was prepared by the method of Gambarjan as modified by Kharasch,[7] and dissolved in the olefin used. The peroxide content was determined by analysis.[8]

A detailed description of the procedure used in a typical trichlorosilane addition to an olefin is given. Essentially this same procedure was employed for the reactions given in Table I.

Olefin, Trichlorosilane and Diacetyl Peroxide.—1-Octene, 17.9 g., 0.16 mole, and trichlorosilane, b. p. 32°, 135.5 g., 1.0 mole, were placed in a three-necked flask with dropping funnel, thermometer, and a reflux condenser connected through a trap cooled in Dry Ice–acetone to a mercury seal 20 cm. in height. The system was swept with nitrogen for two hours, and the reaction mixture was heated to 45° under the slight extra pressure of the mercury. Crystalline diacetyl peroxide, 1.5 g., 0.013 mole, dissolved in 19.1 g., 0.17 mole, of 1-octene was then added during two hours. The mixture was heated at 50–63° for an additional nine hours.

After removal of excess trichlorosilane, the residue was distilled at reduced pressure and then redistilled at atmospheric pressure, giving 80.9 g. of clear colorless liquid, b. p. 231–232° at 728 mm., $n^{20}D$ 1.4480, 99% yield.

Anal. Calcd. for $C_8H_{17}SiCl_3$: Cl, 43.0. Found: Cl, 42.9, 43.0.

n-Octyltrichlorosilane from silicon tetrachloride and *n*-octylmagnesium bromide boils 233° at 731 mm.; 119° at 28 mm.[9]

Treatment of a portion of the product with ethanolic potassium hydroxide gave no hydrogen, indicating the absence of Si-H bonds.[10]

Reaction of the product, 24.8 g., 0.1 mole, with 0.35 mole of methylmagnesium bromide (using a procedure known to form the tetraalkylsilane from *n*-octyltrichlorosilane)[9] gave 13.0 g. of *n*-octyltrimethylsilane, b. p. 201.5° at 733 mm., $n^{20}D$ 1.4242, 74% yield. Constants for this compound[9] are: b. p. 202° at 760 mm., $n^{20}D$ 1.4242. All the data thus conclusively confirm equation (1).

Olefin, Trichlorosilane, and Ultraviolet Light.—1-Octene, 22.4 g., 0.2 mole, and trichlorosilane, 81.3 g., 0.6 mole, were placed in a 500 cc. quartz flask with thermometer and a reflux condenser connected through a trap cooled in Dry Ice–acetone to a mercury seal of 20 cm. height. The system was swept with nitrogen for a half hour, and the reaction mixture was heated to 46° under the slight extra pressure of the mercury. Ultraviolet light was applied from an external source and the solution was heated for twenty-four hours at a temperature range of 46–52°.

After removal of excess trichlorosilane, the residue was distilled at reduced pressure and then redistilled at atmospheric pressure, giving 15.3 g. of clear, colorless liquid, b. p. 231–232° at 728 mm., $n^{20}D$ 1.4481, 31% yield.

Anal. Calcd. for $C_8H_{17}SiCl_3$: Cl, 43.0. Found: Cl, 42.8, 42.9.

Treatment of a portion of the product with ethanolic potassium hydroxide gave no hydrogen, indicating the absence of Si-H bonds.[10]

The above product corresponds completely to the product of the peroxide catalyzed reaction. When ultraviolet light is applied for longer periods of time, better yields of the octyltrichlorosilane are obtained.

Reactions of 1-Octene with Other Silicon Hydrides.—These were carried out under essentially the same conditions as those described above.

Summary

1. A new synthesis of organosilicon compounds is described which involves the addition of trichlorosilane to olefins differing widely in structural type. These reactions are catalyzed by small amounts of diacetyl peroxide or ultraviolet light.

2. New alkyltrichlorosilanes of varying complexity were prepared by this method in good yield.

STATE COLLEGE, PA. RECEIVED MAY 28, 1947

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[7] (a) Gambarjan, *Ber.*, **42**, 4010 (1909); (b) Kharasch, *J. Org. Chem.*, **10**, 393 (1945).

[8] Kokatnur and Jelling, THIS JOURNAL, **63**, 1432 (1941).

[9] Whitmore, Sommer, DiGiorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, THIS JOURNAL, **68**, 475 (1946).

