C. Tetramethylammonium 2-Trifluoromethyl-1,1,3,3-tetracyanopropenide (VII).—A mixture of 1.61 g. (0.01 mole) of 1-amino-1-trifluoromethyl-2,2-dicyanoethylene and 0.88 g. (0.01 mole) of sodiomalononitrile was treated with 7 ml. of water. Solution occurred quickly. The orange-brown solution was boiled briskly for 15 sec., then there was added a solution of 2.2 g. (0.02 mole) of tetramethylammonium chloride in 8 ml. of water. A copious yellow precipitate formed immediately. The product was filtered and dried in air to provide 2.17 g. (77%) of tetramethylammonium 2-trifluoromethyl-1,1,3,3-tetracyanopropenide. Several crystallizations from water provided yellow needles, m.p. 177–179°.

Anal. Calcd. for $C_{12}H_{12}F_3N_5$: C, 50.9; H, 4.3; N, 24.7. Found: C, 50.9; H, 4.2; N, 24.7.

D. Tetramethylammonium 2-Pentafluoroethyl-1,1,3,3-tetracyanopropenide (VII).—A suspension of 2.11 g. (0.01 mole) of 1-amino-1-pentafluoroethyl-2,2-dicyanoethylene in 8 ml. of water was treated with 0.88 g. (0.01 mole) of sodiomalononitrile. Most of the solids dissolved quickly, and the odor of ammonia soon was apparent. The mixture was boiled for 5 min., and a solution of 2.2 g. (0.02 mole) of tetramethylammonium chloride in 7 ml. of water was added. Crystallization of the product began quickly, and the mixture was chilled in ice for 1 hr. Filtration provided 2.34 g. (70%) of bright yellow tetramethylammonium 2-pentafluoroethyl-1,1,3,3-tetracyanopropenide. Crystallization from methanol–ether provided lemon-colored prisms, m.p. 127–129°.

Anal. Calcd. for $C_6H_2F_5N_3$: C, 34.1; H, 0.96; F, 45.0; N, 19.9. Found: C, 34.3; H, 1.2; F, 45.3; N, 20.2.

E. 3-Trifluoromethyl-4-cyano-5-aminopyrazole (X).[5]—A solution of 10.4 g. (0.065 mole) of 1-amino-1-trifluoromethyl-2,2-dicyanoethylene (IV) and 3.5 g. (0.07 mole) of hydrazine hydrate in 250 ml. of ethanol was refluxed 16 hr. The solvent was removed by rapid evaporation to leave an oil which crystallized on standing. Recrystallization from acetone–chloroform provided 4.2 g. (37%) of 3-trifluoromethyl-4-cyano-5-aminopyrazole. Two further crystallizations from chloroform gave white needles, m.p. 172–172.5°.

Anal. Calcd. for $C_5H_3F_2N_4$: C, 34.1; H, 1.7; N, 31.8. Found: C, 34.2; H, 1.6; N, 32.3.

F. Reaction of 1-Amino-1-perfluoroalkylethylenes with Potassium *t*-Butoxide. 1.—A solution of potassium *t*-butoxide was prepared by dissolving 1.96 g. (0.05 g.-atom) of potassium metal in 50 ml. of anhydrous *t*-butyl alcohol. 1-Amino-1-pentafluoroethyl-2,2-dicyanoethylene (5.28 g., 0.025 mole) was added in one portion. The yellow solution was heated under reflux while effluent gases were led from the top of the condenser through an infrared cell. After 16 hr. of reflux, heating was discontinued. The infrared spectrum of the gaseous product contained bands at 7.6, 8.4, 8.8, and 11.5 μ, and identified the material as pentafluoroethane (XII).[6] The yield of pentafluoroethane was not determined.

The ultraviolet spectrum of potassium tricyanomethanide shows $\lambda_{\max}^{\mathrm{EtOH}}$ 272 mμ (ϵ 213), 223 (3220) with the latter appearing as a shoulder on a broad, intense absorption at lower wave lengths. The ultraviolet spectrum of the solid product of the reaction described above contained a maximum at 223 mμ (ϵ 3040), but the weak absorption at 272 was obscured by a strong absorption at 393 (10,900), attributable to starting material.

