chloride. After the precipitate had been washed with ether, the combined ethereal solutions were dried, concentrated, and distilled in a short-path still (130° at 0.25 mm.) to separate 1.314 g. (83%) of the diols **24** identified by comparison of infrared spectra.

A 1.58-g. (0.01 mole) sample of the diols **24** (obtained by reduction of the keto ester **21b** with sodium borohydride) was oxidized with a solution of 2.0 g. (0.02 mole) of chromic acid and 2 ml. of concentrated sulfuric acid in 50 ml. of water. After the mixture had been stirred at room temperature for 3 hr., it was saturated with ammonium sulfate and extracted with ether. Extraction of the ethereal solution with aqueous sodium bicarbonate followed by acidification of the aqueous extract, saturation with ammonium sulfate, and extraction with ether separated 1.5 g. of crude acidic product. Fractional crystallization from cyclohexane-ether mixtures separated 0.843 g. (50%) of the crude keto acid **21a**, m.p. 50–53°, whose melting point was raised to 62–63° by recrystallization. The identity of this oxidation product with the keto acid **21a** was established by a mixed melting point determination and comparison of infrared spectra.

The Chemistry of Carbanions. I. The Reaction of Triphenylmethane with Potassium[1]

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The reaction of triphenylmethane with potassium in 1,2-dimethoxyethane produced solutions of triphenylmethyl potassium containing various cleavage and reduction products derived from triphenylmethane. The addition of butadiene to the reaction mixture prevented the formation of the by-products from triphenylmethane, the diene being converted to *trans*-2-butene and mixtures of octadienes and dodecatrienes.

For a study of the relative stabilities of enolate anions derived from unsymmetrical ketones, we desired a base–solvent system which could be conveniently prepared and would permit rapid and quantitative conversion of a ketone to a solution of its enolate anions. Since distinct advantages, both in terms of the solubility and reactivity of carbanions, are derived from use of the solvents 1,2-dimethoxyethane,[2] dimethylformamide,[2c,3] and dimethyl sulfoxide,[2c,4] we considered use of only these solvents in our study. Of these solvents, we consider 1,2-dimethoxyethane by far the most convenient in preparative work because of its stability and relatively low boiling point facilitating its removal from reaction mixtures. In addition dilute solutions of potassium metal may be obtained[5] in 1,2-dimethoxyethane. Since the most suitable base appeared to be the deeply colored triphenylmethyl anion, we focused our attention on possible methods for the preparation of solutions of metal derivatives of the triphenylmethyl anion in 1,2-dimethoxyethane, preferably in the absence of other contaminants.[6]

In an effort to obtain this base–solvent combination, solutions of triphenylmethane in 1,2-dimethoxyethane were treated with sodium hydride, metallic sodium, and metallic potassium. Although little if any reaction was achieved in the first two cases, reaction of potassium with excess triphenylmethane (**1**) in 1,2-dimethoxyethane effected complete conversion of the potassium to triphenylmethylpotassium (**2**) in approximately eighteen hours. However, it was apparent that this reaction was not to be free from by-products since no hydrogen was evolved in the course of the preparation. The various by-products formed are summarized in Chart I.

The nature of these by-products suggests strongly that the initial reaction of triphenylmethane with potassium forms the ion radical **7**[7] which then dimerizes and cleaves as in **8**.[8,9]

Alternatively the original ion radical **8** may react

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(1) This research has been supported by Grant No. 594A from the Petroleum Research Fund.

(2) (a) G. Wittig and E. Stahnecker, *Ann.*, **605**, 69 (1957); (b) H. D. Zook and T. J. Russo, *J. Am. Chem. Soc.*, **82**, 1258 (1960); (c) H. E. Zaugg, *ibid.*, **83**, 837 (1961).

