General Procedure of Reaction of Fluoro Olefins with Superacids.—Superacid solutions were prepared by dissolving SbF_5–HSO_3F (1/1 mol/mol) in an equal volume of sulfuryl chlorofluoride (Allied Chemical Co.) and cooling to −78°. Fluoro olefins were then introduced into the above solution also at −78°. The acid was always in slight excess over the fluoro olefins. Covalent fluorides were ionized in a solution prepared of antimony pentafluoride in sulfuryl chlorofluoride (1/1.5 v/v) at −78°.

α-Fluoroethyl and α,α-difluoroethyl fluorosulfates were prepared by introducing I and II into neat fluorosulfuric acid at −78°, respectively, until the solutions were saturated. The pure fluorosulfates were obtained by vacuum distillation. Yields are generally high (90–95%) and the fluorosulfates have the following boiling points: $CH_3CHFOSO_2F$, bp 33° (35 mm); $CH_3F_2OSO_2F$, bp 25° (30 mm). Spectral properties (^1H and ^{19}F nmr) and analytical data are in accordance with structures.

Registry No.—I, 75-02-5; II, 75-38-7; III, 1691-13-0; IV, 359-11-5; V, 460-16-2; VI, 79-38-9; VII, 598-73-2; VIII, 359-37-5; IX, 116-14-3; X, 116-15-4; α-fluoroethyl fluorosulfate, 33515-40-1; α,α-difluoroethyl fluorosulfonate, 460-95-7.

Acknowledgment.—Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

The Mechanism of Benzophenone Reduction with the 2-Norbornyl Grignard Reagent

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The reduction of 0.5 equiv of benzophenone with a Grignard reagent from 2-*exo*-chloro-3-*exo*-deuterionorbornane is characterized by deuterium transfer. Carbonation of the unreacted Grignard reagent produces *endo*-norbornane-2-carboxylic acid. These results show that the benzophenone reduction occurs preferentially by a cis–exo eliminative transfer of D and MgCl.

In connection with our work on chiral Grignard reagents,[1-4] it was desirable to know more about the detailed mechanism of ketone reductions with some bicyclic Grignard reagents. A suitable system for a study of the type required appeared to be the reduction of benzophenone with a Grignard reagent from deuterium labeled 2-chloronorbornane.

Recent studies have revealed that the norbornyl Grignard reagent is a relatively slowly equilibrating mixture of epimers.[5-8] On the basis of nmr evidence, Krieghoff and Cowan[6] concluded that either *exo*- or *endo*-chloronorbornane gave an ethereal solution consisting, at equilibrium, of about a 54:46 mixture of endo–exo epimers of the Grignard reagent. Hill[5] similarly concluded that in THF norbornylmagnesium chloride was a 50:50 mixture of epimers. Jensen and Nakamaye[7] prepared norbornylmagnesium bromide in ether and using nmr found it to be a 59:41 mixture of endo–exo isomers. Carbonation of the equilibrium mixture gave a mixture of the epimeric acids, 56–60% the endo isomer. When the equilibrated Grignard reagent was allowed to react with 0.5 equiv of benzophenone at 0°, the nmr signal due to the exo isomer disappeared and the benzophenone was converted to the bromomagnesium salt of benzhydrol. Rapid carbonation of the unreacted Grignard reagent gave almost exclusively *endo*-2-norbornanecarboxylic acid. It was observed that the *endo*-norbornylmagnesium bromide remaining after reaction with benzophenone reequilibrated to the original equilibrium composition if allowed to stand for 1 day at room temperature. These workers also examined the Grignard reagent from norbornyl chloride and found it to be a 57:43 mixture of endo–exo isomers; the behavior toward benzophenone paralleled that of the Grignard reagent from norbornyl bromide.

Davies and Roberts[8] confirmed the results of Jensen and Nakamaye and found that *endo*-norbornylmagnesium bromide did not reequilibrate at 0° over a 3-hr period; at −78° the reagent was still about 95% the endo isomer after 5 days. They also observed that the reduction of benzophenone with equilibrated reagent did not take place at −15°, although an intense red-brown color (presumably due to a Grignard reagent–ketone complex) was produced at this temperature.

The experiments of Jensen and Nakamaye make it clear that the *exo*-norbornyl Grignard reagent reduces benzophenone much more rapidly than the endo isomer. These experiments do not, however, allow one to completely define the stereochemistry of the reduction process. We wanted to know the stereoselectivity associated with the transfer of hydrogen from C-3 of the Grignard reagent. In other words, does the reduction of benzophenone involve transfer of the exo magnesium and the exo hydrogen, the exo magnesium and the endo hydrogen, or a combination of these alternatives? The following experiments led to an answer to this question.