2.—In an experiment identical with that described in 1, except that 4 g. (0.025 mole) of 1-amino-1-trifluoromethyl-2,2-dicyanoethylene was employed, infrared analysis of the gaseous product (8.3, 8.8 μ) showed that it consisted solely of fluoroform.

Acknowledgment.—The author wishes to acknowledge valuable discussions with Dr. S. Proskow who performed some of the early experimental work in this area.

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[5] This reaction was performed by Dr. H. E. Holmquist.

[6] "Fluorine Chemistry," J. H. Simons, Ed., Academic Press, New York, N. Y., 1954, p. 472.

Reactions of *t*-Butyl Hydroperoxide with Olefins

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The decomposition of *t*-butyl hydroperoxide has been studied in the presence of olefins to determine the feasibility of epoxidation with it. Rates were measured at 60 and 100°. Variations in rate with olefin structure were found to be small. Epoxide yields are dependent on structure in a way that suggests that the epoxide-forming reaction is a polar process. By treating hydroperoxide with the geometric isomers of 4-methyl-2-pentene, it was shown that epoxide forms stereospecifically by a *cis* oxidation. A variety of solvents were found to accelerate the over-all reaction, although none was effective in increasing epoxide yield. It is concluded that the reaction between hydroperoxide and olefin proceeds through an intermediate complex and is generally poor for the preparation of epoxide.

The formation of epoxides from the reaction of hydroperoxides with olefins has been described[2] as part of a study of the autoxidation of olefins. The possible utility of this reaction as a synthetic method and the importance of hydroperoxide olefin interactions in hydroperoxide initiated polymerization of olefins[3–5] led us to study some further aspects of hydroperoxide epoxidation.

Experimental

Chemicals.—Olefins were Phillips pure grade. Olefins and solvents were taken from freshly opened bottles and distilled. Purity was checked by gas chromatography. *t*-Butyl hydroperoxide (Lucidol) was distilled (or redistilled) to >90% purity as determined by iodometric analysis.

Kinetics.—New glass equipment was used for kinetic experiments. Samples of 1 to 4 ml. of previously mixed reagents were introduced into small carius tubes which were then degassed with several freezing and thawing cycles and sealed at <0.1-mm. pressure. After thawing and shaking, the tubes were thermostated at 60 or 100° ± 0.02°. Tubes were removed periodically for peroxide and gas chromatographic analyses. Remaining peroxide was determined[6] by titrating aliquots which had been permitted to react in glacial acetic acid–saturated potassium iodide mixtures under carbon dioxide for ~0.25 hr., diluted with distilled water, and titrated with ~0.1 *N* thiosulfate. Gas chromatographic analyses were performed on a Perkin-Elmer Model 154C using a column containing diisodecyl phthalate on Celite (Perkin-Elmer A column), column temperature 130°, helium carrier gas flow 25 p.s.i. Constant volume sampling was achieved with a Hamilton 10-μl. syringe. Epoxide peaks thus obtained were analyzed both by per cent total peak area and by comparison with peak areas obtained from standard solutions of epoxide. The two methods gave essentially the same results implying that the amount of high boiling material, if any, was not enough to interfere with analyses by the first method. Decomposition studies as set forth in Tables I–III were performed on bulk olefin, with

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[2] W. F. Brill, *J. Am. Chem. Soc.*, **85**, 141 (1963).

[3] V. Stannet and R. Mesrobian, *ibid.*, **72**, 4125 (1950).

[4] C. Walling and Y. Chang, *ibid.*, **76**, 4878 (1954).

[5] A. V. Tobolsky and L. R. Matlack, *J. Polymer Sci.*, **55**, 49 (1961).

[6] C. Wagner, R. Smith, and E. Peters, *Anal. Chem.*, **19**, 979 (1947).

