yield, 1-hydroxymethylcyclohexene in a 21% yield, and the expected 2-hydroxymethylcyclohexanol in only an 11% yield. We were able to use all these intermediates to advantage for the synthesis of 3-methylenecyclohexene.[5] The mechanism postulated for this reaction, based partly on the fact that 2-hydroxymethylenecyclohexanone gives the identical products, involves the normal reduction of the ester to the aldehyde, followed by the formation of the corresponding enolate which could undergo attack at either carbonyl group to produce a doubly charged anion which, although stable to further attack by hydride ion, can lose an oxygen ion by analogy with the mechanism for the base-catalyzed dehydration of aldols. One could write a similar mechanism for the reduction of malonic esters. In order to demonstrate that this anomalous reduction would occur with other malonic esters, ethyl methylmalonate was reduced with lithium aluminum hydride to produce, in addition to the expected diol, a 5.2% yield of methallyl alcohol. The methallyl alcohol was identified by vapor phase chromatography and infrared analysis.

Finally as an example that would give an increased opportunity for this anomalous reduction, bimalonic ester, ethyl 1,1,2,2-ethanetetracarboxylate, was reduced as previously described[6] and the forerun from the reductive acetylation was examined carefully. From this reduction was obtained a 15% yield of 2,3-di(acetoxymethyl)-3-butenyl acetate, together with the expected tetraacetate. The structure of this olefin triacetate was proved by pyrolysis to the known 2,3-di(acetoxymethyl)-1,3-butadiene[6] and by independent synthesis by the pyrolysis of 2,3-di(acetoxymethyl)-1,4-diacetoxybutane.

An attempt to isolate 2-phenylallyl alcohol from the reduction of ethyl phenylmalonate failed. It may be that this substituted styrene is formed but is polymerized before isolation.

Experimental[7]

Methallyl Alcohol from Reduction of Ethyl Methylmalonate.—To a slurry of 27.5 g. (0.737 mole) of lithium aluminum hydride and 300 ml. of dry ether in a 1-l., three-necked flask, fitted with a reflux condenser, a dropping funnel, and a stirrer, was added a solution of 75.6 g. (0.435 mole) of ethyl methylmalonate in 100 ml. of ether at a rate such as to maintain gentle reflux of the solvent acid. After the mixture had been heated under reflux for an additional 18 hr., it was poured onto a mixture of ice and dilute hydrochloric acid. The aqueous phase was extracted for 2 days in an exhaustive extractor and the extracts, together with the original ether layer, were dried over anhydrous magnesium sulfate. Distillation of this solution through a 10-in., helix-packed column gave 1.9 g. (5%) of methallyl alcohol, b.p. 112–115°, $n^{25}\mathrm{D}$ 1.4228 (reported[8] b.p. 111.5–112°, $n^{25}\mathrm{D}$ 1.4232), and 28.1 g. (72%) of 2-methyl-1,3-propanediol, b.p. 90–93° (4 mm.), $n^{25}\mathrm{D}$ 1.4436 (reported[9] b.p. 213–214°, $n^{20}\mathrm{D}$ 1.4445). Vapor phase chromatography of this sample of methallyl alcohol at 88° on di-*n*-decyl phthalate column gave a single symmetrical peak with the same retention time as that of an authentic sample of methallyl alcohol.

2,3-Di(acetoxymethyl)-3-butenyl Acetate from the Reduction of Ethyl 1,1,2,2-Ethanetetracarboxylate.—To a slurry of 100 g. (2.63 moles) of lithium aluminum hydride in 3 l. of ether was added dropwise a solution of 318 g. (1 mole) of ethyl 1,1,2,2-ethanetetracarboxylate in 3 l. of ether. After 2 l. of *n*-butyl ether had been added, the mixture was heated under reflux for 8 days. Most of the ethyl ether was removed by distillation with the concurrent addition of an additional 2 l. of *n*-butyl ether. After 500 ml. of glacial acetic acid had been added to decompose the excess hydride, followed by the addition of 1000 ml. of acetic anhydride, the mixture was heated under reflux for 6 days. During this period the mixture became so thick that stirring had to be discontinued and an additional 2 l. of *n*-butyl ether was added. The salts were removed from the solution by filtration and the solvent was removed from the filtrate by distillation. Fractionation of the residue through a 10-in. Vigreux column gave a forerun, b.p. 90–115° (0.2–0.4 mm.), and 151 g. (48%) of 2,3-di(acetoxymethyl)-1,4-diacetoxybutane, b.p. 160–165° (1.8 mm.), m.p. 66–68° (reported[6] 67–68°). The forerun, which contained some solid tetraacetate, was filtered and the solid was washed with ether. The combined filtrates were refractionated through a 10-in., helix-packed column to yield 39 g. (15%) of 2,3-di(acetoxymethyl)-3-butenyl acetate, b.p. 107.5–109° (0.2–0.3 mm.), $n^{25}\mathrm{D}$ 1.4499 [reported[6] b.p. 138–139° (2 mm.), $n^{25}\mathrm{D}$ 1.4518].

