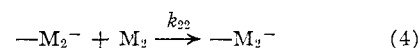
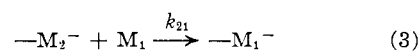
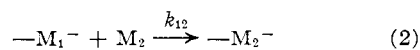
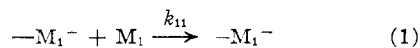


where n is small, such an anion being unable to react further with styrene monomer. The possibility that styrene is introduced into these polymers only through the initiation step does not seem to have been clearly recognized previously.²¹

The reactions which apply to the anionic copolymerization of styrene and methyl methacrylate are shown below, where M_1 is styrene, M_2 methyl methacrylate, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. The present work indicates that reaction 3 does not oc-



cur, and that, therefore, $r_2 \gg 1$; r_1 cannot be determined for polymerizations initiated with fluorenyllithium, as neither of the reactions which determine its value occur. Landler^{2,22} had earlier concluded that there is no alternating effect in anionic copolymerization. All values of the product $r_1 r_2$ were essentially unity, or $k_{11}/k_{12} = k_{21}/k_{22}$, which would mean that the relative reactivities of the two monomers toward different terminal ionic units are the same and that the nature of the carbanion is not important. We conclude from the present work and from the results of Higginson and Wooding⁷ that for the anionic polymerization of a styrene-methyl methacrylate mixture (and probably for all

(21) O'Driscoll and Tobolsky¹³ have described the *n*-butyllithium-initiated copolymerization of an equimolar mixture of these monomers as a "classical anionic polymerization in which the less electro-negative methyl methacrylate polymerizes preferentially to such an extent that little or no styrene (less than 1%) is discernible in the polymer, regardless of the solvent used." These authors have since shown (*J. Polymer Sci.*, **37**, 363 (1959)) that with butyllithium at high ratios of styrene to methyl methacrylate, quite appreciable amounts of styrene are incorporated into low conversion polymers. We find little styrene in similar polymerizations carried to higher conversions (Table I, lines 13-14), which is consistent with the above postulates.

(22) Y. Landler, *J. Polymer Sci.*, **8**, 63 (1952).

systems where the monomers differ greatly in polarity), the nature of the anionic species, both initiating and propagating, is *highly* important. The polymers of Landler are probably not true copolymers, but instead block copolymers (or polymer mixtures), and his experimental results cannot be used to calculate true reactivity ratios for the propagation steps in anionic copolymerization. Interpretations of "anionic copolymerizations"^{20,22,23} should be revised in view of these findings.

Szwarc²⁴ has reported that when methyl methacrylate is polymerized in tetrahydrofuran with sodium-naphthalene complex as initiator and styrene is then added, no polymerization of the styrene is observed. The result is cited as one of the proofs that the poly-(methyl methacrylate) anion is self-terminating in such systems. However, such a result would be expected from the present work and has no bearing on the proof of existence of the "living polymer" anion of poly-(methyl methacrylate), especially as we have shown¹ that the polymeric methyl methacrylate anions are still active even after the addition of styrene. Szwarc²⁴ has also cited as further proof of the self-termination of the poly-(methyl methacrylate) anion the observation that it will not initiate polymerization of more added methyl methacrylate. Evidence that these anions are indeed long-lived and capable of initiating further polymerization of methyl methacrylate has recently been obtained^{1,10} and will be discussed in detail in future publications.

Acknowledgments.—We are grateful to Mr. J. E. Moore, Mr. F. Zimmerman and Dr. F. H. Owens for preparation of initiators, Mr. J. H. Rorapugh for carrying out the polymerization in liquid ammonia, Dr. Aldenlee Spell for infrared determinations and interpretations, and Mr. C. W. Nash for elemental analyses. The advice of Dr. D. L. Glusker is gratefully acknowledged.

(23) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 227.

(24) M. Szwarc and A. Rembaum, *J. Polymer Sci.*, **22**, 189 (1956).