TABLE I

DECOMPOSITION OF 2 *M* *t*-BuOOH IN OLEFINS

	100°		
	Decomposition, %		
Olefin	6 hr.	24 hr.	
Octene-1	35.9	64.1	
Octene-2[a]	26.4	55.0	
4-Vinylcyclohexene	25.5	54.6	
4-Me-2-pentene, *cis*	19.5	31.4	
4-Me-2-pentene, *trans*	22.8	44.9	
	60°		
	48 hr.	216 hr.	456 hr.
Octene-1		16.8	40.0
Octene-2		17.7	37.4
4-Vinylcyclohexene		23.7	34.4
DIB[b]		19.9	35.0
4-Me-2-pentene, *cis*	19.0	31.9	42.7
4-Me-2-pentene, *trans*		25.8	37.7
2-Ethyl-1-hexene		20.0	35.0
Styrene	17.3		
2-Me-1-pentene		35.5	
2-Me-1-butene	18.2	40.0	
Allyl alcohol		35.7	
Allyl chloride		58.0	
2-Butene-1,4-diol		60.0	92.0
Diethyl fumarate		0	0
Di-*n*-butyl maleate		8.5	18.0
2,5-Dihydrofuran		30.0	40.0

[a] Mixture of *cis* and *trans*. [b] 2,4,4-Trimethyl-1-pentene.

TABLE II

SOLVENT EFFECTS. DECOMPOSITION OF *t*-BuOOH
(~1 *M* *t*-BuOOH, ~2 *M* olefin, 60°)

		Decomposition, %		
Olefin	Solvent	72 hr.	168 hr.	336 hr.
Octene-1	C_6H_6			15.0
	MeOH	29.7	45.2	55.4
	Pyridine		15.7	
Octene-2	*t*-BuOH	43.8	58.4	74.4
	CCl_4	72.5		96.5
	HOAc	45.0	60.0	78.0
	DMA[a]	66.0	73.0	89.0
VCH[b]	Styrene oxide	7.1	16.6	31.9
	Furan			31.9
DIB[c]	Pyridine	6.7	15.8	32.3
	DMF[d]	84.0	94.7	98.6
	$MeNO_2$	28.9	36.3	

[a] Dimethylaniline. [b] 4-Vinylcyclohexene. [c] 2,4,4-Trimethyl-1-pentene. [d] Dimethylformamide.

TABLE III

CONCENTRATION EFFECTS. DECOMPOSITION OF *t*-BuOOH IN OCTENE-1[a]

Octene-1, mole/l.	*t*-BuOOH, mole/l.	$k_1 \times 10^7$ sec.$^{-1}$	$k_2 \times 10^8$ l. mole^{-1} sec.$^{-1}$
5.12	1.87	1.95	3.8
3.82	3.88	1.37	3.6
1.98[b]	0.96	0.69	3.5
1.25	7.55	0.52	4.2
			Av. 3.8 ± 0.3 × 10^{-8}

[a] At 60°. [b] In benzene.

TABLE IV

EFFECT OF OLEFIN STRUCTURE ON EPOXIDE YIELD IN *t*-BuOOH EPOXIDATION

Olefin	Epoxide yield, %[a]
Octene-1	5–10
Vinylcyclohexene	10–20[b]
Cyclohexene	10–30
4-Methyl-2-pentene, *cis*	20–25[c]
4-Methyl-2-pentene, *trans*	20–25[c]
2-Ethyl-1-hexene	35–40
Octene-2	25–40[d]
DIB	40–50

[a] Based on *t*-BuOOH consumed. The lowest values represent yields after approximately 60% of the hydroperoxide had been consumed. [b] Mono ring epoxides only. No diepoxide detected. [c] *cis* olefin → *cis* epoxide, *trans* olefin → *trans* epoxide exclusively. [d] Combined yield of *cis* and *trans* epoxide.

solvent, at 60 and 100°, and at various concentrations. Epoxide formation was noted by chemical tests (hydrobromic acid in glacial acetic acid),[7] by comparison of gas chromatographic retention times with those of authentic samples, and by trapping those peaks and comparing their infrared and mass spectra with those of authentic samples. Epoxide yields (Table IV) are all based on hydroperoxide consumed. Products other than epoxide are not considered in this study.