Anal. Calcd. for $C_{12}H_{18}O_6$: C, 55.81; H, 6.96; sapon. equiv., 86. Found: C, 55.98; H, 7.16; sapon. equiv., 85.

The olefin triacetate produced by the pyrolysis of 2,3-di(acetoxymethyl)-1,4-diacetoxybutane was identical to that prepared by the reductive acetylation of ethyl 1,1,2,2-ethanetetracarboxylate.

Pyrolysis of 2,3-Di(acetoxymethyl)-3-butenyl Acetate.—At a rate of 28 drops per min., 35 g. (0.135 mole) of 2,3-di(acetoxymethyl)-3-butenyl acetate was dropped through the pyrolysis tube heated at 490° while the system was flushed with a slow stream of oxygen-free nitrogen.[6] After an ether solution of the pyrolysate was extracted with water, the organic layer was dried over anhydrous magnesium sulfate. (Titration of an aliquot of the aqueous extracts indicated that 55% of the theoretical amount of acetic acid had been eliminated.) The ether was removed by distillation and the residue was fractionated through a 10-in., helix-packed column to give 10.9 g. (41%) of 2,3-di(acetoxymethyl)-1,3-butadiene, b.p. 61–63° (0.25 mm.), m.p. 62–63° (reported[6] m.p. 63–64°), and 14.1 g. of recovered starting material. A mixture melting point determination of this solid with an authentic sample of the diene–diacetate prepared from the pyrolysis of the tetraacetate[6] showed no depression.

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Reactions of Phenyl-Substituted Methanes and Ethanes with Lithium or *n*-Butyllithium

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The chemistry of triphenylmethyllithium has been studied and reviewed recently by Tomboulain.[1] In that investigation, the organometallic compound was prepared in varying yields by reactions of triphenylmethyl chloride with lithium in a variety of solvents. We are now reporting the preparation of this reagent by the reaction of triphenylmethane with lithium or *n*-butyllithium, as well as by the lithium cleavage of 1,1,1,2-tetraphenylethane in tetrahydrofuran (THF) or in mixtures of diethyl ether and THF. Also reported at this time are some related reactions involving toluene, diphenylmethane, and *sym*-tetraphenylethane.

Although lithium wire in THF had been employed previously in the metalation of fluorene,[2a] 9-phenylfluorene[2a,3] and cyclopentadiene,[2a] and in the cleavage

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TABLE I

REACTIONS OF LITHIUM DISPERSION WITH PHENYLMETHANES AND -ETHANES[a]

Hydrocarbon, mole	THF, ml.	Temp., °C.	Reaction time, days	Products, %
Ph_2CH_2 (0.1)[b]	100	25	8	Ph_2CH_2 (78)
Ph_2CH_2 (0.1)	150	25	3	Ph_2CHCO_2H (33)[c]; Ph_2CH_2 (54.5)
Ph_2CH_2 (0.05)	50	25	5	Ph_2CHCO_2H (59)[c]; Ph_2CH_2 (22)
$Ph_2CHCHPh_2$ (0.015)[d]	50	65	7	Ph_2CH_2 (12.35); $Ph_2CH(CH_2)_4OH$ (62.2)[e]
Ph_3CCH_2Ph (0.015)	50	65	2	Ph_3CCO_2H (51)
Ph_3CCH_2Ph (0.015)	50	65	4	Ph_3CCO_2H (72.4)
Ph_3CCH_2Ph (0.004)	30	25	6	Ph_3CCO_2H (82.6)

[a] 100% excess of lithium was used in all reactions and all mixtures were carbonated. [b] Lithium sand was employed in this reaction. [c] M.p. 145–147°. [d] Two additional reactions were carried out under comparable conditions, except for reaction times of 2 and 4 days, respectively. Since work-up of the aqueous layer gave no acid, the organic layers of the three reactions were combined and treated in the usual manner. [e] B.p. 135–137° (0.01 mm.), n^{20}_D 1.5697, d^{20}_{20} 1.049. *Anal.* Calcd. for $C_{17}H_{20}O$: C, 84.8; H, 8.38; MR_D, 75.1. Found: C, 84.75, 84.57; H, 8.63; 8.55; MR_D, 75.4. The infrared spectrum of this material has a sharp band at 3356 cm.$^{-1}$, characteristic of the hydroxyl group.

