarbons. Recently, Forshaw and Tipping have shown that the azine **1** also reacts with olefins such as cyclohexene to give products (cyclopropanes) that would be expected from carbene reactions.[2] However, they concluded that initial formation of bis(trifluoromethyl)carbene followed by attack of this carbene on the olefin is unlikely, since the azine is stable to 240°, and, when it is pyrolyzed at 570°, it does not form products expected from the intermediacy of the carbene.

We have reexamined the reaction of the azine **1** with cyclohexane in the temperature range 129–170° and found that other products in addition to **5** are formed, including the azo compound **7** and the hydrazone **8**. We now concur with Forshaw and Tipping that the azine **1** does not react initially to give the carbene. Instead, a

---

(1) W. J. Middleton, D. M. Gale, and C. G. Krespan, *J. Amer. Chem. Soc.*, **90**, 6813 (1968).

(2) T. P. Forshaw and A. E. Tipping, *Chem. Commun.*, 816 (1969).

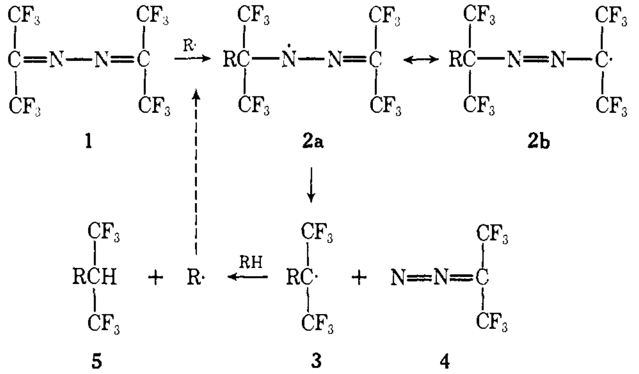
Table I. Reactions of Hexafluoroacetone Azine (1) with Cyclohexane

Reactants			Conditions		Products, % yield				
1, mg	Cyclohexane, µl	Other	Temp, °C	Time, hr	1	5	7	8	Unknown
140	400	None	129	12	0	36	14	18	32
140	400	None	170	12	0	71	11	3	15
140	400	None	155	12	0	51	17	11	21
140	400	Hydroquinone (25 mg)	155	12	100	0	0	0	0
140	0	CCl_4 (400 µl)	170	36	100	0	0	0	0
500	0	None	250	36	100	0	0	0	0
140	0	Benzene (400 µl)	170	12	100	0	0	0	0
140	200	Benzene (200 µl)	170	12	0	67	12	3	14[a]

[a] A 4% yield of 1,1-bis(trifluoromethyl)norcaradiene was also obtained in this reaction.

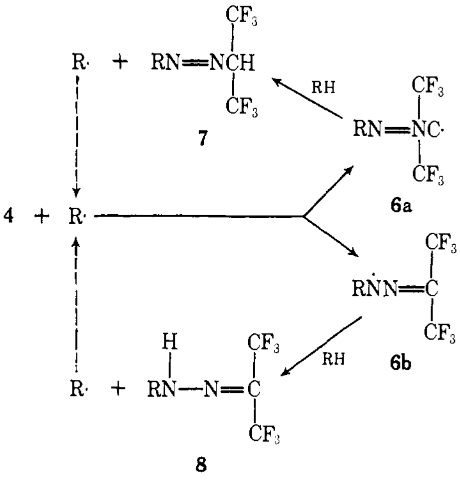
unique radical double chain reaction is believed to occur. This radical double chain mechanism is illustrated in Schemes I and II.

Scheme I



R = cyclohexyl

Scheme II

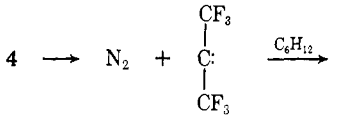


R = cyclohexyl

The first chain reaction is initiated by the addition of a cyclohexyl radical to the azine **1** to give the radical adduct **2** (resonance forms a and b). This adduct then decomposes to give the cyclohexylbis(trifluoromethyl)-methyl radical (**3**) and bis(trifluoromethyl)diazomethane (**4**). Radical **3** then abstracts hydrogen from cyclohexane to give **5**, the major isolated product, and a new cyclohexyl radical to continue the chain (Scheme I).