Epoxidation with *p*-Nitrocumene Hydroperoxide.—*p*-Nitrocumene was prepared by the method of Brown[8] and purified by fractionation on a spinning band column. A cut (b.p. 115° at 13 mm.) containing 97% *p*-nitrocumene (by gas chromatography) was obtained. The only detectable impurities were the *ortho* and *meta* isomers. This material was autoxidized at 60° in a stream of oxygen using a small amount of azobisisobutyronitrile as initiator. After ~5 days an iodometric assay of the autoxidized material indicated it to be ~5 *M* in hydroperoxide. The hydroperoxide unpurified was used in reactions with 1-octene and 2,4,4-trimethyl-1-pentene at 90° in sealed tubes as previously described. The initial hydroperoxide concentrations were 0.5 *M*. After 19 hr., iodometric assays showed that 35 and 25%, respectively, of the hydroperoxide had disappeared to yield (by gas chromatography) 9 and 35% of the respective epoxides based on hydroperoxide reacted.

Stereospecific Epoxidations of 4-Methyl-2-pentenes.—Pure *cis*- or *trans*-4-methyl-2-pentene reacted separately with *t*-butyl hydroperoxide (2 *M*) at 90° for 19 hr. At 30% reaction (20–25% yield of epoxide based on peroxide consumed) the *cis* olefin gave *cis* epoxide and the *trans* olefin gave *trans* epoxide each in more than 10:1 ratios. The epoxides were resolved by gas chromatography on a 2-m. diisodecyl phthalate on Celite (Perkin-Elmer "A") column at 130°, 25-p.s.i. helium pressure. Retention times were *trans* epoxide, 2.4 min.; *cis* epoxide, 2.7 min. The small amounts of nonspecific epoxide might have arisen from impure starting material (the *cis* and *trans* olefins could not be resolved by gas chromatography under the conditions stated above), or by a nonspecific epoxidation similar to those obtained by autoxidative epoxidation.[2]

Epoxide Destruction.—The *separate* effects of heat, olefin, *t*-butyl hydroperoxide, and *t*-butyl alcohol at 60 and 90° were studied on the epoxides of *cis*- and *trans*-4-methyl-2-pentenes, 1,2-epoxyoctane, and the mono ring epoxide of 4-vinylcyclohexene for periods of time up to 30 days in degassed sealed tubes. Epoxide analyses were as previously described. Of all these effects, only hydroperoxide caused measurable, but small, epoxide disappearance.

In a separate experiment it was shown that 1,2-epoxyoctane, 1-pentene, and *t*-butyl hydroperoxide (2 *M*) yielded no detectable quantity of di-*n*-hexyl ketone at 90°, 24-hr. reaction.[9]

Results and Discussion

The decomposition of hydroperoxide has been much studied both in the presence and absence of olefins.[10] Most studies have concluded that the rate equation describing the decomposition differs markedly from those of other common organic free radical sources

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[7] A. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

[8] H. C. Brown and W. H. Bonner, *J. Am. Chem. Soc.*, **76**, 605 (1954).

[9] R. Gritter and T. Wallace [*J. Org. Chem.*, **26**, 282 (1961)] showed that at 150° cyclic ethers and olefins in the presence of di-*t*-butyl peroxide gave ketone. This analogous experiment in which di-*n*-hexyl ketone would have been the expected product indicated that a similar reaction cannot account for low epoxide yields.

