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# Factors Affecting the Ease of Carbanion Formation

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The relative rates of base-catalyzed hydrogen exchange reactions of $HCX_3$, where X = F, $R_F$ ($R_F$ = perfluoroalkyl), Cl, $OCH_2CH_3$ and $SCH_2CH_3$, have been measured employing tritium and deuterium tracer techniques. A comparison of the data with those obtained previously by Hine[1] for $CHCl_3$ and $CHBr_3$ gives the following order of exchange rates:

$$CHI_3 \sim CHBr_3 > CHCl_3 > CH(SCH_2CH_3)_3 \gg CH(OCH_2CH_3)_3$$

These data indicate that the inductive effect and probably polarizability, as measured by atomic refractive constants, are less important than *d*-orbital resonance in determining the above order of exchange rates. Chloroform exchanges faster than fluoroform and probably faster than pentafluoroethane and 1-H-heptafluoropropane. This result is in qualitative agreement with another carbanion formation reaction studied. Whereas phenyltrichloromethylcarbinol forms benzaldehyde and potassium formate when treated with aqueous base, phenylheptafluoro-*n*-propylcarbinol forms only the salt of the alcohol when similarly treated.

Recently, the rates of base-catalyzed transformations of deuterated haloforms to the corresponding protium compounds in aqueous media were measured by Hine and co-workers.[1] α-Halogen substituents were found to facilitate carbanion formation in the order I, Br > Cl > F. The observed order was thought to be due to some combination of the inductive effect, polarizability, and *d*-orbital resonance.

The purpose of the present study was to learn more about the factors which determine carbanion stability. In particular, we studied the factors contributing to the ease of formation of $CX_3^-$ from $HCX_3$ where X = F, $R_F$ ($R_F$ = perfluoroalkyl), RO, RS, and Cl. The relative ease of formation of these anions was determined by measuring the relative rates of base-catalyzed exchanges of $HCX_3$ with a hydroxylic solvent. Tritium and deuterium tracer techniques were employed for this purpose.

## RESULTS

*Base-catalyzed exchange of chloroform-t, triethyl orthothioformate-t, and triethyl orthoformate.* In two separate experiments, chloroform-*t* and triethyl orthothioformate-*t* were permitted to undergo a sodium hydroxide-catalyzed exchange at 35 ± 0.1° in an 80% ethanol–20% water solution (0.65*M* sodium hydroxide 0.78*M* in $HCX_3$). After a predetermined period of time, the two compounds were recovered by techniques which excluded further exchange (see Experimental). The extent to which each tritium-labeled compound had proceeded toward complete equilibration with the solvent was then calculated from its decrease in activity.

In 240 minutes, triethyl orthothioformate-*t* was found to have proceeded 44% toward complete equilibration with the solvent. The more reactive chloroform-*t*, on the other hand, became completely equilibrated with the solvent in less than 0.5 minute. The half-time for the exchange of chloroform-*t* must be <0.05 minute since at least ten half-times are involved for 100% exchange.

Because triethyl orthoformate-*t* is more difficult to prepare, the sodium hydroxide-catalyzed exchange of unlabeled triethyl orthoformate in tritium labeled ethanol-water solution was measured. Even after refluxing for several hours, the recovered triethyl orthoformate remained inactive. In a further attempt to obtain a base-catalyzed exchange, triethyl orthoformate (0.78*M*) was heated at 85 ± 0.1° for 168 hours in a tritium labeled ethanol solution containing sodium ethoxide (0.65*M*). The same experiment was repeated using tritium labeled *t*-butyl alcohol as the solvent and potassium *t*-butoxide as the base. In both cases, the maximum extent of exchange was 0.06%.