(3) (a) N. Kornblum, P. J. Berrigan, and W. J. Le Noble, *ibid.*, **82**, 1257 (1960); (b) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *ibid.*, **82**, 2895 (1960); (c) H. E. Zaugg, *ibid.*, **82**, 2903 (1960); (d) H. E. Zaugg, D. A. Dunnigan, R. J. Michaels, L. R. Swett, T. S. Wang, A. H. Sommers, and R. W. DeNet, *J. Org. Chem.*, **26**, 644 (1961).

(4) (a) D. J. Cram, B. Rickborn and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960); (b) A. Schriesheim, J. E. Hofmann, and C. A. Rowe, *ibid.*, **83**, 3731 (1961); (c) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); (d) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *ibid.*, **83**, 3678 (1961); (e) J. J. Bloomfield, *J. Org. Chem.*, **26**, 4112 (1961); (f) R. Fuchs, G. E. McCrary, and J. J. Bloomfield, *J. Am. Chem. Soc.*, **83**, 4281 (1961).

(5) J. L. Downs, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959).

(6) The following references summarize the methods which have been used to prepare triphenylmethylsodium and triphenylmethylpotassium. (a) K. Ziegler and F. Thielmann, *Ber.*, **56**, 1740 (1923); (b) C. A. Kraus and T. Kawamura, *J. Am. Chem. Soc.*, **45**, 2756 (1923); (c) R. Levine, E. Baumgarten, and C. R. Hauser, *ibid.*, **66**, 1230 (1944); (d) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Synthesis," Coll. Vol. 2, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 607; (e) J. Eisch and W. C. Kaska, 138th National Meeting of the American Chemical Society, New York, N. Y., September 11–16, 1960, Abstracts of Papers, p. 52-P; see also H. Normant and B. Angelo, *Bull. soc. chim. France*, 354 (1960); (f) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); (g) G. W. H. Scherf and R. K. Brown [*Can. J. Chem.* **38**, 2450 (1960)] have reported the formation of triphenylpotassium from triphenylmethane and potassium in 1,2-dimethoxyethane. However, these authors apparently did not examine the reaction mixture to learn what other materials were present.

(7) The ion radicals derived from biphenyl and naphthalene (ref. 6a) have served as strong bases which were used to prepare the triphenylmethyl anion.

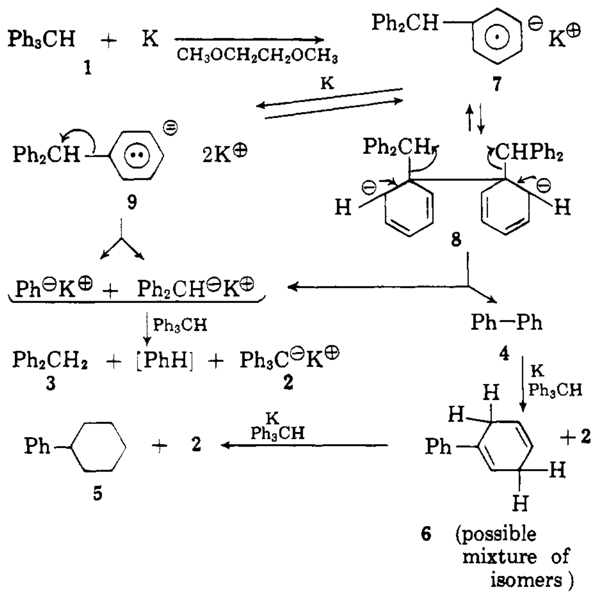

Chart I

with another atom of potassium and then cleave (as in **9**).[8]

Since this preparative sequence produced the variety of undesirable by-products indicated in Chart I, the above mechanistic considerations led us to explore the use of butadiene **10** as a source of the initially formed ion radical **11**. In this way the reduction products of the ion radical might be expected to be volatile and would offer no complications in reaction mixtures. The results of this reaction, summarized in Chart II, confirmed our expectation in that the reaction occurred significantly more rapidly and the various by-products indicated in Chart I were avoided. The only complication proved to be the formation of small amounts of the C_8 dienes **13**[10] from dimerization of the ion radical **11** (or the radical **14**)[11,12] and the C_{12} trienes **15** and **16** from addition of the ion radical **11** (or the radical **14**) followed by coupling of these new ion radicals with **11**. Although, in principle, these C_8 and C_{12} hydrocarbons could be avoided by adding the butadiene sufficiently slowly, in practice we have been unable to eliminate these hydrocarbon by-products.