[10] *Cf.* Sauer, Scheiber and Brewer, *ibid.*, **68**, 962 (1946).

[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY, WASHINGTON, D. C.]

Reaction of Lithium Aluminum Hydride with Compounds Containing Active Hydrogen

BY J. A. KRYNITSKY, J. E. JOHNSON AND H. W. CARHART

The new compound, lithium aluminum hydride, discovered by Finholt, Schlesinger, *et al.*,[1,2] has been shown to be a vigorous agent for the reduction of various types of organic compounds.[3] In addition, many compounds containing active hydrogen decompose the reagent to liberate hydrogen. The purpose of this investigation was to study the latter type of reaction and to explore the possibility of using lithium aluminum hydride as a reagent for the determination of active hydrogen.

In a previous study, it was found that ether solutions of lithium aluminum hydride could be analyzed quantitatively by decomposing with excess water at 0° and measuring the evolved hydrogen by changes in pressure.[4] In the present work, an apparatus was devised so that a known amount of material could be added to an excess of lithium aluminum hydride–ether solution at 0° and the liberated gas measured by changes in pressure. By this method, the apparent active hydrogen content of a number of organic compounds was determined.

Experimental

Apparatus.—A diagram of the apparatus used is shown in Fig. 1. The reaction flask consisted of a 500-ml. round-bottom flask bearing a 35/20 spherical socket joint. A take-off arm was attached to the neck and connected to a manometer by small bore tubing through a T-tube. The T-tube was joined to a drying tube with rubber tubing which could be closed by a pinch clamp. The reaction flask was closed by a spherical ball joint carrying a 12 × 130 mm. guide tube. A clamp with an efficient locking

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[1] Finholt, Schlesinger and Wilzbach, Division of Physical and Inorganic Chemistry, A. C. S., Chicago Meeting, September, 1946.

[2] Finholt, Bond and Schlesinger, THIS JOURNAL, **69**, 1199 (1947).

[3] Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

[4] Krynitsky, Johnson and Carhart, *Anal. Chem.*, in press.

device was used to hold the joint together in order to prevent leakage. The supporting hook was made from glass rod joined to a sealed glass tube containing an iron core. The over-all length of the supporting hook was such that its lower end almost touched the bottom of the flask when the magnet pack was in the lowered position. The magnet pack consisted of two Alnico magnets in opposition mounted so that the pack passed over the guide tube easily. The sample cup was made from 15 mm. tubing and had a capacity of approximately 2 ml. A handle was provided so that the cup could be suspended from the supporting hook.

Before using the apparatus, the volume of the system was determined. In addition to this apparatus, a second one similar in construction but using a one-liter reaction flask was used for many of the determinations.

Procedure.—The reaction flask was clamped into place, connected to the manometer and surrounded with crushed ice and ice water. Approximately 100 ml. of cold lithium aluminum hydride–ether solution (0.3 to 0.7 molar) was placed in the flask and the assembled apparatus allowed to stand with the pinch clamp closed. If a pressure change was observed in five minutes, the pinch clamp was opened momentarily and the standing process repeated until equilibrium was reached. Sometimes over one hour was required to attain this equilibrium.

The material under investigation was weighed into a sample cup which was then hung on the supporting hook. The iron core end of the hook was placed in the guide tube with the magnet pack in the raised position. This assembly was attached to the flask and the joint locked in place.

After equilibrium was re-established (usually ten to fifteen minutes), the magnet pack was lowered so that the sample was brought into the solution. Pressure readings were taken at appropriate time intervals (usually five minutes) until no further change was observed. In some cases, when reaction was slow, the mixture was agitated slightly by raising and lowering the magnet pack.

The apparatus was readied for a subsequent analysis by releasing the pressure and withdrawing the sample cup and supporting hook. The next determination was then started immediately using a fresh sample cup and supporting hook.

The apparent number of active hydrogen atoms in the molecule was calculated from the equation

$$\text{No. active H atoms} = \frac{\text{pressure (mm.)} \times \text{net free vol. (ml.)}}{\text{millimoles sample} \times 17{,}030}$$

The pressure is the observed pressure increase less the small pressure increase found by carrying out a blank determination without a sample. The net free volume is the total volume of the system less the volume of solutions added and the volume of the supporting hook. The factor 17,030 combines the constants R and T.