*Attempted base-catalyzed exchange of fluoroform, pentafluoroethane, and 1-H-heptafluoropropane.* A vessel containing 90 ml. of 1.11*N* sodium hydroxide in deuterium oxide was pressured to 520 p.s.i.g. by adding 0.60 mole of fluoroform. After shaking for 1121 hours at room temperature, <0.05% exchange could be detected. In a similar experiment at atmospheric pressure, chloroform underwent complete exchange in < two hours. Even though fluoroform and chloroform may be soluble in basic deuterium oxide to different extents,[2] it seems quite certain that the former exchanges much more slowly.

Equal molar quantities of pentafluoroethane, 1-*H*-heptafluoropropane and chloroform were sealed in separate ampoules containing basic, aqueous dioxane and then vigorously agitated. Whereas chloroform underwent complete exchange in < two hours, no detectable exchange of the fluorocarbons

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

[2] The solubilities of fluoroform and chloroform in water at atmospheric pressure at 20° are 0.033 and 0.083 moles/liter, respectively (*Handbook of Chemistry and Physics*, 40th edition, 1958–59). Fluoroform under 520 p.s.i.g. pressure may be equally as soluble as is chloroform at atmospheric pressure.

TABLE I

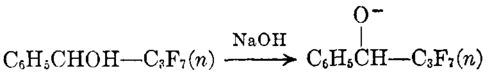
RELATIVE RATES OF BASE-CATALYZED HYDROGEN EXCHANGE OF $HCX_3$

| Compound exchanged | $HC(OCH_2CH_3)_3$ | $HCF_3$ | $HC(SCH_2CH_3)_3$ | $HCCl_3$ | $HCBr_3$[a] | $HCI_3$[a] |
|---|---|---|---|---|---|---|
| Relative rates of exchange | $<6 \times 10^{-8}$ | — | 1.0 | $>5 \times 10^3$ | $>6 \times 10^5$ | $>6 \times 10^5$ |
| Electronegativity[b,d] | 3.5 | 4.0 | 2.5 | 3.0 | 2.8 | 2.5 |
| σ *meta* values[e] | 0.11[f] | 0.337 | 0.15[f] | 0.373 | 0.391 | 0.352 |
| Atomic refractive constants[b,c] | 1.64 | 1.25 | 7.97 | 5.97 | 8.87 | 13.9 |

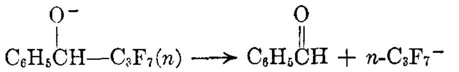
[a] From data of Hine and co-workers.[1] [b] Values are for the atom of X attached directly to the methide carbon. [c] Values are from Lange's *Handbook of Chemistry*, 6th ed., Handbook Publishing Co., Sandusky, Ohio, p. 1025. The value for fluorine is given by A. Fainberg, Cornell University Ph.D. Thesis (1950) as a better value for this atom in polyfluoro compounds. [d] Values are from L. Pauling, *Nature of the Chemical Bond*, 3rd ed., Cornell University press, Ithaca, N. Y., 1960, p. 90. [e] See Ref. 18. [f] Values for $CH_3O—$ and $CH_3S—$.

occurred in 500 hours at room temperature. The fluorocarbons were observed to have a definite but small solubility in the solvent. Although quantitative solubility data for these systems are not available, the experiments suggest that the chloroform exchanges more readily than either pentafluoroethane or 1-H-heptafluoropropane.

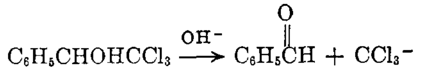
*Attempted generation of the heptafluoro-n-propyl anion from phenylheptafluoro-n-propylcarbinol and aqueous potassium hydroxide.* An attempt was made to generate the heptafluoro-*n*-propyl anion by treating phenylheptafluoro-*n*-propylcarbinol with aqueous sodium hydroxide (Equations 1 and 2). However, only the sodium salt of the alcohol was formed. Under similar conditions, phenyltrichloromethylcarbinol is converted to benzaldehyde and formate salts[3] (Equations 3 and 4).