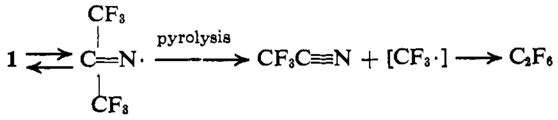
The second chain (Scheme II) has already been described in an earlier report.[1] A cyclohexyl radical adds to the diazo compound **4** to give the resonance-stabilized radical **6**, which can abstract hydrogen from cyclohexane in two different ways to give either azo compound **7** or hydrazone **8** and a new cyclohexyl radical to complete the chain. Since the diazo compound **4** can also decompose directly to give bis(trifluoromethyl)-carbene and nitrogen[1] (Scheme III), some of the product

Scheme III



5 from the reaction of the azine **1** with cyclohexane must also arise from a carbene reaction.

The cyclohexyl radical necessary to initiate these chain reactions may be formed by reaction of the imine radical, $(CF_3)_2C{=}N\cdot$, with cyclohexane. This imine radical is believed to be present in an equilibrium concentration when the imine is heated, for the azine initiates the polymerization of acrylonitrile at 95°. Also, the pyrolysis products of the azine[2] suggest that the azine first dissociates into imine radicals.



$$1 \rightleftarrows (CF_3)_2C{=}N\cdot \xrightarrow{\text{pyrolysis}} CF_3C{\equiv}N + [CF_3\cdot] \longrightarrow C_2F_6$$

We have the following evidence to support this proposed radical double chain mechanism.

(1) No reaction occurs when the azine is heated by itself at 250° or with carbon tetrachloride at 170°. Since bis(trifluoromethyl)carbene generated from bis-(trifluoromethyl)diazirine at 165° does add to carbon tetrachloride, initial formation of the carbene from the azine appears unlikely.

(2) Hydroquinone, a radical trap, completely prevents the reaction of the azine with cyclohexane at 155°, although the reaction proceeds quite readily at this temperature in the absence of hydroquinone. This experiment establishes the radical nature of the reaction.

(3) The ratio of the three principal products (**5**, **7**, and **8**) is temperature dependent. Higher temperatures favor **5** as expected, for when the diazo compound **4** is formed (Scheme I) at higher temperatures, it would be more likely to decompose to the carbene (Scheme III)

because of excess thermal energy, and therefore less likely to react with a cyclohexyl radical (Scheme II).

(4) The azine **1** does not react with benzene at 170°. However, if cyclohexane is added, the benzene does react and 1,1-bis(trifluoromethyl)norcaradiene is formed. This reaction of the diazo compound **4** with benzene to give a norcaradiene has been previously demonstrated.[3] It is likely that the benzene is intercepting some of the diazo compound **4** (or the carbene derived from it) that was formed from the reaction of the azine with cyclohexane.

Experimental Section

Reactions of Hexafluoroacetone Azine with Cyclohexane. The reactants listed in Table I were sealed in glass tubes and heated as indicated in an oil bath. The reaction products were identified and analyzed by glc and ^{19}F nmr and ir spectroscopy. All products were compared with authentic[1] samples for positive identification. The azine used in these experiments was prepared by photolysis of *N*-bromohexafluoroacetone imine.[4]

Polymerization of Acrylonitrile with Hexafluoroacetone Azine. A mixture of 400 µl of acrylonitrile and 40 µl of hexafluoroacetone azine was sealed in a glass tube and heated at 95° for 17 hr. A hard, solid block of white polymer formed. No change occurred to a control sample of acrylonitrile that contained no azine but was also heated at 95° for 17 hr.

