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.), $n^{25}\text{D}$ 1.4411 [lit., b.p. 119–120° (20 mm.),[20] $n^{25}\text{D}$ 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.), $n^{26}\text{D}$ 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.), $n^{24}\text{D}$ 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 $m\text{-}C_6H_4F_2 > 1,2,4\text{-}C_6H_3Cl_3 > m\text{-}FC_6H_4Cl > m\text{-}C_6H_4Cl_2$. 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 $RI > RBr > RCl \gg RF$[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).

tion in the order I ~ Br > Cl > F, almost the reverse of the order to be expected from the inductive effect.[4]

From the experiments of Roberts and coworkers on the reactions of potassium amide with *o*-deuteriofluorobenzene and *o*-deuteriochlorobenzene it seems clear that carbanions are produced more rapidly from the former.[5] However, for neither compound was a rate constant reported. Bunnett, Miles, and Nahabedian studied the formation of *m*-dihalobenzenes from 2,6-dihalobenzaldehydes and alkali, a reaction that appears to involve the intermediate formation of a 2,6-dihalophenyl anion.[6] The variation in reaction rate was less than threefold for the series bromochloro, dichloro, chlorofluoro, and difluoro, perhaps because the greater activating inductive effect of fluorine was counteracted by steric acceleration of the cleavage of the bromo and chloro aldehydes.

To add to our knowledge of the effect of β-halogen substituents on ease of carbanion formation we have studied the rates of deuterium exchange of several fluoro- and chlorobenzenes and also the reaction of 1,1-difluoro-1,2,2-trichloroethane with base.

Experimental

Reagents.—Methanol was purified by the method of Fieser;[7] deuteriomethanol (Merck Sharpe & Dohme of Canada, Ltd.) was found by n.m.r. measurements to be 95% deuteriomethanol and 5% methanol. Some deuteriomethanol was prepared from anhydrous sodium methoxide and heavy water; the resultant solution was fractionally distilled, the methanol dried with Drierite and refractionated to give ~65% deuteriomethanol–35% methanol. The refractive indices of the halogenated benzene derivatives used (*m*-difluorobenzene, $n^{21}\text{D}$ 1.4379, $n^{29}\text{D}$ 1.4339; *m*-chlorofluorobenzene, $n^{29}\text{D}$ 1.4907; *m*-dichlorobenzene, $n^{29}\text{D}$ 1.5430; 1,2,4-trichlorobenzene, $n^{27}\text{D}$ 1.5685) are all within 0.0010 of values reported in the literature.

Refractionation of 1,1-difluoro-1,2,2-trichloroethane, prepared by the method of Henne and Ladd, gave material of b.p. 70.5–70.9° (740 mm.), $n^{21}\text{D}$ 1.3910 (reported $n^{20}\text{D}$ 1.3889).[8]

Preparation of Deuterio Di- and Trihalobenzenes.—In a typical preparation, 0.6 ml. of *m*-difluorobenzene and 2.40 ml. of 1.327 *M* sodium methoxide in deuteriomethanol were kept at 50° for 97 hr. in a 12-ml. sealed tube. The tube was cooled, the contents shaken with 3 ml. of water, and the resultant nonaqueous layer shaken with another 3 ml. of water. The wet deuterio-*m*-difluorobenzene was dried with little silica gel to give 0.45 ml. of product, having a slight straw color that disappeared on standing overnight. A similar process was used for the deuteriation of *m*-chlorofluorobenzene, *m*-dichlorobenzene, and 1,2,4-trichlorobenzene, except that the materials were exposed to the basic deuteriomethanol at 100° for 18, 68, and 10 hr., respectively.

Deuterium Analyses.—Upon treatment as described in the preceding paragraph the halogenated benzene derivatives were found to acquire new absorption maxima in their infrared spectra and to lose old maxima. It was further found that this spectral change could be completely reversed by treatment with sodium methoxide in ordinary methanol. For each of the compounds studied it was found that at least one of the new absorption bands due to the deuteriated compound appeared at a wave length at which absorption by the protium compound is negligible. This band was used in analysis for the deuterium compound, and for the protium compound the band that decreased most in intensity on deuteriation was used. To calculate the extent of deuteriation it was assumed that the pure deuterio compound would not absorb at all at the latter wave length; it was shown previously that the validity of this assumption has no effect on the values of the rate constant obtained in the deuterium-exchange experiments so long as the base concentration always remains constant within a given run.[4] Using a Perkin–Elmer Model 21 infrared spectrophotometer the *m*-difluorobenzene, *m*-chlorofluorobenzene, *m*-dichlorobenzene, and 1,2,4-trichlorobenzene prepared were analyzed for their deuterium content at 9.812, 10.933, 13.484, and 8.430 μ and for their protium content at 11.755, 8.165, 10.001, and 9.135 μ, and found to be 74.9, 74.0, 67.25, and 87.06% deuteriated,[9] respectively.