$$C_6H_5CHOH—C_3F_7(n) \xrightarrow{NaOH} C_6H_5\overset{O^-}{\overset{|}{C}}H—C_3F_7(n) \quad (1)$$



$$C_6H_5\overset{O^-}{\overset{|}{C}}H—C_3F_7(n) \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}H + n\text{-}C_3F_7^- \quad (2)$$



$$C_6H_5CHOHCCl_3 \xrightarrow{OH^-} C_6H_5\overset{O}{\overset{\|}{C}}H + CCl_3^- \quad (3)$$

$$CCl_3^- \xrightarrow[OH^-]{H_2O} HCO_2^- \quad (4)$$

*Relative rates of exchange of $HCX_3$.* The assumed exchange mechanism is similar to the one postulated by Hine[1] for the base-catalyzed exchange of deuterohaloforms.[4]

The base-catalyzed exchange reactions are pseudo first order since the base concentration does not change. From the above data, first order rate constants were calculated for the sodium hydroxide-catalyzed exchange of chloroform and $HC(SCH_2CH_3)_3$ at 35° in 80% ethanol–20% water solution. Since the exchange of chloroform was too fast to measure accurately, the calculated rate is a minimum value only. The maximum rate constant for the sodium ethoxide-catalyzed exchange of $HC(OCH_2CH_3)_3$ at 35° was calculated, using the absolute rate equation,[5] from the value obtained at 85° in pure ethanol,[6] assuming the energy of activation to be at least as large as that determined by Hine[1] for the exchange of $DCFCl_2$. This is a reasonable assumption since $HC(OCH_2CH_3)_3$ exchanges much more slowly than $HCFCl_2$.

The relative rate constants, assigning a value of 1.0 to the rate of exchange of $HC(SCH_2CH_3)_3$, are listed in Table I. Physical properties of the atom or group attached to the methide carbon are included in the table for the purpose of discussion. These values were calculated assuming equal isotope effects for the hydrogen abstraction reactions involving the different $HCX_3$ compounds. In view of the large variation in rates, corrections for isotope effects of different magnitudes would be minor. The rates of exchange of bromoform and iodoform are included in Table I assuming that they exchange about 120 times faster than chloroform, as was found by Hine[1] to be the case for aqueous media. The relative rates of exchange of fluoroform, pentafluoroethane, and 1-H-heptafluoropropane included in the table since their values are considered to be less reliable.

## DISCUSSION

The ability of the α-substituents to stabilize carbanions is probably reflected in the relative rates of base-catalyzed exchanges of $HCX_3$ ($X = F, R_F, Cl, Br, I, OCH_2CH_3, \text{and } SCH_2CH_3$). This as-

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(3) M. Bossneck, *Ber.*, **18**, 1516 (1855); P. Hebert, *Bull. Soc. Chim.*, (4) **27**, 49 (1920).

(4) Hine[1] demonstrated that the rate of hydrolysis, *via* the dihalocarbene, of chloroform, bromoform and iodoform were slow relative to the rates of base-catalyzed deuterium exchange. This is probably true of triethyl orthoformate and triethyl orthothioformate as well. All efforts to detect diethoxy- and dithioethoxycarbene intermediates by addition to cyclohexene were unsuccessful.

$$TCX_3 + B^- \rightleftarrows CX_3^- + TB$$

$$HCX_3 + B^- \rightleftarrows CX_3^- + HB$$

$$CX_3^- \xrightarrow{slow} CX_2 + X^-$$

(5) S. Glasstone, K. J. Laidler and H. Eyring, *Theory of Rate Processes*, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

(6) The rate for the sodium ethoxide–catalyzed exchange of $HC(OCH_2CH_3)_3$ in pure ethanol was calculated rather than the value for the sodium hydroxide–catalyzed exchange in aqueous ethanol since a longer exchange period and more drastic conditions were employed for the former. This should give a maximum value for the rate of exchange of $HC(OCH_2CH_3)_3$.

sumption has received support from several other similar investigations.[1,7–11] Shatenshtein[11] has pointed out the close parallel between the exchange rate constants for several weak acids in $ND_3$ containing potassium amide and the ionization constants reported by Conant and Wheland[12] and McEwen.[13] With a few exceptions, Pearson and Dillon[14] found a rough parallel between exchange rate constants and ionization constants for a variety of weak acids. The validity of the above assumption will depend, in large part, upon the extent to which carbanions are developed in the transition state. Streitwieser,[10] in keeping with the above assumption, concluded from the magnitude of $\alpha$ and $\beta$ deuterium isotope effects that there was considerable bond breaking in the transition state during the base-catalyzed exchange of several hydrocarbons.