of 9,9-diphenylfluorene,[2a] no reaction occurred with triphenylmethane after five days at room temperature.[2a] Reaction does occur with potassium in 1,2-dimethoxyethane.[2b] The same results were obtained by us when the last-mentioned reaction with lithium and triphenylmethane was repeated during this investigation. When the solution was refluxed for four days, however, a red color developed in the mixture, and a 15.9% yield of triphenylacetic acid was realized subsequent to carbonation after refluxing for an additional fourteen days with stirring.

The yield of acid was not increased to any appreciable extent when lithium sand was employed. However, the use of dispersed lithium in refluxing THF gave triphenylacetic acid in yields ranging up to 72% over a reaction period of seven days. In most of these runs, the stirrer was allowed to rub against the bottom of the flask in order to expose a fresh surface on the metal continuously. In one run where such scraping was not allowed, the yield of acid was only 20.5%. This was considerably lower than the yields obtained after comparable reaction times when rubbing was allowed.

It was also noticed that the yield of triphenylacetic acid varied considerably in the reactions employing a given form of lithium. This variation may possibly have been due to variations in intensity of rubbing by the stirrer, a factor which was difficult to control. The length and variations in induction periods observed for these reactions may also be explained on the same basis. Although care was taken to exclude moisture from these reactions, this induction period was probably due to small amounts of moisture in the system. Once the reactions began, as evidenced by the red color of the organometallic compound, the yields in comparable reactions were of the same order of magnitude. Attempts to effect the metalation with dispersed lithium in diethyl ether or tetrahydropyran both failed, indicating that the basicity of the solvent is a predominant factor in these reactions.

As noted in Table I, lithium sand failed to metalate diphenylmethane after stirring for eight days at room temperature. The reaction of dispersed lithium with this compound at room temperature, however, gave a 33% yield of diphenylacetic acid after three days and a 58% yield after five days. No phenylacetic acid could be detected from the reaction of toluene with lithium dispersion after refluxing for either six or twelve days in THF.

Three reactions of symmetrical tetraphenylethane with lithium dispersion were carried out, but no diphenylacetic acid was isolated after carbonation at various intervals, although several color changes were observed. When the organic layers were combined and distilled, diphenylmethane (12.25%) and an alcohol, which is presumed to be 5,5-diphenyl-1-pentanol (62.2%) were obtained. These reaction mixtures never attained the red colors observed in the reactions of diphenylmethane with lithium.

This solvent cleavage is rather surprising since triphenylmethylsodium does not effect this reaction under reflux conditions unless complexed with triphenyl boron[4] or triphenylaluminum.[5] Also, the reaction of symmetrical tetraphenylethane with potassium in diethyl ether gave diphenylacetic acid subsequent to carbonation.[6] Although a higher temperature was used in the reactions of tetraphenylethane with lithium than in the metalation of diphenylmethane, the failure to observe a red color in the former reaction suggests that a free-radical mechanism may be involved in the formation of 5,5-diphenyl-1-pentanol. Hydrogen abstraction by the radical could also account for the isolation of diphenylmethane from this reaction. In this connection, it is interesting to note that triphenylmethylmagnesium bromide is capable of cleaving THF under reflux conditions, apparently because of the ability of Grignard reagents to coordinate with the solvent.[7]

Unsymmetrical tetraphenylethane similarly was cleaved by lithium, and the mixtures were carbonated to give triphenylacetic acid in yields ranging up to 82.6%. These reaction mixtures did not have the characteristic odor of phenylacetic acid indicating the absence of benzyllithium at the time the mixtures were carbonated. Apparently, the benzyllithium underwent further reaction with the solvent; however, no products derived from it were isolated. Similar results were obtained by Ziegler and Thielmann when potassium was used in an analogous reaction.[6]

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TABLE II

METALATION OF PHENYLMETHANES WITH *n*-BUTYLLITHIUM

Compound metalated, mole	BuLi, mole	Solvent, ml. Et_2O:THF	Temp., °C.	Time, hr.	Acid, %	Other products, %
Ph_3CH (0.0204)	0.021	20:50	25	0.25	77.6	. . .
Ph_3CH (0.0204)	.023	20:50	0	1	51.5	Ph_3CH (37)
Ph_3CH (0.0204)	.022	22:50	25	1	74.0	Ph_3CH (11.6)
Ph_3CH (0.0204)	.03	30:50	0	4	86.5	Ph_3CH (8.2)
$PhCH_3$ (0.19)	.05	50:40	0	1	. . .	Valeric acid (53.5)[a]
$PhCH_3$ (0.1)	.12	120:50	10	1	. . .	Valeric acid (48.5)[b]
$PhCH_3$ (0.05)	.075	75:50	25	1	20.7[c]	. . .
$PhCH_3$ (0.15)	.21	235:80	25	24	24.3[d]	. . .