[10] See, for example, C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 503.

such as diacyl peroxides, azobisisobutyronitrile or di-*t*-butyl peroxides which show rates (except for special cases) describable mainly as simple first order homolysis.[10] The presence of olefins in these systems has either no effect or a tendency to eliminate side reactions such as induced decomposition. In sharp contrast, the presence of olefins in hydroperoxide systems has the effect of increasing decomposition rates. The hydroperoxide decomposition rates rarely, if ever, fit the relatively simple schemes which describe the other common free radical sources. The reason advanced for these differences are (1) radical-induced decomposition[4,11–13]; (2) primary decomposition that is not unimolecular[8,14,15]; (3) polar side reactions between olefin and hydroperoxide.[1,4,5,14]

Rates.—The work described here falls in good general agreement with earlier[10] observations that olefins accelerate the decomposition of hydroperoxides. The rate of decomposition of *t*-butyl hydroperoxide in olefin is not very sensitive to the olefin structure as demonstrated by the data in Table I. The markedly lower rates in unsaturated esters could arise from the formation of peresters by transesterification. From rates at 60 and 100°, the activation energy in all cases where data was available was estimated to be 20 ± 1 kcal./mole contrasted to 39 kcal./mole estimated in octane at 150–180°,[16] strongly indicating the participation of olefin in the decomposition.

The effect of solvents, as shown in Table II, was such that an increased over-all rate of decomposition was noted in each case except benzene, strongly supporting prior evidence[5,14] for solvent hydroperoxide interaction. In the cases of carbon tetrachloride and dimethylformamide the increased rate is probably the result of induced decomposition accompanying chain addition of solvent to olefin and/or telemer formation.[17,18]

Concentration dependence in the system *t*-butyl hydroperoxide and 1-octene (Table III) confirms the importance of olefin hydroperoxide interactions. The individual runs gave reasonably good first-order plots for decomposition rates, k_1, dependent in an orderly way on the olefin concentration. The second-order rate constant, k_2, is obtained by dividing k_1 by the octene-1 concentration. The data imply that the reaction proceeds through an intermediate which leaves the olefin concentration essentially unchanged. A rather simple scheme, such as the one that follows,

$$t\text{-BuOOH} + \text{olefin} \xrightarrow{1} \text{complex}$$

$$\text{complex} \xrightarrow{2} \text{epoxide} + t\text{-BuOH}$$

$$\text{complex} \xrightarrow{3} \text{olefin} + t\text{-BuOH} + 0.5\ \text{O}_2$$

fits the data if rate 3 > rate 2, leaving the olefin concentration not much depleted over the course of the reaction. In cases where olefin is consumed by polymerization, hydroperoxide disappearance does appear to be more truly first order in olefin and first order in hydroperoxide.[4,5]

Epoxide yields based on reacted *t*-butyl hydroperoxide obtained in bulk olefin at 60 and 100° (Table IV), ranged from 5–10% in the case of the least substituted olefin to as much as 50% for the most highly substituted olefin examined, 2,4,4-trimethyl-2-pentene. There was a tendency in all cases for the epoxide yield to diminish with time and also a tendency toward slightly lower yields at higher temperatures. The nature of the epoxide destroying reactions was not studied in great detail since the effects examined (see Experimental) were not important in accounting for the low yields of epoxide. Since the epoxide forming reaction is *not* rate determining and since no consecutive epoxide destroying reaction was found to be significant, it must be concluded that the variation in yield over the range of olefin structures examined represents a competition between reactions that produce epoxide and those that do not as in the scheme outlined above. Further, it may be stated that the competition is governed by the stability of the resultant epoxide, by the electron supplying nature of the groups in the vicinity of the double bond, or by whether or not the transition state of the postulated complex is similar to epoxide.

Epoxide yields in the presence of all solvents (except benzene) were lower than in bulk. In several instances (*t*-butyl alcohol, carbon tetrachloride, dimethylformamide, acetic acid, and dimethylaniline) no epoxide was detected at all indicating that the solvent–hydroperoxide interaction outweighed the olefin–hydroperoxide interaction. In fact, it is possible that the inevitable production of *t*-butyl alcohol (which is nearly quantitative in all cases described here) in the decomposition of *t*-butyl hydroperoxide provides a solvent–hydroperoxide interaction that precludes the possibility of quantitative epoxide formation in these reactions.