Addition of gaseous DCl to a pentane solution of norbornene[9] at −78° gave 2-*exo*-chloronorbornane in 81% yield. The amount, location, and orientation of deuterium in the chloride had to be rigorously determined (see below). Stille and coworkers treated 2,3-dideuterionorbornene with HCl in pentane at −78° and obtained approximately a 50:50 mixture of *endo*-

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[1] J. D. Morrison and R. W. Ridgway, *J. Amer. Chem. Soc.*, **91**, 4601 (1969).

[2] J. D. Morrison, D. L. Black, and R. W. Ridgway, *Tetrahedron Lett.*, 985 (1968).

[3] (a) J. D. Morrison, A. Tomash, and R. W. Ridgway, *ibid.*, 565 (1969); (b) J. D. Morrison and R. W. Ridgway, *ibid.*, 569 (1969).

[4] For a review of asymmetric reduction using chiral Grignard reagents, see J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, Chapter 5.

[5] E. A. Hill, *J. Org. Chem.*, **31**, 20 (1966).

[6] N. G. Krieghoff and D. O. Cowan, *J. Amer. Chem. Soc.*, **88**, 1322 (1966).

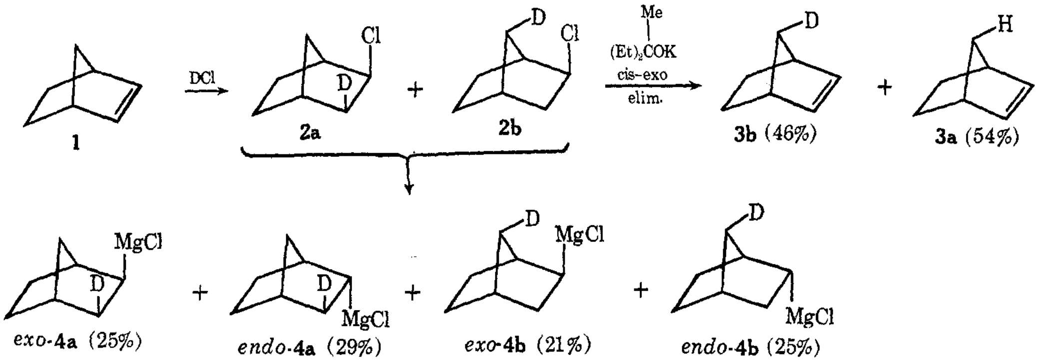
[7] (a) F. R. Jensen and K. L. Nakamaye, *ibid.*, **88**, 3437 (1966); (b) K. L. Nakamaye, Ph.D. Thesis, University of California, Berkeley, 1967.

[8] A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 317 (1969).

[9] L Schmerling, *J. Amer. Chem. Soc.*, **68**, 195 (1946).

SCHEME I

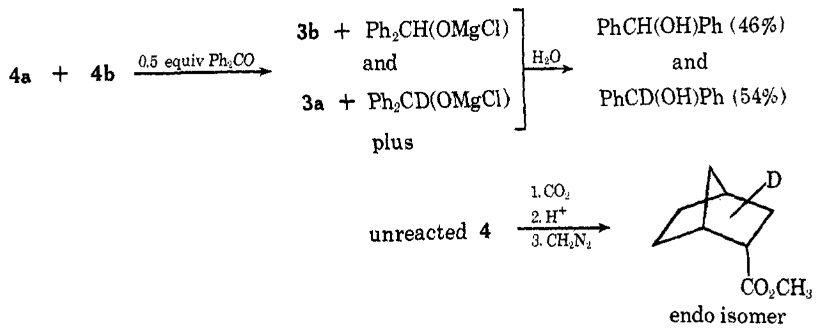
COMPOSITION OF THE GRIGNARD REAGENT FROM MONODEUTERIO-*exo*-NORBORNYL CHLORIDE[a]



[a] The approximate percentage of each isomer is calculated on the assumption that the chloromagnesium exo–endo ratio is the same (47:53)[6,7] for both the 3-exo and 7-syn deuterated isomers.