By application of either of these procedures we have been able to prepare conveniently solutions of triphenylmethylpotassium in 1,2-dimethoxyethane which are approximately one molar in the base. The solutions, which are stable for at least 24 hours, could be used to convert simple ketones, *e.g.* 2-heptanone, to a solution of mixtures of the corresponding enolate anions. Our studies of the position of equilibrium between various enolate anions will be reported in a subsequent paper.

Experimental[13]

Reaction of Potassium with Triphenylmethane.—After a mixture of 6.2402 g. (0.0256 mole) of triphenylmethane-0.9437 g. (0.0241 g.-atom) of potassium, and 25 ml. of 1,2, dimethoxyethane[14] had been stirred at room temperature under a nitrogen atmosphere for 16 hr., 2.0781 g. (0.02078 mole or 0.86 equiv. corresponding to a 0.83 *M* solution of potassium triphenylmethyl) of 4-methyl-2-pentanone was required to discharge the red color of the solution. The mixture was diluted with 2 ml. of water and extracted with ether. The ethereal extract was dried, mixed with 4.7052 g. of phenanthrene (as a standard), and then concentrated. Analysis of the crude product[15] indicated the presence of 4.85 g. (78%) of triphenylmethane. Comparison of the mass spectrum of the crude product with the mass spectrum of pure triphenylmethane indicated the presence of no peaks above *m/e* 244 not attributable to triphenylmethane. Thus, no significant quantities of partially reduced triphenylmethane derivatives are present.

From a comparable reaction employing 10.056 g. (0.041

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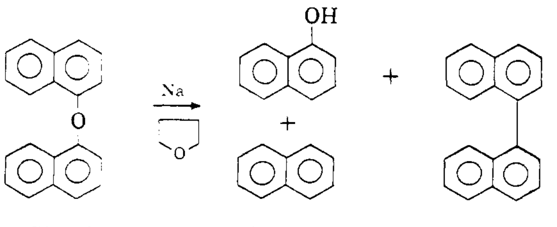
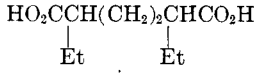
(8) D. H. Eargle, Jr. [141st National Meeting of the American Chemical Society, Washington, D. C., March 26–29, 1962, Abstracts of Papers, p. 33-O] has reported the reaction of aryl ethers with alkali metals in 1,2-dimethoxyethane or tetrahydrofuran to form an ion radical which subsequently reacts as indicated in the accompanying equation. We believe processes analogous to those represented in structures **8** and **9** provide a satisfactory explanation for these results.



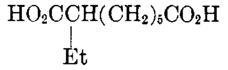
(9) The subsequent reaction of triphenylmethane (**1**) with potassium and biphenyl (**4**) is analogous to the probable mechanism of the Birch reduction. (a) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959); *ibid.*, **82**, 751 (1960); (b) A. Streitweiser, Jr., and S. Suzuki, *Tetrahedron*, **16**, 153 (1961); (c) H. E. Zimmerman, *ibid.*, **16**, 169 (1961).

(10) The preparation and characterization of these dienes has recently been reported by W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

(11) The formation, dimerization and carbonation of the butadiene ion radical to form, after reduction, acids *i* to *iii* has been reported by National Distillers and Chemical Corp., British Patent 756,385, September 5, 1956; *Chem. Abstr.*, **51**, 15557 (1957).