In general, the size of the sample was chosen so that a pressure change of approximately 100 mm. was obtained. For the apparatus described, the amount of material ordinarily used varied from 0.1 to 0.4 g. depending on its molecular weight and the number of active hydrogen atoms. Materials which were suspected of not being dry were dried using anhydrous calcium sulfate or phosphorus pentoxide.

Results and Discussion

The values found for the apparent active hydrogen content of a number of typical organic compounds are presented in Table I.

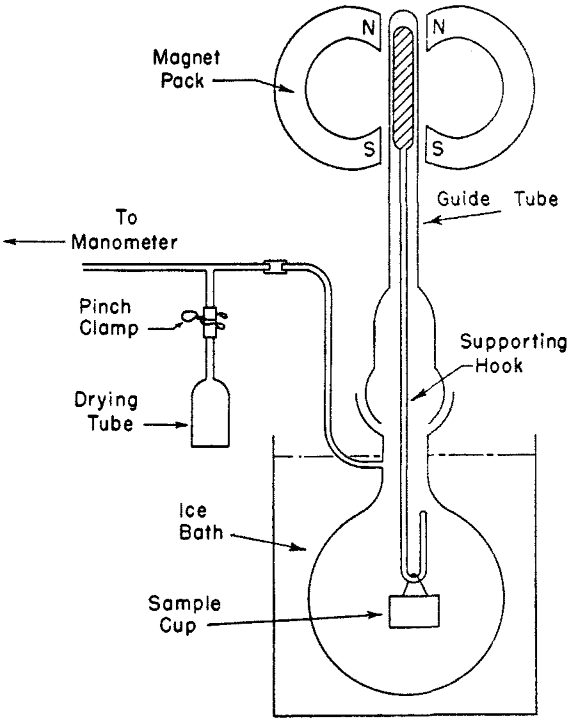

Fig. 1.—Apparatus for determining active hydrogen.

From this table, it can be seen that many of the simple alcohols, phenols and acids react with lithium aluminum hydride in ether to liberate hydrogen in the expected manner and give results which are in good agreement with the theoretical values. Although the reactions usually appeared to be complete within a few seconds, several minutes were required to reach equilibrium. The inconclusive results obtained with hydroquinone, succinic acid and terephthalic acid may be due to the formation of insoluble material which coats the crystals and inhibits further reaction. The anomalous results obtained with resorcinol may be due to the formation of an insoluble product or to partial reaction in the keto form. With the Grignard reagent, resorcinol has been reported to show from one to two atoms of active hydrogen.[5,6,7]

The amines and amides tested showed the expected number of active hydrogen atoms, and with the exception of acetanilide required prolonged reaction periods. The extreme slowness of the reaction of diamylamine was unexpected. The liberation of two hydrogens by primary amines and unsubstituted amides by this reagent at 0° is of interest since it has been reported that the Grignard reagent liberates one hydrogen from such compounds at ordinary temperatures and the second on heating.[8] Whereas the time required

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[5] Ciusa, *Gazz. chim. ital.*, **50**, II, 53 (1920).

[6] Fuchs, Ishler and Sandhoff, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 507 (1940).

[7] Lehman and Basch, *ibid.*, **17**, 428 (1945).

[8] Zerewitinoff, *Ber.*, **41**, 2233 (1908).