SCHEME II

REACTION OF THE GRIGNARD REAGENT 4 WITH 0.5 EQUIV OF BENZOPHENONE FOLLOWED BY CARBONATION OF THE UNREACTED 4



2,3-dideuterio-2-*exo*-chloronorbornane and 2-*exo*-chloronorbornanes with scrambled deuterium; the distribution of deuterium in the latter was not determined.[10] From a similar reaction in chloroform at −78°, Brown and McIvor[11] obtained norbornyl chloride which was, on the basis of a 220-MHz nmr analysis, about 55% 2-*exo*-chloro-3-*exo*-deuterionorbornane (**2a**) and 45% 2-*exo*-chloro-7-*syn*-deuterionorbornane (**2b**). It was concluded that there was less than 2%, if any, of a 5-deuterio isomer produced. Brown and Liu[12] reported that at −78° in methylene chloride DCl addition to norbornene produced about 60% of **2a**, 34% of **2b**, and 6% of a 2-*exo*-chloro-5-*exo*-deuterio isomer.

Our *exo*-norbornyl chloride from DCl addition in pentane at −78° contained one deuterium per molecule.[13] The amount of the 3-*exo*-deuterio isomer present was determined in the following way. Treatment of a sample of **2** with the potassium salt of 3-methyl-3-pentanol gave norbornene containing 46% of one deuterium per molecule (Scheme I). Since this elimination is known to proceed in a cis–exo manner,[10,12] 54% of one deuterium per molecule must have been present at the 3-exo position in the norbornyl chloride; *i.e.*, there was 54% deuterium and 46% hydrogen at the 3-exo position. A 220-MHz nmr spectrum of our chloride was virtually identical with that of the chloride prepared by Brown and McIvor,[11] a finding in excellent agreement with the conclusion from the above experiment and evidence that about 46% of the deuterium was at the 7-syn position in our *exo*-norbornyl chloride. For our purposes it is only important to know that about 54% of the deuterium is 3-exo, the exact distribution of the remainder is not critical, so long as none of it is 3-endo. The absence of 3-*endo*-deuterium was confirmed by the 220-MHz nmr spectrum.

Having established the composition of the chloride to be as shown in Scheme I,[14] the Grignard reagent was prepared and titrated to determine the exact amount present,[15] and then the equilibrated reagent was allowed to react with 0.5 equiv of benzophenone in ether at 0° (Scheme II). After the addition of the benzophenone (20 min) the reaction mixture was filtered, under nitrogen pressure, through a fritted glass filter into a flask cooled to −78°. The filtered solution was carbonated, thus converting the unreacted Grignard reagent to norbornane-2-carboxylic acid which was, in turn, converted to the methyl ester with diazomethane[16] (Scheme II). Glpc analysis of the methyl norbornane-2-carboxylate revealed the

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[10] J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *J. Amer. Chem. Soc.*, **88**, 4922 (1966).

[11] J. M. Brown and M. C. McIvor, *Chem. Commun.*, 238 (1969).

[12] H. C. Brown and K. Liu, *J. Amer. Chem. Soc.*, **89**, 3900 (1967).

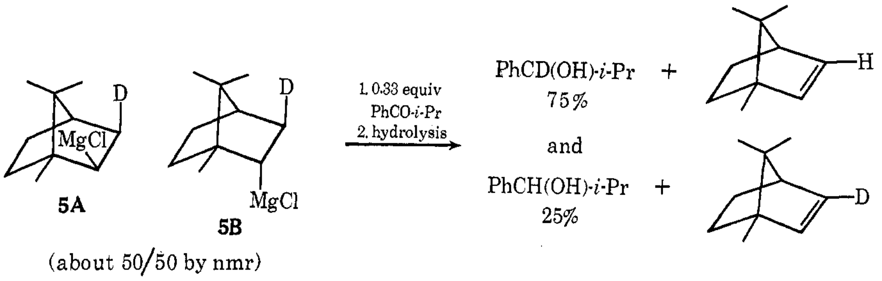
[13] Deuterium analysis by Josef Nemeth, Urbana, Ill.; supported by mass spectrometric and 220-MHz nmr analysis. We thank Dr. Peter Kleinhomer for the nmr work.

[14] In Scheme I only one enantiomer of each isomer is shown, but the *exo*-norbornyl chloride was, of course, racemic. The other enantiomer is omitted for clarity of illustration.

[15] S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 165 (1967). We have found that this method is much more accurate than acid–base titration.

[16] The carbonation and esterification sequences were carried out following the directions and observing the precautions of Nakamaye.[7b] Numerous control experiments confirmed the reliability of the method and the analytical procedure.