$HO_2CCH(CH_2)_2CHCO_2H$ with Et under each CH: $HO_2C\underset{Et}{C}H(CH_2)_2\underset{Et}{C}HCO_2H$

i


$HO_2C\underset{Et}{C}H(CH_2)_5CO_2H$

ii

$HO_2C(CH_2)_8CO_2H$

iii

(12) For other recent examples of ion radical dimerizations see (a) C. C. Overberger and A. M. Schiller, *J. Org. Chem.*, **26**, 4230 (1961); (b) J. W. Dodd, F. J. Hopton, and N. S. Hush, *Proc. Chem. Soc.*, **61** (1962).

(13) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Baird Model B or a Perkin-Elmer Model 21 infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11MS. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory. Unless otherwise stated magnesium sulfate was employed as a drying agent. The n.m.r. spectra were determined at 60 Mc. with a Varian Model A-60 n.m.r. spectrometer. The mass spectra were determined with a CEC Model 21-130 mass spectrometer.

(14) 1,2-Dimethoxyethane which had been distilled from sodium was dried immediately prior to use by distillation from lithium aluminum hydride.

(15) A gas chromatographic column packed with Dow Corning Silicone Fluid, No. 710, suspended on ground firebrick was employed for this analysis.

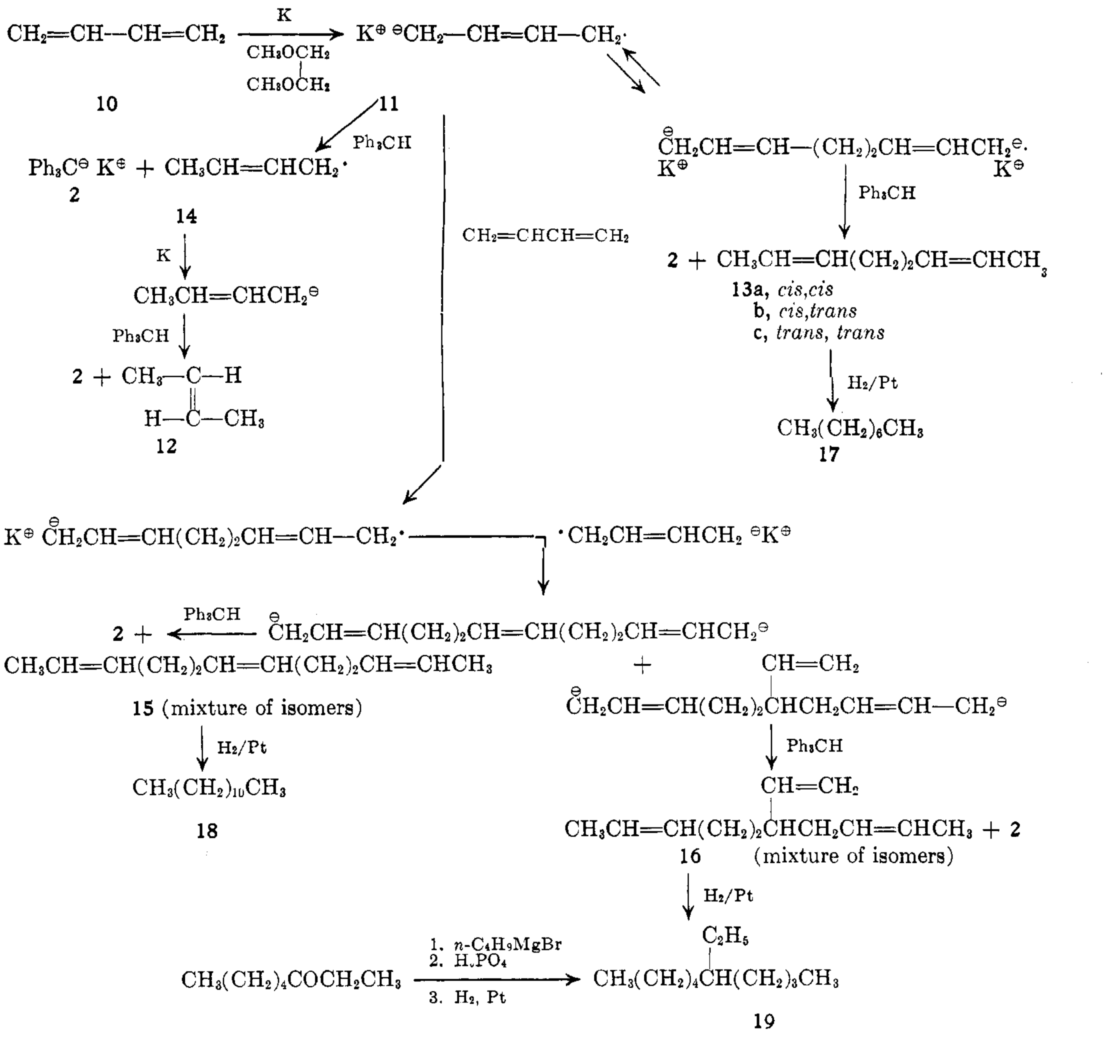


Chart II

mole) of triphenylmethane, 1.5256 g. (0.039 g.-atom) of potassium, and 50 ml. of 1,2-dimethoxyethane, a 5-ml. aliquot of the solution was added, with stirring, to 4 ml. of deuterium oxide. After the resulting mixture had been extracted with ether, the extract was dried and concentrated. Recrystallization of the residue from methanol-*d*, afforded 0.37 g. (37%) of monodeuteriotriphenylmethane with infrared absorption[16] at 3015 and 3050 cm.$^{-1}$ (aromatic C—H) and at 2130 cm.$^{-1}$ (C—D). The n.m.r. spectrum[16] lacks absorption at 4.56 τ where the spectrum of the nondeuterated sample exhibits a singlet (aliphatic C—H).

A solution of potassium triphenylmethyl, prepared from 10.8737 g. (0.044 mole) of triphenylmethane, 1.5268 g. (0.039 g.