*Factors influencing the ease of carbanion formation.* The slower rate of exchange of fluoroform, pentafluoroethane, and 1-H-heptafluoropropane relative to chloroform indicates, in agreement with the results of Hine,[1] that $\alpha$-chlorine facilitates carbanion formation more than the more electronegative $\alpha$-fluorine. This result is in qualitative agreement with another carbanion formation reaction studied. Whereas phenyltrichloromethylcarbinol is known to form benzaldehyde and potassium formate when treated with aqueous potassium hydroxide[3] (see Equations 3 and 4), a similar treatment of phenylheptafluoro-*n*-propylcarbinol produced no aldehyde but instead gave only the salt of the alcohol (see Equation 1). This difference in reactivity is similar to that for the decarboxylation of trichloroacetic acid[15,16] and trifluoroacetic acids,[17] *i.e.*, $Cl_3CCO_2^- > F_3CCO_2^-$. The rate determining step is probably the elimination of $CX_3^-$ from the carboxylate anion.

Although the inductive effect may play a role in stabilizing carbanions, the above data indicate that it is not the most important participant. The minor role of the inductive effect is also evidenced by the large difference ($>1.7 \times 10^7$) in the rates of exchange of $CH(OCH_2CH_3)_3$ and $CH(SCH_2CH_3)_3$ (see Table I). Due to a lack of available data, it is difficult to assign relative inductive values to $CH_3CH_2S$— and $CH_3CH_2O$—. However, if the $\sigma$ *meta* values[18] for $CH_3S$— and $CH_3O$— are taken as representative, it would appear that the inductive effects for the two groups are about equal. It is unfortunate that Taft's $\sigma^*$ or Roberts' $\sigma'$ values for the two groups are not available[19] since these are more representative of the indictive effect than are $\sigma$-meta values.[19]

Polarizability of the atom attached to the methide carbon may also assist carbanion formation. However, polarizability, as measured by atomic refractive constants, cannot determine by itself the order of exchange reactivity listed in Table I. For example, the atomic refractive constant of sulfur is 7.97 compared with 5.97 for chlorine. Nevertheless, chloroform exchanges at least $5 \times 10^3$ times faster than $CH(SCH_2CH_3)_3$.

Probably, the most important single factor for carbanion stabilization is *d*-orbital resonance, that is, the resonance contribution of structures having ten electrons in the outer shell of the atom attached to the methide carbon $(\text{R-}\underset{\cdot\cdot}{\ddot{X}}\text{-}\overset{|}{\underset{|}{C}}{}^- \longleftrightarrow \text{R-}\underset{\cdot\cdot}{\ddot{X}}{}^-\!=\!\overset{|}{\underset{|}{C}})$. *d*-Orbital resonance is thought to be important only for elements below the first row in the periodic table. This could easily explain the much faster rates of exchange of $CH(SCH_2CH_3)_3$ compared with $CH(OCH_2CH_3)_3$ and of chloroform, bromoform, and iodoform compared with fluoroform, pentafluoroethane, and 1-H-heptafluoropropane. Doering and Hoffmann[7] similarly concluded that *d*-orbital resonance is primarily responsible for the much greater rate of base-catalyzed deuterium exchange of tetramethylphosphonium iodide compared to that of tetramethylammonium iodide.