SCHEME III
REDUCTION OF ONE-THIRD EQUIVALENT OF PHENYL ISOPROPYL KETONE WITH THE ISOBORNYL (**5a**)/BORNYL (**5b**) GRIGNARD REAGENT[a]



[a] Reference 17.

presence of only the endo isomer. The precipitate from the Grignard reaction was hydrolyzed to yield benzhydrol. The benzhydrol contained 54% of one deuterium per molecule.

These experiments indicate that when an equilibrated Grignard reagent from norbornyl chloride is allowed to react with 0.5 equiv of benzophenone, reduction of the benzophenone occurs, in a formal sense, *via* a cis–exo eliminative transfer of H and MgCl. Within the limits of experimental error this is the exclusive mode of reduction under the conditions of this experiment.

After this work was completed it was reported[17] that the Grignard reagent (**5**) from *α-exo*-deuterioisobornyl chloride reduces phenyl isopropyl ketone with preferential transfer of deuterium. With **5** cis–exo eliminative transfer of "DMgCl" was judged to be preferred over cis–endo transfer of "MHgCl" by a factor of 3:1 (Scheme III). In the present work with the norbornyl system no cis–endo transfer was observed. Less preference for a cis–exo reduction mode in the isobornyl–bornyl Grignard system is probably a reflection of the influence of *gem*-dimethyl substitution in the C-7 bridge which reduces the energy difference between exo and endo transfer. In the absence of this influence there is, within the limit of detection, exclusive eliminative transfer of "DMgCl" from the exo direction when the exo and endo reagents (**4a**) compete for a limited amount of benzophenone. With the available information, however, one cannot exclude the possibility that the structure of the ketone is also a factor in determining the stereoselectivity of the eliminative transfer process.

Experimental Section

Deuterio-*exo*-norbornyl Chloride (2a + 2b).—Deuterium chloride, generated by the dropwise addition of phosphorus trichloride (9.15 g, 0.67 mol, distilled before use) to deuterium oxide (40 g, 2.0 mol, 99.8% deuterated), was passed into a well-stirred solution of norbornene (70.6 g, 0.75 mol) in pentane (250 ml, purified by percolation through a silica gel column) at −78°. After all the phosphorus chloride had been added to the D_2O, the mixture was heated until DCl was no longer evolved.

The reaction mixture was allowed to come to room temperature overnight. It was then washed with 0.1 *M* sodium bicarbonate solution (until neutral to litmus) and two 50-ml portions of water before drying ($MgSO_4$). The pentane solution was then filtered, combined with a pentane wash of the magnesium sulfate, and concentrated by distillation at atmospheric pressure. The residual oil was distilled through a Vigreux column and gave **2** as a colorless liquid, bp 49° (12 mm), 80 g (81% yield). Observed in the infrared spectrum of this liquid were characteristic norbornyl C–H stretching absorptions at 2865 and 2960 cm^{-1} and a C–D stretching absorption at 2180 cm^{-1}. The purity of the sample was established by glpc analysis on a 3-ft Pyrex column of 20% Carbowax 20M on Chromosorb W (acid washed) at 125° and 7 psi (retention time, 1.9 min). The sample was analyzed for deuterium content by mass spectrometric, 220-MHz nmr and falling drop methods,[13] which indicated 1 deuterium per molecule. The 220-MHz nmr spectrum was virtually identical with that reported by Brown and McIvor.[11]

Preparation of the Grignard Reagent (4) from Monodeuterated *exo*-2-Chloronorbornane.—Magnesium (2.4 g, 0.1 mol) was placed into a dry, 250-ml round-bottomed, three-necked flask equipped with dry condenser and magnetic stirrer. The flask was then flamed under dry nitrogen and allowed to cool. Dry ether (30 ml) and monodeuterated *exo*-2-chloronorbornane (about 30% of the total amount; *i.e.*, 30% of 13.1 g, 0.1 mol) were placed in the flask and allowed to stand undisturbed for 0.75 hr after which time a cloudiness appeared. The mixture was then stirred, and the reaction began. The remainder of the chloride, as the neat liquid, was added dropwise to the reaction mixture. Once the reaction ceased, dry ether (40 ml) was added to the mixture, and the reagent was refluxed under nitrogen for 2 hr. The solution was then pumped through a fritted glass filter into a dry, 250-ml, round-bottomed, three-necked flask filled with nitrogen. Titration of an aliquot of the filtered reagent with 1 *M* 2-butanol in xylene[15] indicated that the Grignard reagent had been produced in 96% yield.