-atom) of potassium, and 45 ml. of 1,2-dimethoxyethane was poured into 25 ml. of water. After the ether extract of the resulting mixture had been dried and concentrated, distillation of the residue afforded 1.5435 g. of fractions, b.p. 38–62° (1.3 mm.), n^{25}_{D} 1.5739–1.5804, containing (in order of elution)[15] phenylcyclohexane (*5*, 2% yield), one or more phenylcyclohexadienes (**6**, 2% yield), biphenyl (**4**, 6% yield), and diphenylmethane (**3**, 16% yield). From similar reactions the proportion of phenylcyclohexane (**5**) was found to decrease when excess triphenylmethane was employed. The diphenylmethane (**3**), biphenyl (**4**), and phenylcyclohexane (**5**) were shown to be identical with authentic samples by comparison of retention times,[15] infrared[16] and mass spectra. The remaining peak, tentatively identified as one or more phenylcyclohexadienes **6**, was collected and its mass spectrum was found to exhibit intense peaks at *m/e* 156, 155, 154, 153, and 152 (molecular ion and fragments resulting from loss of hydrogen) and at 91 ($C_7H_7^{\oplus}$).

Reaction of Potassium with Triphenylmethane and Butadiene.—A mixture of 22.383 g. (0.0917 mole) of triphenylmethane, 3.2824 g. (0.0843 g.-atom) of potassium, and 100 ml. of 1,2-dimethoxyethane was placed in a flask fitted with a Dry Ice condenser and 15 ml. (10 g. or 0.18 mole) of 1,3-butadiene[17] was distilled into the mixture with stirring over a 20-min. period. The reaction was complete within 30 min. Analysis[15] of the gases above the reaction solution indicated the presence of *trans*-2-butene (**12**) and butadiene. Addition of 8.7333 g. (0.0766 mole or 0.91 equiv.) of 2-heptanone discharged the red color of the potassium triphenylmethyl. The resulting mixture was diluted with 20 ml. of water and extracted with ether. After the ethereal extract had been dried and concentrated, 8.5709 g. of ethylbenzene was added as an internal standard and the mixture was analyzed by gas chromatography.[15] The mixture was estimated to contain 8.48 g. (97% recovery) of 2-heptanone, 1.7 g. of the octadienes **13** and 1.6 g. of the dodecatrienes **15** and **16** as well as 1.0 g. of a mixture of higher molecular weight components believed to be a mixture of hexadecatetraenes. A collected sample of this

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(16) Determined in carbon tetrachloride solution.