One can only speculate on the reasons for the reactivity order $CH(SCH_2CH_3)_3 <$ chloroform $<$ bromoform, iodoform. It may be due to an unresolved combination of *d*-orbital resonance, inductive effects, and polarizability. However, the contribution of *d*-orbital resonance may be most important for iodine or bromine and least important for sulfur. It is not impossible that this alone could account for the above order. There is one other factor, probably small, which may account in part for the slower rate of exchange of $CH(SCH_2CH_3)_3$ compared to chloroform, bromoform, and iodoform. That is, the thioethoxy groups may sterically shield the central hydrogen atom against base attack more than do the halogen atoms.

*Attempts to make carbene adducts.* One common method of preparing carbenes is to generate the anion $CX_3^-$ which by $\alpha$-elimination gives $CX_2$ +

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(7) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

(8) D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

(9) H. Hart and R. E. Crocker, *J. Am. Chem. Soc.*, **82**, 418 (1960).

(10) A. Streitwieser, Jr., Abst. of the Sixteenth National Organic Chemistry Symposium, Seattle, Wash. (1959).

(11) A. I. Shatenshtein, *Doklady Acad. Nauk S.S.S.R.*, **70**, 1029 (1950) [*Chem. Abstr.*, **44**, 5194 (1950)].

(12) J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932).

(13) W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936).

(14) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(15) F. H. Verhoek, *J. Am. Chem. Soc.*, **56**, 571 (1934).

(16) R. A. Fairdough, *J. Chem. Soc.*, 1186 (1938).

(17) I. Auerbach, F. H. Verhoek, and A. L. Henne, *J. Am. Chem. Soc.*, **72**, 299 (1950).

(18) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(19) Newman, M. S., *Steric Effects in Organic Chemistry*, John Wiley & Sons, New York, 1956. See Chapter 13 by R. W. Taft, Jr.

$X^-$. Subsequently, $CX_2$ may react *in situ* with an olefin, *e.g.*, cyclohexene, to give a cyclopropane derivative.

As would be expected from the exchange results, $C(OCH_2CH_3)_2$ could not be generated from potassium *t*-butoxide and triethyl orthoformate. A similar treatment of triethyl orthothioformate in cyclohexene likewise produced no cyclopropane derivative. Even though the anion $C(SCH_2CH_3)_3^-$ is readily formed (*vide supra*), it apparently does not decompose to give $C(SCH_2CH_3)_2$ in significant yields.[20]

## EXPERIMENTAL

*Triethyl orthothioformate.* By the procedure of Holmberg,[21] triethyl orthothioformate was prepared in 90% yields from ethyl formate (2.0 moles) and ethanethiol in the presence of hydrogen chloride gas. The pale yellow orthoester was purified by careful distillation, b.p. 124–126° (10 mm.), $n_D^{20}$ 1.5424.

*Anal.* Calcd. for $C_7H_{16}S_3$: C, 42.8; H, 8.2; S, 49.0. Found: C, 42.7; H, 8.1; S, 48.8.

*Triethyl orthothioformate-t.* To a 2*N* ethanolic solution of sodium ethoxide (120 ml.) was added 1 mc. of tritiated water (~0.1 ml.). Triethyl orthothioformate (0.34 mole) was added and the solution maintained at 95 ± 1° for 16 hr. A dry nitrogen atmosphere was maintained in the flask at all times. The ethanol was removed under vacuum at room temperature and the remaining slurry extracted with *n*-pentane.

After washing repeatedly and drying over calcium chloride, distillation of the solution gave triethyl orthothioformate-*t* (30% recovery), b.p. 124–126° (10 mm.). Repeated water washing of the triethyl orthothioformate-*t* did not reduce the measured activity of $2.29 \times 10^5$ d.p.m./mmole. The relative activities of the original ethanol-*t* and the recovered orthothioformate indicated that exchange was ~100% complete.

The tritium was shown to be present on the central carbon atom since ethanethiol recovered from the triethyl orthothioformate-*t* by the procedure of Mochel, Agre, and Hanford[22] was found to be inactive.