2-Chloro-2-(trichloromethyl)-1,1,1,3,3,3-hexafluoropropane. A mixture of 50 ml of carbon tetrachloride and 20 g of bis(trifluoromethyl)diazirine was heated at 150° for 12 hr in a 400-ml stainless steel tube. The tube was cooled and vented, and the contents were distilled to give 8.65 g of 2-chloro-2-(trichloromethyl)-1,1,1,3,3,3-hexafluoropropane as a colorless liquid, bp 134–135°, that solidified upon cooling: mp 100–101° (sealed capillary); ^{19}F nmr (CCl_3F) δ 64.5 ppm from CCl_3F (s).

Anal. Calcd for $C_4Cl_4F_6$: C, 15.81; Cl, 46.67; F, 37.52. Found: C, 16.19; Cl, 47.01; F, 37.32.

---

[3] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, 88, 3617 (1966).

[4] W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

The Behavior of Photochemically Generated Ketyl Radicals. A Modified Mechanism for Benzophenone Photoreduction

Steven A. Weiner

Contribution from the Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121. *Received June 23, 1970*

Abstract: The photoreductions of benzophenone by isopropyl alcohol and of acetone by benzhydrol produce both benzpinacol and $(C_6H_5)_2C(OH)C(OH)(CH_3)_2$. In isopropyl alcohol solution, the latter product can only arise from a cage reaction. The fraction of cage reaction, *a*, has been measured to be 0.11 ± 0.02. This value demonstrates that electron spin flipping in a caged radical pair is fast compared with diffusive destruction of the cage.

While the photoreduction of benzophenone in isopropyl alcohol solution has been studied intensively, the exact mechanism is still a matter of controversy.[1–3] One of the most perplexing aspects is the failure to detect the mixed pinacol, $(C_6H_5)_2C(OH)C(OH)(CH_3)_2$ (I), in the reaction mixture. Analogous cross-coupled products have been reported in the photoreduction of benzophenone in toluene and cumene solutions,[1] and in methanol and ethanol solutions.[4] Furthermore the statistical distribution of these products was taken to mean that the products were not formed from the initial caged species. However, more recently the absolute termination constants of benzophenone ketyl, cumyl, and benzyl radicals have been measured.[5,6] The very high values obtained for these constants would seem to demand a cage reaction in these systems.

Despite the intense interest in photoreductions, very little work has been done on the system of benzhydrol in acetone solution. Earlier workers reported that the products were benzpinacol and isopropyl alcohol[7] while later workers said the reaction was not repeatable.[2] These reports are equally disturbing. If the reaction goes at all, one would expect compound I as a product even if there were no cage reaction. This comes about because there is no benzophenone in the solution to serve as a trap for the acetone ketyl radical, $(CH_3)_2\dot{C}(OH)$. Consequently, one would expect statistical product distribution unless the ketyl radicals disproportionated. Accordingly, it was decided to take a closer look at this system and at benzophenone in isopropyl alcohol solution in an attempt to shed some light on the seemingly odd behavior of ketyl radicals generated under these conditions.

Experimental Section

All solvents were Matheson Coleman Bell spectroscopic grade and were used as received except for isopropyl alcohol which was distilled from magnesium turnings. Benzophenone, benzhydrol, and benzpinacol were recrystallized from ethanol. Camphorquinone was recrystallized from hexane. The melting points were in agreement with literature values.

1,1-Diphenyl-2-methyl-propane-1,2-diol (I) was synthesized by the addition of excess methylmagnesium bromide to an ether solution

---

[1] G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Amer. Chem. Soc.*, 83, 2795 (1961).

[2] J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, and R. B. Martin, *ibid.*, 81, 1068 (1959).

[3] N. Filipescu and F. L. Minn, *ibid.*, **90**, 1544 (1968).

[4] H. Mauser and V. Bihl, *Z. Naturforsch. B*, 22, 1077 (1968).

[5] G. S. Hammond and S. A. Weiner, *Intra-Sci. Chem. Rep.*, **3**, 241 (1969).

[6] R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968).

[7] A. Schönberg and A. Mostafa, *J. Chem. Soc.*, 276 (1943).