All compounds listed in Table I gave at least trace quantities of epoxide by chemical tests (reaction with hydrobromic acid in glacial acetic acid[7]), but only those in Table IV were analyzed by gas chromatography and characterized.

p-Nitrocumene hydroperoxide was treated with olefin in a few experiments to establish whether or not some drastic change in hydroperoxide structure would increase epoxide yields and/or reaction rates. Both decomposition rates and epoxide yields were very similar to those obtained using *t*-butyl hydroperoxide. It is known that electron-withdrawing groups on perbenzoic acid enhance epoxidation rates.[19] No direct analogy is permitted by the results obtained since comparison with cumene hydroperoxide would be necessary. It appears unlikely that drastic alteration of the hydroperoxide structure will provide a quantitative route to epoxide.

Comparison with Peracid Oxidations.—Although the well-known peracid epoxidation of olefins[20] produces generally higher yields and faster rates, the similarity of the two systems invites comparison. Both reactions are first order in olefin and peroxide.[19] Both reactions

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[11] F. Seubold, F. Rust, and W. Vaughan, *J. Am. Chem. Soc.*, **73**, 18 (1951).

[12] D. H. Johnson and A. V. Tobolsky, *ibid.*, **74**, 938 (1952).

[13] B. Bayral and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).

[14] L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952).

[15] A. V. Tobolsky, D. Metz, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 1942 (1950).

[16] E. Bell, J. Raley, F. Rust, F. Seubold, and W. Vaughan, *Discussions Faraday Soc.*, **10**, 242 (1951).

[17] L. Friedman and H. Shechter, *Tetrahedron Letters*, **7**, 238 (1961).

[18] M. S. Kharasch, E. Jensen, W. Urry, *J. Am. Chem. Soc.*, **69**, 1100 (1947).

[19] B. Lynch and K. Pausacker, *J. Chem. Soc.*, 1525 (1955).

[20] D. Swern, "Organic Reactions" Coll. Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 378.

have activation energies in the neighborhood of 20 kcal./mole[19] compared to values of at least 30 kcal./mole found for most O–O homolyses.[10] Electron-releasing groups substituted on the double bond enhance the rate and yield of epoxide formation in both reactions.[19] Both reactions are stereospecific in the sense that they give *cis* epoxidation.[20] The evidence presented speaks strongly in favor of a polar mechanism for hydroperoxide epoxidation with at least certain similarities to peracid epoxidation. It is consistent with the previously reported opinion that unbound free radicals are not significantly involved.[2] The conceivable advantages of hydroperoxide over peracid as epoxidizing agents are the potentially low cost of the reagent and the possibility of epoxidations in acid sensitive systems.

The Grignard Reagents of *p*- and *m*-Bromophenylferrocene[1a]

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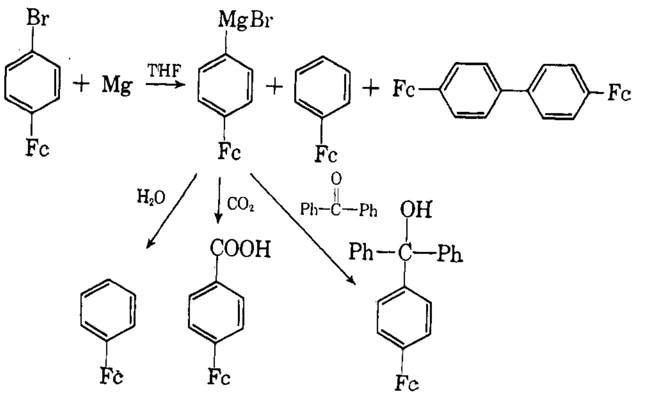
The Grignard reagent of *p*-bromophenylferrocene has been prepared in tetrahydrofuran, accompanied by the formation of phenylferrocene, and has been found to react normally with water, carbon dioxide, and benzophenone. Attempts to prepare the reagent at higher temperatures in dimethylcarbitol yielded only phenylferrocene and *p,p'*-diferrocenylbiphenyl. Similarly, *m*-bromophenylferrocene reacted with magnesium at high temperatures in dimethylcarbitol to yield only phenylferrocene and *m,m'*-diferrocenylbiphenyl, but even at lower temperatures in tetrahydrofuran only these two products could be obtained.