*Chloroform-t.* Chloroform (0.3 mole) and sodium hydroxide (0.8 g.) were added to 18 ml. of tritiated water (~3 mc.). The mixture was mechanically agitated at room temperature for 3 hr. and the chloroform-*t* recovered in a separatory funnel. The chloroform-*t* was diluted to 100 ml., dried over excess calcium chloride and distilled, b.p. 61.3°. The activity of the chloroform-*t* was $9.63 \times 10^5$ d.p.m./mmole.

*Exchange of triethyl orthothioformate-t in alkaline ethanol-water solution.* An alkaline solution was prepared by dissolving sodium hydroxide (0.473 mole) in a solution consisting of ethanol (540 ml., 7.50 moles) and water (90 ml., 5.0 moles). The resulting solution (670 ml.) was 0.6449*M* in sodium hydroxide and 0.783*M* in orthothioformate. The flask containing the solution was placed in a constant temperature bath regulated at 35 ± 0.1°. While vigorously agitating, triethyl orthothioformate-*t* (113.4 g., 0.570 mole) was quickly injected into the solution and heated for 4 hr. A dry nitrogen atmosphere was maintained at all times during the preparation of the alkaline solution and the exchange reaction.

After 4 hr., the solution was quickly added to cold *n*-pentane (900 ml.) in a separatory funnel. The *n*-pentane was washed five times with 200 ml. of water and dried over calcium chloride. Pure triethyl orthothioformate-*t* was recovered (65%) by vacuum distillation. In an independent experiment, it was shown that tritium was not removed from triethyl orthothioformate-*t* by the above water washing procedure.

Measured tritium activities: Triethyl orthothioformate-*t* before base-catalyzed exchange, $2.91 \times 10^4$ d.p.m./mmole; triethyl orthothioformate-*t* after base-catalyzed exchange, $1.66 \times 10^4$ d.p.m./mmole. From the decrease in activity that is required for complete equilibration with the exchangeable hydrogens in the solution, the exchange is calculated to be 44.1% complete.

*Exchange of chloroform-t in alkaline ethanol-water solution.* The exchange of chloroform-*t* in alkaline ethanol-water solution was carried out exactly as above for triethyl orthothioformate-*t* using the same molar quantities of reagents.

After a 30 seconds exchange period, the solution was quickly poured into a separatory funnel containing 1500 ml. of 1.1*N* hydrochloric acid and 100 ml. of chlorobenzene. The chlorobenzene solution was washed five times with 200 ml. of 1.1*N* hydrochloric acid, dried over calcium chloride and distilled through a helices packed column to collect chloroform-*t* (60%), b.p. 61.3°.

Measured tritium activities: Chloroform-*t* before base-catalyzed exchange, $1.05 \times 10^5$ d.p.m./mmole; chloroform-*t* after exchange, $3.16 \times 10^3$ d.p.m./mmole. Knowing the decrease in activity that is required for complete equilibration with the exchangeable hydrogens in solution, the exchange is calculated to be 100.1% complete.

To demonstrate that tritium was not lost from the chloroform-*t* during the quenching and washing procedure the following experiment was performed. An alkaline ethanol-water solution, like the exchange media above, was poured into 1500 ml. of 1.1*N* hydrochloric acid. To this acidic solution was added chloroform-*t* (0.570 mole) followed by 100 ml. of chlorobenzene. The chlorobenzene solution was washed five times with 200 ml. of 1.1*N* hydrochloric acid, dried over calcium chloride and distilled. The activity ($9.63 \times 10^5$ d.p.m./mmole) of the recovered chloroform-*t* was the same as the starting material.