BRISTOL, PENNA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Preparation of Silyl- and Germylmetallic Compounds

BY M. V. GEORGE, DONALD J. PETERSON AND HENRY GILMAN

RECEIVED JUNE 22, 1959

Triphenylsilyllithium was prepared by the reaction of chlorotriphenylsilane and lithium in solvents like tetrahydrofuran, 2-methyltetrahydrofuran and tetrahydropyran. Similarly, dimethylphenylsilyllithium, triphenylsilylpotassium, triphenylsilylrubidium, triphenylsilylcesium, tri-*o*-tolylsilyllithium and tri-*o*-tolylsilylcesium were prepared by the treatment of the respective chlorosilanes with corresponding alkali metals. Hexaphenyldisilane was the product when either sodium or magnesium was treated with chlorotriphenylsilane. The reaction of bromotriphenylgermane and lithium gave a fair yield of triphenylgermyllithium. Some tentative observations concerning the probable course of the reaction are made.

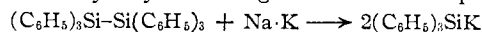
The first report of the successful preparation of a triarylsilylmetallic compound was the formation of triphenylsilylpotassium by the cleavage of triphenyl-(phenylisopropyl)-silane with sodium-potassium alloy.¹ Shortly thereafter² an improved

(1) R. A. Benkeser and R. G. Severson, *THIS JOURNAL*, **73**, 1424 (1951).

procedure was reported for the preparation of triphenylsilylpotassium, by the cleavage of hexaphenyldisilane with sodium-potassium alloy in diethyl

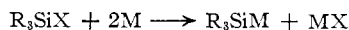
(2) H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951); H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, *ibid.*, **74**, 561 (1952); H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953); A. G. Brook and H. Gilman, *THIS JOURNAL*, **76**, 278 (1954).

ether. Not only is the hexaphenyldisilane more accessible, but the triphenylsilylpotassium is unaccompanied by any other organometallic compound.



This distinct improvement in a general procedure still had two drawbacks. One was the troublesome excess of sodium-potassium alloy; but this was soon corrected by amalgamation subsequent to cleavage of the disilane. The other was the inconvenience of working with a suspension of the triphenylsilylmetallic compound in diethyl ether. This was overcome by operating in ethylene glycol dimethyl ether, although slow cleavage to give methyltriphenylsilane was still a problem. The most significant development was the use of tetrahydrofuran as a solvent for the preparation of organosilylmetallic compounds.³ There is some cleavage of this solvent by the R_3SiM compound, but this is only significant in cases of slow reaction, and most reactions proceed quite promptly in tetrahydrofuran.

Although the cleavage reactions of disilanes have been used extensively for the preparation of a wide variety of organosilylmetallic compounds, little attention has been paid to the possibility of preparing these reagents by the direct reaction of chlorosilanes with alkali metals.⁴



It now appears that this procedure is of broad applicability and that such organosilylmetallic compounds can be prepared in essential accordance with conventional techniques used for the preparation of Grignard reagents and of organolithium compounds (RLi). Some of our observations in this area were reported in a preliminary communication,⁵ and we are now providing new experimental work involving not only organosilylmetallic but also an organogermylmetallic compound, as well as direct reactions of halides with metals such as cesium and rubidium, and the use of solvents in addition to tetrahydrofuran.

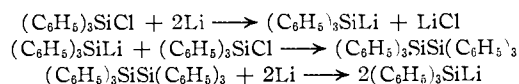
Treatment of chlorotriphenylsilane with lithium in tetrahydrofuran gave an 89.5% yield of triphenylsilyllithium. The same product was obtained in 61.7 and 64.1% yields, respectively, on use of 2-methyltetrahydrofuran and tetrahydropyran as the solvents.