(17) The diene was purified by passing it through a drying tube containing activated molecular sieves, no. 4A.

latter mixture of components has mass spectral peaks at m/e 218, 203, 189 etc. attributable to a $C_{16}H_{26}$ hydrocarbon and lacks peaks at 168 and 160 attributable to the molecular ions of diphenylmethane and phenylcyclohexane. A peak of very low intensity at m/e 154 suggests the presence of a very small amount of biphenyl in the mixture.

A combination of fractional distillation and collection from a gas chromatographic column[15] separated a mixture of the three 2,6-octadienes which has infrared absorption[18] at 3000 cm.$^{-1}$ (vinyl C—H), 2910 and 2840 cm.$^{-1}$ (saturated C—H), 1650 cm.$^{-1}$ (unconj. C=C), and 965 cm.$^{-1}$ (*trans* CH=CH) with an intense peak in its mass spectrum at m/e 110 ($C_8H_{14}^{\oplus}$). A solution of 35.2 mg. (0.32 mmole) of the diene mixture **13** in ethanol was hydrogenated over the catalyst derived from 10.7 mg. of platinum oxide at room temperature and atmospheric pressure. After 38 min. the hydrogen uptake (16.0 ml. or 2.06 equiv.) ceased and the mixture was filtered. The filtrate exhibited a single gas chromatographic peak[18] with the retention time of *n*-octane other than the solvent peak; the mass spectrum of a collected sample of the product was identical with the spectrum of *n*-octane. Samples of each of the three dienes **13** were collected[19] from the mixture (containing 31% of **13c**, 26% of **13b**, and 43% of **13a**) were identified by comparison of their infrared spectra with published spectra.[10]

Fractional distillation and subsequent collection[15] separated a mixture of the dodecatrienes **15** and **16**; the chromatogram of the mixture exhibits two triplets. The triplet first eluted has infrared absorption[16] at 965 cm.$^{-1}$ (*trans* CH=CH) and 912 cm.$^{-1}$ (CH=CH$_2$) and has a peak in the mass spectrum at m/e 164 ($C_{12}H_{20}^{\oplus}$). The second triplet eluted has infrared absorption[16] at 968 cm.$^{-1}$ (*trans* CH=CH) with a peak in the mass spectrum at m/e 164 ($C_{12}H_{20}^{\oplus}$). A solution of 14.9 mg. (0.09 mmole) of the triene mixture **15** and **16** in ethanol was hydrogenated over the catalyst from 15.9 mg. of platinum oxide at room temperature and atmospheric pressure. After 39 min. the hydrogen uptake (6.12 ml. or 2.79 equiv.) ceased. After filtration, analysis[15] of the filtrate indicated the presence of 5-ethyldecane (**19**, 52%, first eluted) and dodecane (**18**, 48%, last eluted). Collected samples of each hydrocarbon were identified with authentic samples by comparison of retention times and mass spectra.