TABLE I

Name of compounds	Time to reach equilibrium, min.	No. of active H atoms found	
Alcohols and Phenols			
n-Decanol	5–10	1.00	1.02
Benzyl alcohol	5–10	1.06	
Heptanol-2	5–10	1.02	
Cyclohexanol	5–10	0.98	1.01
t-Amyl alcohol	5–10	0.97	1.00
2-Methyl-2,4-pentanediol	5–10	2.01	2.01
α-Naphthol	10–20	1.05	1.03
β-Naphthol	5–10	1.05	1.08
Resorcinol	50–140	1.53	1.56
Hydroquinone		....[a]	
Acids			
n-Caprylic acid	5–10	1.03	1.03
2-Ethylhexoic acid	5–10	1.02	
Benzoic acid	5–10	0.99	0.99
o-Bromobenzoic acid	10–15	1.00	
Succinic acid		....[a]	
Terephthalic acid		....[a]	
Amines and Amides			
Cyclohexylamine	115	2.08	
Diamylamine	375	0.94	
Tributylamine		None[b]	
Aniline	50	1.99	2.05
β-Naphthylamine	70–80	2.04	1.99
2-Ethylhexanoamide	60	2.05	
Acetanilide	5–10	0.98	
Nitro Compounds			
Nitrobenzene	35	2.08	
o-Nitrotoluene	100	2.03	
Nitromethane	120–250	2.40	2.75
Tautomeric Compounds			
Acetyl acetone	5–10	0.94	0.95
Ethyl acetoacetate	5–10	.56	.57
Diethyl malonate	5–10	.56	.57
Diethyl methylmalonate	5–10	.25	.28
Diethyl ethylmalonate	5–10	.22	.25
Diethyl *i*-propylmalonate	5–10	.18	.21
Diethyl *n*-butylmalonate	5–10	.22	.26
Diethyl *i*-butylmalonate	5–10	.22	.25
Diethyl benzylmalonate	5–10	.19	.21
Miscellaneous			
Acetophenone	5–10	0.07	0.05
Propiophenone	5–10	0.05	0.08
Octyl mercaptan	5–10	1.00	1.01
Dioctyl thioether		None[b]	
Ethyl palmitate		None[b]	
Phenylhydrazine	70–125	Erratic[c]	

[a] Reaction with these compounds was slight and too slow to obtain significant results. [b] These compounds gave less than 0.02 atom of active hydrogen. [c] Values obtained were 3.01, 2.68, 3.47, 3.90 and 3.20.

for complete liberation of hydrogen by primary amines and unsubstituted amides was rather long, in every case the first hydrogen was liberated rapidly, usually within five minutes. This behavior was also observed for all other compounds tested showing more than one atom of apparent active hydrogen.

Nitrobenzene and nitrotoluene showed two apparent active hydrogen atoms. With the Grignard reagent nitrobenzene has been reported as showing from 1.0 to 1.9 active hydrogens depending on the reagent used.[9] In contrast to the aromatic nitro compounds, nitromethane gave erratic results showing more than two apparent active hydrogens. With the Grignard reagent, values of less than one have been reported for nitromethane.[5,10]

The reaction of lithium aluminum hydride with compounds exhibiting keto–enol tautomerism was rapid and the results indicated that the compounds tested behaved as though they were partially enolized. In this connection it is interesting to note that diethyl malonate reacted as though it were approximately 56% enolized, yet the substituted diethyl malonates gave values which ranged from 18 to 28%. With the Grignard reagent acetylacetone, ethyl acetoacetate and diethyl malonate have been reported to react as though they existed entirely in the mono-enol form.[6,8] In contrast to the Grignard reagent, it appears that lithium aluminum hydride reacts with the keto form of these compounds rapidly enough so that complete enolization cannot occur.

Definite conclusions cannot be drawn from the values obtained for acetophenone and propiophenone. However, it is indicated that these compounds reacted as though they were partially enolized. In this respect, it is of interest that acetophenone has been reported to react with the Grignard reagent as though it were approximately 12–15% enolized in isoamyl ether and 78% in pyridine or dioxane.[11,12]

Although the reaction of phenylhydrazine with lithium aluminum hydride gave erratic results, it was surprising that in three out of five determinations, more than three apparent active hydrogen atoms were found. This suggested partial cleavage of the N–N bond. Confirmation of this cleavage was obtained by detection of ammonia upon hydrolysis of such a reaction mixture. In every case, the liberation of the first two hydrogens was rapid and occurred within five minutes.

Acknowledgment.—The authors are indebted to Dr. W. E. Weaver of this Laboratory who courteously furnished the substituted malonic esters used in this work.

Summary

The apparent active hydrogen content of a number of organic compounds was determined by means of an ether solution of lithium aluminum hydride. In the majority of cases, this reagent behaved in a manner similar to that of the Grignard reagent and the expected number of hydro-

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(9) Gilman and Fothergill, THIS JOURNAL, **49**, 2815 (1927).

(10) Zerewitinoff, *Ber.*, **43**, 3590 (1910).

(11) Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

(12) Lieff, Wright and Hibbert, *ibid.*, **61**, 865 (1939).

gen atoms was found. However, in some instances, the reaction was more vigorous in that it proceeded at a lower temperature and further toward completion.

With lithium aluminum hydride, the keto–enol tautomers investigated behaved as though they were only partially enolized, whereas similar compounds with the Grignard reagent act as though they exist in the enol form only.