The first step in the reaction of chlorotriphenylsilane with lithium seems to be the formation of triphenylsilyllithium by a route analogous to that of the formation of a Grignard reagent. Triphenylsilyllithium would then react with an excess of chlorotriphenylsilane present in the system to give hexaphenyldisilane. The actual isolation of a 63.4% yield of hexaphenyldisilane by arresting the reaction before completion is in agreement with this view.⁵ Further reaction of lithium with hexaphenyldisilane would bring about the cleavage of the Si-Si bond to give two moles of triphenylsilyllithium. The second stage of the reaction involving the symmetrical cleavage

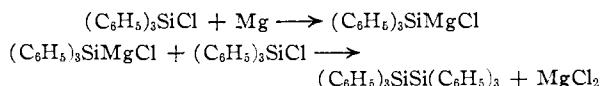
(3) H. Gilman and G. D. Lichtenwalter, *THIS JOURNAL*, **80**, 608 (1958).

(4) See H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951); and A. G. Brook and R. J. Mauris, *ibid.*, **79**, 971 (1957).

(5) H. Gilman, D. J. Peterson and D. Wittenberg, *Chemistry & Industry*, 1479 (1958).



of the disilane in a much slower process compared to the initial formation of triphenylsilyllithium and is effected by only the most electropositive elements. Thus it has been observed that the reaction of chlorotriphenylsilane with magnesium gave only hexaphenyldisilane, even after a reaction period of 24 hr. This would clearly indicate that magnesium is less effective in rupturing the Si-Si bond to give, as the final product, the corresponding triphenylsilylmagnesium derivative. However, it is significant that a 60.5% yield of hexaphenyldisilane is formed from the reaction of chlorotriphenylsilane and magnesium. The initial step in the reaction seems to be the formation of a "silyl Grignard reagent" namely, triphenylsilylmagnesium chloride, or triphenylsilylmagnesium, which then combines with excess of chlorotriphenylsilane to give hexaphenyldisilane. The reaction was initiated by the addition of two drops of ethyl iodide, although subsequent studies by W. Stuedel with diphenylchlorosilane show that an alkyl iodide is unnecessary. The recent work of Selin and West⁶ supports the formation of a triphenylsilyl Grignard reagent.



Similarly, the reaction of chlorotriphenylsilane with sodium in tetrahydrofuran gave only hexaphenyldisilane (44.8%). Prolonged stirring for one week failed to bring about the cleavage of the disilane to give triphenylsilylsodium. On the other hand, when metals like rubidium and cesium were treated with chlorotriphenylsilane, a prompt reaction occurred and the yields of triphenylsilylrubidium and triphenylsilylcesium were 69.1 and 43.4%, respectively. Use of sodium-potassium alloy gave a 75.1% yield of triphenylsilylpotassium. The high reactivity of triphenylsilylcesium and the marked ability of this reagent to cleave the solvent (tetrahydrofuran) would account for the comparatively low yield.

The reaction of chloro-*o*-tolylsilane with lithium gave a 55.5% yield of tri-*o*-tolylsilyllithium, characterized as tri-*o*-tolylsilane after acid hydrolysis. Tri-*o*-tolylsilyllithium is an example of a highly hindered silylmetallic compound. If this reaction is assumed to proceed by a route similar to the reaction of chlorotriphenylsilane and lithium, then hexa-*o*-tolylidisilane would be formed as a reaction intermediate. However, earlier studies showed that it was uncommonly difficult to prepare any hexa-*o*-tolylidisilane by conventional coupling procedures. Though the hindrance in hexa-*o*-tolylidisilane due to the aryl substituents is appreciable, the existence of such a compound is not highly improbable. Thus, the isolation of the different forms of tetra-*o*-tolylsilane, compounds in which the hindrance due to substituent groups is considerable,⁷ has been effected. Similarly, from

(6) T. C. Selin and R. West, *Tetrahedron*, **5**, 97 (1959).

(7) G. N. R. Smart, H. Gilman and H. W. Otto, *THIS JOURNAL*, **77**, 5193 (1955); see also H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**,

the reaction of chlorotri-*o*-tolylsilane and cesium, a 21.4% yield of tri-*o*-tolylsilylcesium was obtained.