Ferrocene as a substituent on other aromatic systems has been of interest in these laboratories,[4,5] and in the course of these studies attempts have been made to prepare *m*- and *p*-ferrocenylphenylmagnesium bromides.

The Grignard reagent from *p*-bromophenylferrocene has been prepared in refluxing tetrahydrofuran, and in many ways the behavior of the system resembles the experiments reported by Shechter and Helling[6] on the preparation of ferrocenyl Grignard reagents. *p*-Bromophenylferrocene, like the haloferrocenes, reacts sluggishly with magnesium and requires, for a satisfactory reaction, tetrahydrofuran (THF) as a solvent and entrainment with alkyl halides, such as ethyl bromide.

Once formed, the Grignard reagent reacts normally with water, carbon dioxide, and benzophenone (see Scheme I); however, in all of these reactions phenylferrocene is a major product, despite rigorous precautions to exclude moisture. Of course deliberate hydrolysis of the Grignard reagent produced phenylferrocene (43%), but in the carbonation experiment phenylferrocene (25%) was produced along with *p*-ferrocenylbenzoic acid (44%). Upon addition of benzophenone to the Grignard reagent solution, phenylferrocene (58%) as well as *p*-ferrocenyltriphenylcarbinol (11%) was obtained. This behavior is quite analogous to the production of ferrocene accompanying the formation of ferrocenyl Grignard reagents[6] from haloferrocenes, and similarly this compound may arise from decomposition of the Grignard reagent to *p*-ferrocenylphenyl radicals, followed by abstraction of hydrogen from the solvent.

SCHEME I



Fc = ferrocenyl

Shechter and Helling also report the formation of biferrocenyl from the ferrocenyl Grignard reagents, especially at higher temperatures. The analogy was observed when *p*-bromophenylferrocene was treated with magnesium (with entrainment) at 100° in dimethylcarbitol (diethylene glycol dimethyl ether). Such a reaction mixture yielded only phenylferrocene (58%) and *p,p'*-diferrocenylbiphenyl[7] (15%) when carbonated, and phenylferrocene (58%) and *p,p'*-diferrocenylbiphenyl (18%) on treatment with benzophenone. Yields up to 57% of phenylferrocene were obtained on deliberate hydrolysis of the original reaction mixtures. It is most likely that at this higher temperature of formation the Grignard reagent does not survive to add to carbon dioxide or ketones.

m-Bromophenylferrocene also reacts with magnesium in refluxing tetrahydrofuran (with entrainment), but no addition products with carbon dioxide or benzophenone could be obtained. Hydrolysis yielded phenylferrocene (77%) and, in one attempted carbonation, a small amount *m,m'*-diferrocenylbiphenyl was obtained along with phenylferrocene (54%). Also in dimethylcarbitol, attempted preparations of the Grignard reagent, followed by addition to carbon dioxide

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(1) (a) Taken in part from the Ph.D. dissertation of A. K. Clark, The University of North Carolina, 1960; (b) Union Carbide Fellow, 1958–1959.

(2) Petroleum Research Fund Scholar, 1960–1961.

(3) National Science Foundation Undergraduate Research Participation Program participant.

(4) W. F. Little and A. K. Clark, *J. Org. Chem.*, **25**, 1979 (1960).

(5) W. F. Little, R. A. Berry, and P. Kannan, *J. Am. Chem. Soc.*, **84**, 2525 (1962).

(6) H. Shechter and J. F. Helling, *J. Org. Chem.*, **26**, 1034 (1961).

(7) This compound has been prepared by an independent synthesis from the arylation of ferrocene with bisdiazonium salts of benzidine and will be described more fully in a later publication.