Reaction of Benzophenone with the Grignard Reagent (4) from Monodeuterated *exo*-2-Chloronorbornane.—The flask containing the Grignard reagent was equipped with a dry condenser and a magnetic stirrer. Benzophenone (8 g, 0.044 mol) dissolved in sodium-dried ether (40-ml) was added to the flask containing the filtered Grignard reagent cooled to 0°. The reaction was characterized by the immediate appearance of a red color which faded as a white precipitate formed. After the addition of benzophenone (20 min), the reaction mixture was filtered through a fritted glass filter into a dry, 500-ml, round-bottomed, three-necked flask filled with nitrogen and cooled to −78°. An ether wash of the solid remaining behind was also pumped into the flask.

The solid diphenylmethoxymagnesium chloride on the fritted glass filter was hydrolyzed with saturated ammonium chloride solution. The resulting mixture was extracted several times with ether, and the combined extracts were dried ($MgSO_4$). The ether solution was filtered, combined with an ether wash of the magnesium sulfate, and concentrated by distillation at atmospheric pressure. A white solid (4.05 g) melting at 65–66° crystallized from a solution of the residual oil in petroleum ether (lit.[18] for benzhydrol, 69°).

A C–D stretching absorption at 2240 cm^{-1} and an OH absorption were observed in the infrared spectrum of the solid (Nujol and halocarbon mulls). Glpc analysis of an ether solution of the solid indicated the presence of a small amount of benzophenone. Deuterium content of the benzhydrol as determined by mass spectral analysis was 0.54 deuterium atom per molecule, the same as that determined by nmr using the phenyl protons as an internal integration reference. Comparison of the nmr spec-

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[17] J. F. Fauvarque, *C. R. Acad. Sci., Ser. C*, 1053 (1971).

[18] "Heilbron's Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965, p 1286.

tra of benzophenone and benzhydrol showed that the aromatic protons of the former absorb further downfield than those of the latter, so that the presence of a small amount of benzophenone in the sample would not interfere with the deuterium analysis.

Carbonation of the Remaining Grignard Reagent.—The carbonation was begun 20 min after the reaction of the Grignard reagent with 0.5 equiv of benzophenone. Crushed Dry Ice contained in a 250-ml erlenmeyer flask was slowly added through Gooch tubing to the unconsumed Grignard reagent contained in a round-bottomed flask equipped with condenser and mechanical stirrer. Once all the Dry Ice had been added, the reaction mixture was allowed to attain room temperature overnight.

The mixture was then treated with 6 *N* hydrochloric acid until two clear layers separated. The aqueous layer was extracted several times with ether, and the extracts were combined with the organic layer. The yield of norbornyl acid was 62% of the theoretical amount as determined by titration of an aliquot of the ethereal solution in 65% methanol with standard sodium hydroxide solution to a phenolphthalein end point. The solution of norbornyl acid was then extracted with three 50-ml portions of 2 *N* sodium hydroxide solution and one 50-ml portion of water. The combined base extracts were held for the methylation step.

Reaction of Norbornyl Acid with Diazomethane.—Diazomethane was prepared from Diazald (21.5 g, 0.1 mol).[19]

Just prior to the reaction with diazomethane, the norbornyl acid was liberated from the sodium salt by acidification and extraction with ether. Esterification was accomplished by the dropwise addition of the dried norbornyl acid solution to diazomethane at 0°. The mixture was allowed to stand until nitrogen was no longer evolved and was then treated with 3 *M* sulfuric acid until the disappearance of the yellow color. The two layers were separated, and the aqueous layer was extracted several times with ether. The extracts were combined with the organic layer, washed with two 50-ml portions of 0.05 *M* sodium carbonate solution, and then dried ($MgSO_4$). The ethereal solution was then filtered, combined with an ether wash of the magnesium sulfate, and concentrated by distillation at atmospheric pressure. Analysis of the residual oil by glpc gave one peak, with a retention time of 9.5 min. Glpc analysis was carried out using a 6 ft × 0.25 in., 15% Apiezon L on Chromosorb W-HP, 80–100 mesh column coupled to a 6 ft × 0.25 in., 20% Carbowax 20M on Chromosorb W-HP, 80–100 mesh column, 210°, 120 ml/min He flow rate. An authentic sample of the methyl ester of *endo*-norbornane-2-carboxylic acid gave one peak with the same retention time, whereas a mixture of the endo and exo isomers gave a second peak at 12.0 min. Analysis of the oil was repeated using a 10 ft × 0.25 in. column of 25% castorwax on 60–80 Chromosorb P at 120° and 60 ml/min. One peak was observed at 73 min, the retention time of the endo isomer under these conditions.