The direct preparation procedure is applicable to the synthesis of germymetallic compounds also. Thus the reaction of bromotriphenylgermane with lithium in tetrahydrofuran gave a 52.5% yield of triphenylgermyllithium, characterized as triphenyl-(triethylsilyl)-germane after treatment with chlorotriethylsilane.

Experimental

All melting points are uncorrected. Reactions were carried out under an atmosphere of dry, oxygen-free⁸ nitrogen. Tetrahydrofuran, boiling at 65–66°, 2-methyltetrahydrofuran, boiling at 76–77°, and tetrahydropyran, boiling at 85–86°, were freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride. The chlorotriphenylsilane employed was the pure grade (95%) purchased from the Dow-Corning Co. Chlorodimethylphenylsilane was kindly supplied through the courtesy of Dr. R. N. Meals of the General Electric Co. The authors are also grateful to Dr. A. P. Dunlop of the Quaker Oats Co. for some of the 2-methyltetrahydrofuran. Chlorotri-*o*-tolylsilane⁹ and bromotriphenylgermane¹⁰ were prepared by standard procedures.

Triphenylsilyllithium in Tetrahydrofuran.—Tetrahydrofuran (50 ml.) was slowly added, with rapid stirring, to a mixture of 5.9 g. (0.02 mole) of chlorotriphenylsilane and 0.55 g. (0.08 g. atom) of finely cut lithium wire. Four minutes after the addition of the solvent had commenced, the solution turned cloudy and soon a white precipitate was noticed. Within about 20 min. the reaction mixture turned light yellow; the color then gradually turned brown and finally black-brown, after 3 hr. of stirring at room temperature. The solution was clear, free of any white precipitate and gave a positive Color Test I.¹¹ The triphenylsilyllithium solution was filtered through glass wool and treated with 5.9 g. (0.02 mole) of chlorotriphenylsilane. Subsequent to hydrolysis with water, the insoluble white precipitate of hexaphenyldisilane was removed by filtration and repeatedly washed with ether. The product weighed 9.2 g. (89.5%) and melted at 363–365°. It did not depress the melting point of an authentic sample of hexaphenyldisilane.

In a second run using the same quantities of reactants and solvent, the triphenylsilyllithium solution was derivatized by treatment with chlorotrimethylsilane. A 82.0% yield of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 106–108° (mixed m.p.), was obtained.

Triphenylsilyllithium in 2-Methyltetrahydrofuran.—To a mixture of 7.4 g. (0.025 mole) of chlorotriphenylsilane and 0.69 g. (0.1 g. atom) of lithium was added, during 2 hr., 75 ml. of 2-methyltetrahydrofuran. A white precipitate of hexaphenyldisilane was observed which was slowly cleaved by excess lithium to give a deep black-brown solution, after 24 hr. of stirring at room temperature. The solution was filtered through glass wool and treated with 7.4 g. (0.025 mole) of chlorotriphenylsilane to give 8.0 g. (61.7%) of hexaphenyldisilane, m.p. 363–365° (mixed m.p.).

Triphenylsilyllithium in Tetrahydropyran.—A solution of 14.7 g. (0.05 mole) of chlorotriphenylsilane in 120 ml. of tetrahydropyran was added to 1.4 g. (0.2 g. atom) of lithium, with constant stirring. As in previous experiments, the formation of a white precipitate was noticed, within the first few minutes of adding the solvent. The mixture turned light yellow after 45 min. and became black-brown on stirring for 4 hr. at room temperature. Derivatization by treatment with 14.7 g. (0.05 mole) of chlorotriphenylsilane gave 19.1 g. (64.1%) of hexaphenyldisilane, m.p. 363–365° (mixed m.p.).

720 (1950); 16, 424 (1951); 19, 441 (1954), as well as a paper presented by Dr. G. N. R. Smart at the Delaware Regional Meeting of the A.C.S. in February, 1956.