Reaction of 3-octanone with butylmagnesium bromide afforded 51% of 5-ethyl-5-decanol, b.p. 100–101° (9 mm.), $n^{25}\mathrm{D}$ 1.4411 [lit., b.p. 119–120° (20 mm.),[20] $n^{25}\mathrm{D}$ 1.4401[21]]. Dehydration of this alcohol by reaction with 85% phosphoric acid at 95–105° for 5 hr. produced a mixture of at least[15] three olefins, b.p. 27–68° (12 mm.), $n^{26}\mathrm{D}$ 1.4352; yield 85%. A solution of 458.5 mg. (2.74 mmoles) of this olefin mixture in acetic acid was hydrogenated over the catalyst from 30.2 mg. of platinum oxide at room temperature and atmospheric pressure. After the hydrogen uptake (65.6 ml. or 1.00 equiv.) ceased (32 min.), filtration followed by distillation of the filtrate afforded 177.6 mg. (38%) of 5-ethyldecane (**19**), b.p. 67–78° (12 mm.), $n^{24}\mathrm{D}$ 1.4424 [lit.,[22] 94.7° (20 mm.)].

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[18] A column packed with Dow Corning Silicone Fluid No. 550 suspended on ground firebrick was employed for this analysis.

[19] A column packed with a solution of silver nitrate in tetraethylene glycol suspended on ground firebrick was employed.

[20] N. Rabjohn and M. J. Latina, *J. Am. Chem. Soc.*, **76**, 1389 (1954).

[21] O. R. Quayle and K. O. Smart, *ibid.*, **66**, 935 (1944).

[22] K. Ziegler, H. Grimm, and R. Willer, *Ann.*, **542**, 90 (1939).

The Carbanion Mechanism for β-Elimination Reactions. IV. The Effect of β-Chlorine and Fluorine Substituents on Ease of Carbanion Formation[1]

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The rates of sodium methoxide-catalyzed hydrogen exchange of four aromatic halides have been found to stand in the order m-$C_6H_4F_2$ > 1,2,4-$C_6H_3Cl_3$ > m-FC_6H_4Cl > m-$C_6H_4Cl_2$. The hydrogen atom that undergoes exchange is almost undoubtedly the one that has two *ortho* halogen substituents. From the reactivity sequence observed it follows that β-fluorine substituents facilitate carbanion formation more than β-chlorine substituents do. The rate of dehydrohalogenation of 1,1-difluoro-1,2,2-trichloroethane has been found to be 55 times as large as the rate of carbanion formation of 1,1,1-trifluoro-2,2-dichloroethane, but since the dehydrohalogenation is not accompanied by deuterium exchange in deuterium oxide or deuteriomethanol, it does not necessarily involve carbanion formation.

Among the strongest arguments that most alkaline β-dehydrohalogenations of organic halides proceed by a concerted rather than a carbanion mechanism is the fact that the reactivity sequence is usually RI > RBr > RCl ≫ RF[2] and dehydrohalogenation in a deuteriated solvent is not accompanied by deuterium exchange of the unreacted starting material.[3] The lack of deuterium exchange shows that any carbanion formation that occurs is not reversible. If the reaction involves irreversible carbanion formation, the dehydrohalogenation rate must be equal to the carbanion-formation rate. However, it would be expected that the various halogens would stabilize β-carbanions only by the inductive effect so that a reactivity sequence RF > RCl > RBr > RI, the opposite of that observed, would be expected for dehydrohalogenation *via* rate-controlling carbanion formation. One of the weak points in this argument, however, is the dearth of direct quantitative measurements on the effect of β-halogen on reactivity in carbanion formation. This brings to mind the acidity of the hydrogen atom of haloforms, which was once thought due to the inductive effect of the α-halogens; kinetic experiments showed that α-halogens facilitate carbanion forma-

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[1] Abstracted from the Ph.D. thesis of Paul B. Langford, 1962. J. Hine and O. B. Ramsay, *J. Am. Chem. Soc.*, **84**, 973 (1962) and ref. 3 and 2 therein are considered parts III, II, and I, respectively.

[2] *Cf.* E. D. Hughes, C. K. Ingold, *et al.*, *J. Chem. Soc.*, 2043, 2049 (1948); N. B. Chapman and J. L. Levy, *ibid.*, 1673 (1952), and references cited therein.

[3] P. S. Skell and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 1661 (1945); D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor, and C. R. Hauser, *ibid.*, **74**, 5599 (1952).