Kinetics of Deuterium-exchange Reactions.—In a typical run 10 μl. of deuterio compound and 10 ml. of 0.09932 *M* sodium methoxide in methanol were sealed in a 12-ml. tube, placed in a constant temperature bath for a recorded length of time, removed, and cooled. The tube was broken and its contents poured into 20 ml. of 0.1044 *M* aqueous perchloric acid. The resultant solution was extracted with 4 ml. of carbon disulfide which was then dried with a little silica gel. The dry carbon disulfide solution was analyzed for its deuterio and protio halide content by infrared measurements. First order rate constants were determined from the equation[10]

$$k_1t = 2.303 \log \left(p + p\frac{[\text{H}]_t}{[\text{D}]_t}\right) \qquad (1)$$

where $[\text{H}]_t$ and $[\text{D}]_t$ are the concentrations of protio and deuterio compound and p is equal to $[\text{D}]_0/([\text{H}]_0 + [\text{D}]_0)$. Satisfactory first order rate constants were obtained thus for all compounds except *m*-difluorobenzene. When the deuteriated *m*-difluorobenzene was subjected to all the procedure of a kinetic run, except that the sealed tube was not placed in the constant temperature bath, the infrared analysis corresponded to a deuterio content of 67.4% instead of the expected 74.9% (the conditions were such that only a negligible amount of exchange should have occurred). When a value of 0.674 was used for p instead of 0.749 the plots of the right side of equation 1 *vs.* t were linear and passed through the origin. For each compound an acidimetric titration was made at a time corresponding to the last kinetic point taken (usually around 70% reaction) and in no case was a detectable amount of base found to have reacted. Values of k_1 from the plots of equation 1 were turned into second order rate constants by division by the sodium methoxide concentration. The k_2 values are listed in Table I.

Kinetics of the Reaction of 1,1-Difluoro-1,2,2-trichloroethane with Sodium Methoxide.—In a typical run 5 ml. of 0.5119 *M* methanolic sodium methoxide at 0° was pipetted into a solution of 0.281 ml. (2.54 mmoles) of the difluorotrichloroethane in 95 ml. of methanol, also at 0°. At various times 10-ml. samples of the reaction solution were pipetted

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[4] J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957).

[5] G. E. Hall, R. Piccolini, and J. D. Roberts, *ibid.*, **77**, 4540 (1955); J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956).

[6] J. F. Bunnett, J. H. Miles, and K. V. Nahabedian, *ibid.*, **83**, 2512 (1961).

[7] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Inc., Boston, Mass., 1955, p. 289.

[8] A. L. Henne and E. C. Ladd, *J. Am. Chem. Soc.*, **58**, 402 (1936).

[9] These are minimum values; if the assumption described in the previous sentence is in error, the values are higher.

[10] J. Hine, R. C. Peek, Jr., and B. D. Oakes, *J. Am. Chem. Soc.*, **76**, 827 (1954).

TABLE I

RATE CONSTANTS FOR METHOXIDE ION-CATALYZED DEUTERIUM EXCHANGE IN METHANOL

	10^6k_2 (l. mole^{-1} sec.$^{-1}$)		ΔH‡,	ΔS‡,
Reactant	70.0°	100°	kcal./mole	e.u.
2,6-$F_2C_6H_3D$	2.88 ± 0.04[a]	978 ± 35	27.3 ± 0.2	−4.3 ± 0.7
2,6-$ClFC_6H_3D$	4.47 ± 0.13	151 ± 3	29.2 ± 0.5	−2.9 ± 1.4
2,6-$Cl_2C_6H_3D$	153 ± 6[b]	20.2 ± 0.8	28.6 ± 1.0	−8.6 ± 2.8
2,3,6-$Cl_3C_6H_2D$	4.78 ± 0.23	244 ± 6	32.8 ± 0.5	7.6 ± 1.5

[a] At 50.0°. [b] At 120°.

into excess aqueous acid and back-titrated with standard base. The average rate constant calculated from seven points taken between 14 and 64% reaction was $(43.7 \pm 1.4) \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$. A similar run gave a k value of $(45.7 \pm 2.1) \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$.