(8) L. J. Brady, *Ind. Eng. Chem., Anal. Ed.*, **20**, 1034 (1948).

(9) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950).

(10) O. H. Johnson and D. M. Harris, *This Journal*, **72**, 5566 (1950).

(11) H. Gilman and F. Schultze, *ibid.*, **47**, 2002 (1925).

Dimethylphenylsilyllithium.—A solution of 3.6 g. (0.021 mole) of chlorodimethylphenylsilane in 30 ml. of tetrahydrofuran was added slowly to 0.69 g. (0.1 g. atom) of finely cut lithium wire. A prompt reaction took place soon after adding the first 5 ml. of the solution as evidenced by the formation of a brown color, the evolution of heat and a positive Color Test I. The brown color of the solution was temporarily discharged on adding the remainder of the solution, indicating the formation of the disilane intermediate. After stirring for 3 hr. at room temperature, the deep brown silylmetallic solution which formed was filtered through glass wool and derivatized with chlorotriphenylsilane. Work-up by the usual procedure gave 2.7 g. (32.6%) of 1,1-dimethyl-1,2,2,2-tetraphenyldisilane, m.p. 86–87°. A mixed melting point with an authentic sample¹² was not depressed.

Triphenylsilylpotassium.—To a mixture of 5.9 g. (0.02 mole) of chlorotriphenylsilane and 2.5 ml. (0.05 g. atom) of sodium-potassium alloy was added 75 ml. of tetrahydrofuran. After adding about 2 ml. of the solvent the surface of the alloy became deep brown indicating that the reaction had started. However, the brown color was rapidly discharged and soon a white precipitate was formed when the mixture was stirred after adding more solvent. After 15 min. of stirring the mixture became light yellow and gradually turned brown. The reaction was slightly exothermic and the flask was kept cool in an ice-bath. After stirring for 3 hr. the deep brown and clear solution of triphenylsilylpotassium was filtered through glass wool under nitrogen. The solution gave a positive Color Test I and was treated with 2.2 g. (0.02 mole) of chlorotrimethylsilane. Subsequent to hydrolysis and work-up in the usual manner there was obtained 5.0 g. (75.1%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 106–108°. A mixed m.p. with an authentic sample was not depressed.

Triphenylsilylrubidium.—Tetrahydrofuran (50 ml.) was added during 30 min. to a mixture of 2.95 g. (0.01 mole) of chlorotriphenylsilane and 2.58 g. (0.03 g. atom) of rubidium. After adding about 2 ml. of the solvent the mixture turned light yellow; a white precipitate was also observed. The flask was cooled in an ice-bath and stirring was continued for 3 hr. The clear, deep brown solution of triphenylsilylrubidium gave a positive Color Test I and derivatization with 1.1 g. (0.01 mole) of chlorotrimethylsilane gave 2.3 g. (69.1%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 106–108° (mixed m.p.).

Triphenylsilylcesium.—Gradual addition of tetrahydrofuran (50 ml.) to a mixture of 2.95 g. (0.01 mole) of chlorotriphenylsilane and 3.31 g. (0.03 g. atom) of cesium metal resulted in a prompt reaction as indicated by the light brown color of the solution. After about 15 min. of stirring, the mixture turned deep brown and became nearly black at the end of 1 hr. The clear solution of triphenylsilylcesium gave a positive Color Test I and was derivatized by treatment with 2.95 g. (0.01 mole) of chlorotriphenylsilane. Work-up of the mixture gave 2.0 g. (38.6%) of hexaphenyldisilane, m.p. and mixed m.p. 363–365°. Other products isolated were 1.2 g. (43.3%) of triphenylsilanol, m.p. 153–155°, and 0.3 g. (10.9%) of hexaphenyldisiloxane, m.p. 226–228°. The identities of these products were established by mixed melting point determinations with authentic samples.

In a second run using the same quantities of reactants and solvent the reaction was carried out at –50° (approx.). After 4 hr. of stirring the solution was derivatized using chlorotrimethylsilane to give a 46% yield of 1,1,1-trimethyl-2,2,2-triphenyldisilane.