*Attempted base-catalyzed exchange of triethyl orthoformate.* A solution of potassium *t*-butoxide in *t*-butyl alcohol was prepared by dissolving 0.21 mole of potassium in 188 ml. of the alcohol (previously dried by distilling from dissolved potassium). To this solution was added 0.1 ml. of tritiated water (~1 mc.). The flask, equipped with condenser, drying tube, and helium inlet, was placed in a constant temperature bath at 85 ± 0.1°. Purified triethyl orthoformate (0.337 mole) was added with vigorous agitation and the solution maintained at 85° for 168 hr. A dry helium atmosphere was maintained throughout the entire experiment. The solution was then poured into excess water and extracted with *n*-pentane. The triethyl orthoformate was recovered by distillation (b.p. 142.2°) after the *n*-pentane solution had been washed with water several times and dried over calcium chloride.

Measured tritium activities: *t*-Butyl alcohol-*t*, $3.36 \times 10^4$ d.p.m./mmole; recovered triethyl orthoformate, <27 d.p.m./mmole. It is apparent that <0.06% exchange occurred. An independent experiment demonstrated conclusively that tritium was not lost from the triethyl orthoformate by the washing process. That is, triethyl orthoformate was found to be inactive after washing with tritium labeled water followed by drying over calcium chloride.

The use of ethanol-*t* and water-ethanol-*t* solvents with sodium ethoxide and sodium hydroxide, respectively, failed also to give any detectable tritium exchange with triethyl orthoformate, even after prolonged heating at 85°. In these

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[20] Interestingly, Hine [*J. Am. Chem. Soc.*, **72**, 2438 (1950)] has shown that the thiophenolate anion is an excellent scavenger for $CCl_2$ and that triphenyl orthothioformate can be obtained in 85% yields from a basic solution of chloroform and thiophenol. This would seem to indicate that the equilibrium

$$C_6H_5S^- + C(SC_6H_5)_2 \rightleftharpoons C(SC_6H_5)_3^-$$

lies far to the right in agreement with the present results.

[21] B. Holmberg, *Ber.*, **40**, 1741 (1907).

[22] W. E. Mochel, C. L. Agre, and W. E. Hanford, *J. Am. Chem. Soc.*, **70**, 2268 (1948).

last two cases, the base and triethyl orthoformate concentrations were $0.65M$ and $0.78M$, respectively.

*Radioactivity measurements.* The tritium activities of the compounds were determined by the liquid scintillation method[23] employing toluene as the organic solvent. In general, counting efficiencies were about 20%. All net counting rates were converted to disintegrations per minute (d.p.m.) by measurement of the exact counting efficiencies with calibrated $H^3$ solutions.

*Hydrogen exchange between fluoroform and deuterium oxide catalyzed by 1.11N sodium hydroxide.* A stainless steel pressure vessel was charged with 90 ml. of $1.11N$ sodium hydroxide in deuterium oxide. The vessel was pressured up to 520 p.s.i.g. with 42 g. (0.60 mole) of fluoroform then shaken for 1121 hr. at 15–25°. From time to time, small gas samples were taken *via* a needle valve. After 1121 hr., <0.05% exchange could be detected by mass spectrometric analysis. Titration of the fluoroform saturated solution after venting showed that 98% of the sodium hydroxide charged was present. A qualitative test for fluoride ion (titanium(IV); hydrogen peroxide) was negative.

*Hydrogen exchange between chloroform and deuterium oxide catalyzed by 1.11N sodium hydroxide.* A heterogeneous mixture of chloroform (0.50 mole) and $1.11N$ sodium hydroxide (20.0 ml.) in deuterium oxide was shaken vigorously at 25° for 2 hr. The chloroform, dried over calcium chloride and distilled, had undergone complete exchange with the solvent according to mass spectrometric analysis. Titration of the aqueous layer showed that only 3.3% of the chloroform had undergone decomposition to formate salts.