Reaction of 1,1-Difluoro-1,2,2-trichloroethane with Base in Heavy Water and in Deuteriomethanol.—A number of experiments were run, under conditions sufficient to bring about the reaction of 25 to 90% of the difluorotrichloroethane, in which the organic halide was allowed to react with sodium deuterioxide in heavy water or with sodium methoxide in about 65% deuteriomethanol-35% methanol, and the resultant solution was extracted (after neutralization in some cases, and after the addition of water in the cases where methanol was used) with isooctane, carbon disulfide, or carbon tetrachloride. In no case were any infrared absorption bands found in the organic extract that were not also found (in about the same intensity) when an analogous experiment was carried out using a nondeuteriated solvent.

Discussion

In view of the observations of Roberts[4] and Shatenshtein[11] and their co-workers that electron-withdrawing substituents increase the rate of carbanion formation much more in the *ortho* than in the *meta* and *para* positions,[4] it seems very probable that the *m*-dihalobenzenes should undergo base-catalyzed deuterium exchange much more rapidly at the position between the two halogen atoms than at any other position. We have therefore assumed that our measurements refer in each case to the only hydrogen atom in the molecule that is *ortho* to two halogens. From Table I it is seen that the replacement of an *ortho* chlorine atom by fluorine increases the rate constant for carbanion formation by about sevenfold. The replacement of a *meta* hydrogen by chlorine (*cf.* *m*-dichlorobenzene and 1,2,4-trichlorobenzene) increases the reactivity by about twelvefold.

Viewing our results in conjunction with those of Roberts and co-workers and Bunnett, Miles, and Nahabedian it seems that in our case the inductive effect of the halogens is the most important effect influencing the reactivity. It is possible that the larger *ortho* chlorine atoms interfere somewhat with the attack of the hydroxide ion and slow the reaction somewhat by a steric effect, but if such a steric effect were very large it does not seem very likely that the rate constant for exchange of *m*-chlorofluorobenzene would be so nearly the geometric mean of those for *m*-dichlorobenzene and *m*-difluorobenzene. Steric effects are usually not so linear.[12]

The enthalpy and entropy of activation for 1,2,4-trichlorobenzene are higher than those for the other compounds by more than the combined average deviations listed. We have no explanation for this but cannot rule out the possibility that because of some systematic error these differences are not significant.

Having thus learned that a β-fluorine substituent increases the ease of carbanion formation more than a β-chlorine substituent does in the case of haloaromatics, where both α- and β-carbon atoms are sp^2 hybridized, we decided to investigate a case where the α- and β-carbon atoms are saturated. The rate constant for the removal of the proton from 1,1,1-trifluoro-2,2-dichloroethane by the action of methoxide ions in methanol at 0° is about 8.2×10^{-4} l. mole^{-1} sec.$^{-1}$ (allowing for a kinetic isotope effect of 1.26).[13] The change of one of the fluorine atoms in this molecule to chlorine gives 1,1-difluoro-1,2,2-trichloroethane. Attempts to measure the rate constant for carbanion formation by this difluorotrichloroethane were unsuccessful, since the compound reacted with base without any observable hydrogen exchange. Since the rate of reaction of the compound with base should give a maximum value for its rate of carbanion formation,[14] we determined the rate constant for reaction with sodium methoxide in methanol at 0°. The value obtained, 4.5×10^{-2}, is about 55 times as large as the rate constant for carbanion formation by 1,1,1-trifluoro-2,2-dichloroethane. Actually, we believe it is more probable that even in saturated compounds β-fluorine facilitates carbanion formation relative to β-chlorine and that the reaction of 1,1-difluoro-1,2,2-trichloroethane with sodium methoxide is a concerted dehydrohalogenation, although it is a reaction fairly near the borderline between those eliminations that involve intermediate carbanions and the concerted E2 type.

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(11) A. I. Shatenshtein, Yu. I. Ranneva, and T. T. Kovalenko, *Zh. Obshch. Khim.*, **32**, 967 (1962); A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962).

(12) Cf. J. Hine and R. G. Ghirardelli, *J. Org. Chem.*, **23**, 1550 (1958).

(13) J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *J. Am. Chem. Soc.*, **83**, 1219 (1961).

(14) This depends on the assumption that the reaction with base is a dehydrohalogenation, an assumption that seems plausible in view of the observations that have been made on 1,1,1-trifluoro-2,2-dihaloethanes.[15]

(15) J. Hine, R. Wiesboeck, and O. B. Ramsay, *J. Am. Chem. Soc.*, **83**, 1222 (1961).