Tri-*o*-tolylsilyllithium.—To a mixture of 8.42 g. (0.025 mole) of chlorotri-*o*-tolylsilane and 0.69 g. (0.1 g. atom) of finely cut lithium wire, 75 ml. of tetrahydrofuran was added during 1 hr. Twenty minutes after the solvent addition was commenced, the mixture turned light brown, indicating that the reaction had started. The reaction was slightly exothermic and the flask was cooled in a water-bath (approx. 15°). On stirring for 3 hr. the solution turned deep brown and gave a positive Color Test I. The silyllithium solution was filtered through glass wool and hydrolyzed by pouring into an excess of ice-cold dilute sulfuric acid. Extraction with ether and removal of the solvent gave 4.2 g. (55.5%) of tri-*o*-tolylsilane, which melted at 87–88°, after crystallization from ethanol. The infrared spectrum

(12) H. Gilman, R. K. Ingham and A. G. Smith, *J. Org. Chem.*, **18**, 1743 (1953).

of this compound in carbon tetrachloride showed a strong Si-H absorption band at 2125 cm^{-1} . The identity of this substance was confirmed by a mixed melting point determination and also by a comparison of the infrared spectrum with an authentic sample of tri-*o*-tolylsilane.⁹

Tri-*o*-tolylsilylcesium.—Tetrahydrofuran (75 ml.) was added during 1 hr. to a mixture of 3.4 g. (0.01 mole) of chlorotri-*o*-tolylsilane and 3.31 g. (0.03 g. atom) of cesium. The mixture became light red-brown within 5 min. and the reaction was exothermic. The flask was cooled in an ice-bath and stirred for 2 hr. The deep red-brown solution obtained gave a positive Color Test I. Subsequent to acid hydrolysis, work-up as in the previous experiment gave 0.9 g. (21.4%) of tri-*o*-tolylsilane, m.p. 87–88° (mixed m.p.).

Reaction of Chlorotriphenylsilane with Magnesium.—To 14.7 g. (0.05 mole) of chlorotriphenylsilane and an excess of magnesium turnings was added 50 ml. of tetrahydrofuran. Stirring was started, 2 drops of ethyl iodide was added, and the reaction mixture was warmed to reflux temperature. A yellow color and hexaphenyldisilane were observed within 15 minutes indicating initiation of the reaction. After stirring for 24 hr. the mixture was hydrolyzed by filtering through glass wool into dilute hydrochloric acid. Filtration and purification yielded 7.8 g. (60.5%) of hexaphenyldisilane, m.p. 356–359°.

Reaction of Chlorotriphenylsilane with Sodium.—A mixture of 1.15 g. (0.05 g. atom) of finely cut sodium metal was fused slowly with 7.35 g. (0.025 mole) of chlorotriphenylsilane. Subsequently, 40 ml. of tetrahydrofuran was slowly added. After stirring for 24 hr. the solution was yellow and gave a positive Color Test I, indicating the presence of triphenylsilylsodium. However, the color test faded on prolonged stirring. Work-up of the reaction mixture after one week of stirring yielded 2.9 g. (44.8%) of hexaphenyldisilane.

Triphenylgermyllithium.—To a stirred mixture of 3.84 g. (0.01 mole) of bromotriphenylgermane and 0.69 g. (0.1 g. atom) of lithium, 50 ml. of tetrahydrofuran was added during a 1-hr. period. A white precipitate was formed inside the flask after about 15 min. of stirring and the solution turned light yellow at the end of 4 min. Stirring was continued for 3 hr. at room temperature and the deep red-brown solution was filtered through glass wool. The solution gave a positive Color Test I and was treated with 1.5 g. (0.01 mole) of chlorotriethylsilane. The mixture was hydrolyzed and extracted with ether. Removal of the solvent gave 2.2 g. (52.5%) of triphenyl-(triethylsilyl)-germane, which melted at 95–96° after crystallization from ethanol. The identity of this product was established by a mixed melting point determination and comparison of the infrared spectrum of an authentic sample.¹³

Acknowledgment.—This research was supported in part by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors are grateful to Dan Aoki and Leonard Tushaus for assistance. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to Dr. V. A. Fassel and Mr. R. Kniseley for the spectra.