Dehydrohalogenation of Monodeuterated *exo*-2-Chloronorbornane.—Potassium (3 g, 0.075 mol) was slowly introduced under nitrogen into a dry flask containing 3-methyl-3-pentanol (51 g, 0.5 mol) and equipped with condenser and magnetic stirrer. As the concentration of potassium alkoxide increased, the solution acquired a reddish-brown hue, and the reaction became less vigorous. Completion of reaction was effected by heating.

Monodeuterated *exo*-2-chloronorbornane (6.6 g, 0.05 mol) was added all at once to the solution of potassium alkoxide, and the mixture was refluxed under nitrogen for 1 hr. Refluxing was then continued for a total of 17 hr while sweeping continuously with nitrogen. The norbornene (0.6 g) which formed was scraped from the inner surface of the condenser and from the tube leading into a trap cooled with a Dry Ice–isopropyl alcohol mixture.

Glpc analysis of an ether solution of the collected norbornene indicated the presence of less than 1% 3-methyl-3-pentanol. The sample was analyzed for deuterium content by low voltage mass spectroscopy, 0.46 deuterium atoms per molecule.

Registry No.—**2a**, 33495-71-5; **2b**, 33495-72-6; *exo*-**4a**, 33495-73-7; *endo*-**4a**, 33495-74-8; *exo*-**4b**, 33495-75-9; *endo*-**4b**, 33495-76-0; benzophenone, 119-61-9.

Acknowledgment.—We thank the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. G. L. was an NDEA Fellow for the period 1967–1970.

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(19) Th. J. de Boer and H. J. Backer, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 943.

The Nucleophilic Reactivity of Peroxy Anions[1]

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We report rate data on the reactivity of several peroxy anions with the anions of bromoacetic acid, α-bromo-*p*-toluic acid, *p*-cyanobenzoic acid, *p*-nitrophenylsulfuric acid, and with *p*-nitrophenylacetate and 2,4-dinitrochlorobenzene. The magnitude of the α effect, as measured by the ratio log (k_{HOO^-}/k_{HO^-}), appears to be linearly correlated with the magnitude of the product $|\alpha\beta|$ of the coefficients of the Edwards equation (the oxibase scale): $\log k/k_0 = \alpha E_n + \beta H$.

Edwards and Pearson[3] recognized a class of nucleophiles which showed exceptionally high reactivity toward a variety of substrates relative to their basicity toward hydrogen. This class is structurally characterized by an unshared pair of electrons on the atom adjacent or α to the nucleophilic atom. This rate enhancement is known as the α effect. Both uncharged nucleophiles such as hydrazine and hydroxylamine as well as anionic nucleophiles such as the peroxy anions exhibit this effect but to varying degrees toward various substrates. There have been a number of recent discussions of the α effect.[4] In this study, we have examined the reactivity of the anions of hydrogen peroxide, methyl hydroperoxide, *tert*-butyl hydroperoxide, and several peroxycarboxylic acids toward several substrates with a view toward defining more precisely the factors influencing the magnitude of the α effect.

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(1) Presented in part at the 156th National Meeting of the American Chemical Society, Sept 1968, ORGN 70.

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(3) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

(4) (a) G. Klopman, K. Tsuda, J. B. Louis, and R. E. Davis, *Tetrahedron*, **26**, 4549 (1970); (b) J. D. Aubort and R. F. Hudson, *Chem. Commun.*, 937, 938, 1378 (1970); (c) L. A. Kaplan and H. B. Pickard, *ibid.*, 1500 (1969); (d) M. Goodman and C. B. Glaser, *J. Org. Chem.*, **35**, 1954 (1970); (e) M. J. Gregory and T. C. Bruice, *J. Amer. Chem. Soc.*, **89**, 4400 (1967); (f) T. C. Bruice, A. Donzel, R. W. Huffman, and A. R. Butler, *ibid.*, **89**, 2106 (1967); (g) A. R. Fersht and W. P. Jencks, *ibid.*, **92**, 5442 (1970); (h) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, pp 107–111; (i) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 452–453; (j) J. E. Dixon and T. C. Bruice, *J. Amer. Chem. Soc.*, **93**, 3248 (1971).