WASHINGTON, D. C. RECEIVED JULY 22, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY]

Claisen Condensation of Methyl Esters

BY E. EARL ROYALS

Investigations of the acetoacetic ester condensation[1] have been largely confined to the study of ethyl esters; particularly, relatively few methyl ester condensations have been reported in the literature. The present commercial availability of sodium methoxide, and observations[2] that sodium methoxide is a condensation catalyst considerably less sensitive to adverse experimental conditions than sodium ethoxide make further investigation of methyl ester condensations desirable. The present research was undertaken to determine the utility of sodium methoxide as a reagent for the condensation of the simpler methyl esters, and, more specifically, to develop methods of synthesis for certain keto-esters which have not previously been satisfactorily prepared by direct ester condensation.

McElvain and co-workers made an extensive study of the self-condensation of ethyl esters in the presence of sodium ethoxide under both equilibrium and forcing conditions.[3] Our results on the self-condensation of methyl esters, shown in Table I, are quite similar to those of McElvain in the ethyl ester series. Our forcing procedure, however, is considerably simpler and requires less of the pure ester than the one described by McElvain.

The condensation of methyl benzoate with methyl acetate has been reported to give yields of methyl benzoylacetate ranging from 45 to 85% depending on the conditions employed.[4] Dorsch and McElvain[5] condensed ethyl benzoate in the presence of sodium ethoxide with ethyl acetate, propionate, and *n*-butyrate and obtained yields of 37, 19 and 4%, respectively, of the α-benzoyl esters. We have investigated the condensation of methyl benzoate with methyl acetate, propionate and *n*-butyrate; our results are summarized in Table II. The methyl propionate condensation was chosen for pilot work. The yield of methyl α-benzoylpropionate from equivalent quantities of the two esters and sodium methoxide was found to be essentially the same whether the reactants were directly mixed, or whether the propionate was added dropwise to a mixture of methoxide and benzoate. The yield was not increased by lengthening the reaction time from four to twenty-four hours. It was found, however, that the use of excess methyl propionate and sodium methoxide greatly increased the yield of methyl α-benzoylpropionate (calculated on methyl benzoate); indeed, the second and third equivalents of propionate were utilized in inter-ester condensation with almost the same efficiency as the first. Similar results were obtained in the condensation of methyl acetate with methyl benzoate; somewhat lower yields were obtained, however, than in the corresponding methyl propionate condensations. The best conditions found for the condensation of methyl benzoate with methyl propionate were applied to the analogous methyl *n*-butyrate condensation. A negligible yield of methyl α-benzoylbutyrate was obtained. It was observed, however, that even with a reaction period of forty hours, considerable quantities of methyl *n*-butyrate were recovered unreacted, indicating that the low yield of inter-ester condensation product might be due to an unfavorable equilibrium rather than to a preference of methyl *n*-butyrate for self-condensation. Accordingly, methyl *n*-butyrate (4 moles) was condensed with methyl benzoate (1 mole) in the presence of sodium methoxide (2

TABLE I

SELF-CONDENSATIONS OF METHYL ESTERS IN THE PRESENCE OF SODIUM METHOXIDE

Methyl ester	Moles ester per mole CH_3ONa	Temp., °C.	Time, hr.	% yield β-ketoester
Acetate	6	60	8	43
Acetate (forced)[a]	6	80	8	43–50
Propionate	4	80	16	29
Propionate	6	80	16	42
Propionate (forced)	6	100	16	71
n-Butyrate (forced)	6	125	30	79
Phenylacetate (forced)	2	100[b]	6	80

[a] See text and Experimental Part for description of forcing conditions. [b] Pressure slowly reduced from atm. to final value of 10 mm.

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(1) See Hauser and Hudson in Adams, "Organic Reactions," John Wiley and Sons, New York, N. Y., 1942, Chap. 9.

(2) Freri, *Gazz. chim. ital.*, **68**, 616 (1938); Royals, THIS JOURNAL, **67**, 1508 (1945).

(3) McElvain, THIS JOURNAL, **51**, 3124 (1929); Briese and McElvain, *ibid.*, **55**, 1697 (1933); Roberts and McElvain, *ibid.*, **69**, 2007 (1937).

(4) Ref. 1, pp. 278, 283.

(5) Dorsch and McElvain, THIS JOURNAL, **54**, 2960 (1932).