(13) H. Gilman and C. W. Gerow, *THIS JOURNAL*, **77**, 4676 (1955).

AMES, IOWA

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY AND FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Chromic Acid Oxidation of Diisopropyl Ether^{1,2}

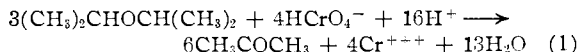
BY ROBERT BROWNELL, ALBERT LEO, Y. W. CHANG AND F. H. WESTHEIMER

RECEIVED JUNE 26, 1959

Chromic acid in aqueous sulfuric acid solution oxidizes diisopropyl ether to acetone in good yield without prior hydrolysis to isopropyl alcohol. The reaction proceeds about five times as fast as does the corresponding reaction of $(\text{CH}_3)_2\text{C}(\text{OCD}(\text{CH}_3)_2)$, but only about $1/1500$ as rapidly (per secondary hydrogen atom) as does that for isopropyl alcohol under the same experimental conditions. The mechanisms of chromic acid oxidations are discussed.

The kinetics of the chromic acid oxidations of alcohols^{3,4} and of aldehydes^{5,6} has been extensively investigated. Two mechanisms for the reactions have been advanced. One requires the preliminary formation of an ester⁷ of chromic acid which then undergoes decomposition to products; the other^{3a,8} mechanism involves the direct removal of a hydride ion (or hydrogen atom) from the secondary car-

bon atom of the alcohol. In order to help elucidate the mechanisms of oxidation-reduction processes, the reaction of chromic acid with isopropyl ether has been investigated.



Experimental

Materials.—Eastman Kodak Co. white label diisopropyl ether was freed from peroxides with acidified ferrous sulfate solution, washed, dried and distilled. Ether of half-degree boiling range, with an index of refraction,⁹ n_D^{20} 1.3679, was stored in a brown bottle over sodium wire. The ether, stored in this way, gave no peroxide test with acidified potassium iodide for several months; when the test became positive, the compound was discarded, and a fresh lot prepared.

The sulfuric acid solutions were prepared from distilled water and J. T. Baker "Sulfuric Acid, Special. Low in N and As. Subs. Oxid. by KMnO_4 (as SO_2): 0.0005%." Ordinary C.P. sulfuric acid contains impurities which react with chromic acid, and even the special reagent reacted slowly; a 0.0002 *M* solution of chromic acid in 5.47 *M* sulfuric acid decreased in optical density 4.2% in 30 hours. Other materials were of reagent grade, or were prepared as described in earlier publications.

(9) H. R. Fife and E. W. Reid, *Ind. Eng. Chem.*, **22**, 513 (1930).

(1) Taken in part from the thesis of Robert Brownell (University of Chicago, 1949) and the thesis of Albert Leo (University of Chicago, 1952).

(2) Presented at the Symposium on the Oxidation of Organic Compounds, Queen Mary College, London, April 13–14, 1959.

(3) (a) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); (b) W. Watanabe and F. H. Westheimer, *ibid.*, **17**, 61 (1949); (c) N. Nicolaides and F. H. Westheimer, *THIS JOURNAL*, **71**, 25 (1949); (d) M. Cohen and F. H. Westheimer, *ibid.*, **74**, 4387 (1952); (e) F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949), and Errata, June, 1950.

(4) H. Kwart and P. S. Francis, *THIS JOURNAL*, **77**, 4907 (1955); **81**, 2116 (1959).

(5) K. B. Wiberg and T. Mill, *ibid.*, **80**, 3022 (1958).

(6) G. Graham and F. H. Westheimer, *ibid.*, **80**, 3030 (1958).

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