*Hydrogen exchange between pentafluoroethane and deuterium oxide catalyzed by sodium hydroxide.* A glass ampoule was charged with 5.0 ml. of $1.65N$ sodium hydroxide in deuterium oxide, 5.0 ml. dioxane, and 2.0 g. (0.0167 mole) of pentafluoroethane.[24] The mixture was shaken at room temperature for 22 days. An infrared examination of the recovered pentafluoroethane (10 cm. gas cell) showed no diminution in the intensity of the single sharp carbon-hydrogen peak at $3.3\ \mu$ and no C-D band. A qualitative test on the aqueous layer (which was saturated with pentafluoroethane) indicated that no fluoride ion was produced. Likewise, the recovered pentafluoroethane was free of tetrafluoroethylene as indicated by its infrared spectra and negative permanganate test.

Chloroform, when similarly treated, underwent complete exchange in <2 hours as determined by mass spectrometric analysis as previously described.

*Hydrogen exchange between 1-H-heptafluoropropane and deuterium oxide catalyzed by sodium hydroxide.* A glass ampoule was charged with 5.0 ml. of $1.65N$ sodium hydroxide in deuterium oxide, 5.0 ml. dioxane and 6.5 g. (0.038 mole) of 1-H-heptafluoropropane.[24] The mixture was shaken at room temperature for 21 days. The recovered gas, examined by infrared spectroscopy, showed no detectable sign of exchange. Likewise, no hexafluoropropene, resulting from β-elimination, was detectable. The aqueous layer was free of fluoride ion.

Chloroform, when similarly treated, underwent complete exchange in <2 hours as determined by mass spectrometric analysis as previously described.

*Attempted generation of heptafluoro-n-propyl anion from phenylheptafluoro-n-propylcarbinol and aqueous sodium hydroxide.* One gram of the subject carbinol when suspended in 5 ml. of $1.3N$ sodium hydroxide formed a white solid which regenerated starting material on dilution with water. When the suspension was warmed on the steam bath for approximately one hour and the mixture diluted, only starting carbinol, free of benzaldehyde, was found in the oil layer (infrared spectrum and negative dinitrophenylhydrazine test). The aqueous layer, on acidification, gave a negative dinitrophenylhydrazine test. The white solid is presumably the sodium salt of the carbinol.

*Attempted generation of dithioethylcarbene.* To a suspension of 36 g. (0.32 mole) of potassium *t*-butoxide in 102 g. (1.24 moles) of dry cyclohexene was added 61.5 g. (0.314 mole) of triethyl orthothioformate. The mixture warmed up to 34° and turned red-brown. The mixture was stirred for 1 hr., warmed at 75–82° for an hour, cooled, and vacuum stripped. The 111 g. of volatiles contained approximately 93% of the starting cyclohexene contaminated with *t*-butyl alcohol. A total of 76% of the starting triethyl orthothioformate was recovered by petroleum ether extraction of the residual salts and distillation. There was no indication that dithioethylcarbene was trapped by cyclohexene.

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[24] Procedure for preparation is published elsewhere. E. Bergman, *J. Org. Chem.,* **23,** 476 (1958).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# The Magnesium Enolate of 2,2-Diphenylcyclohexanone[1,2]

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The magnesium enolate of 2,2-diphenylcyclohexanone (I) has been prepared and its reactions have been investigated. In addition, two benzal derivatives of 2,2-diphenylcyclohexanone have been examined.

This paper records the preparation and reactions of the magnesium enolate of 2,2-diphenylcyclohexanone (I). The 2,2-diphenylcycloalkanone ring systems have been the subject of several recent reports.[3–12] The anticipated steric hindrance of the adjacent bulky phenyl groups is manifested by the

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[1] From the Ph.D. dissertation of James P. Collman, University of Illinois, 1958. Inquiries should be addressed to James P. Collman, Department of Chemistry, University of North Carolina, Chapel Hill, N. C. The author wishes to express his gratitude to Professor R. C. Fuson, who directed his graduate studies during the period in which this work was carried out, and to the National Science Foundation for a fellowship.

[2] Presented before the Organic Division of the American Chemical Society at the 134th Meeting at Chicago, Ill., September 7–12, 1958.

[3] N. R. Easton and S. J. Nelson, *J. Am. Chem. Soc.,* **75,** 640 (1953).