[a] B.p. 188–190°, $n^{20}D$ 1.4108. [b] B.p. 187–189°, $n^{20}D$ 1.4112. [c] M.p. 76–77°, from petroleum ether (b.p. 60–70°). [d] M.p. 75–77°, from petroleum ether (b.p. 60–70°).

In Table II, are recorded several reactions of triphenylmethane and toluene with *n*-butyllithium. All of these reactions were carried out in a mixture of diethyl ether and THF since this combination of solvents had previously been shown to be well suited for metalation reactions.[8,9] Apparently, dilution of THF with ether does not decrease the effectiveness of this solvent in facilitating metalation reactions; however, it does stabilize the organometallic compounds, since these reagents are known to be more stable in diethyl ether than in THF.[10] This is also exemplified by the yields of triphenylacetic acid in the reactions recorded in Table II; the best yield was obtained when *ca.* a 50% excess of *n*-butyllithium was employed in a reaction at 0°.

The reactions of toluene with *n*-butyllithium at 0° or 10° failed to give any of the metalated product, whereas stirring at room temperature with an excess of *n*-butyllithium did cause metalation to occur. No indication for the presence of valeric acid was observed after twenty-four hours at room temperature, indicating that the *n*-butyllithium and, undoubtedly, some of the benzyllithium were consumed by a reaction with the solvent. Previously, toluene was metalated in very low yield by *n*-butyllithium in ether solution.[11] These results again indicate the advantage of using THF in metalation reactions. It might be mentioned that metalation of toluene is not the best method for preparing benzyllithium since better yields of this reagent have been obtained by cleavage reactions.[12,13]

Experimental[14]

General Procedure.—The lithium sand used in several reactions was prepared by heating lithium wire in mineral oil to *ca.* 200° and shaking the round-bottomed flask, in which it was contained, very vigorously as it cooled below the melting point of lithium. This was done under an atmosphere of dry, oxygen-free nitrogen. The material was then washed into a separatory funnel with dry benzene and the oil was removed through the stopcock. The finely divided lithium was washed several times with benzene, then with diethyl ether and finally with THF, before being transferred to the reaction flask with dry THF.

The lithium dispersion was kindly supplied by the Lithium Corporation of America, Inc. The material having a particle size of less than 25 μ was dispersed in heavy petrolatum as a 30% dispersion. The petrolatum was removed by washing with benzene and THF before use.

All of the reactions using lithium metal were carried out in three-necked flasks fitted with a mechanical stirrer, reflux condenser, and nitrogen inlet and outlet tube. The stirrer was adjusted so as to fit flush, but not tight against the bottom of the flask. The mixtures were then stirred continuously for the reaction times indicated in the tables and carbonated by pouring through glass-wool into a slurry of Dry Ice and diethyl ether.

In the reactions involving *n*-butyllithium, this organometallic compound was prepared in diethyl ether and added to a solution of the hydrocarbon in tetrahydrofuran. All of these reactions were terminated by carbonation. All products except 5,5-diphenyl-1-pentanol were identified by mixture melting points and infrared spectra if solids, and by their physical constants and infrared spectra if liquids.

Lithium Metal and Triphenylmethane.—A series of runs involving the interaction of triphenylmethane and different physical forms of lithium metal in tetrahydrofuran was carried out, in order to establish optimal reaction conditions. In a typical run, 5.0 g. (0.0204 mole) of triphenylmethane and *ca.* 0.115 g.-atom of lithium metal were stirred (with paddle scraping on the bottom of the flask) together in 50 ml. of tetrahydrofuran. Three types of runs were conducted. First, with cut pieces of lithium wire a 15.9% yield of triphenylacetic acid and a 60% recovery of triphenylmethane were obtained after 18 days at the reflux temperature. Second, with lithium sand the maximum yield of triphenylacetic acid (21.3%) observed was obtained after 9 days of refluxing. Third, with lithium dispersion the maximum yield obtained after 7 days at room temperature was 66% (20.2% of the starting triphenylmethane being recovered). When the reaction was conducted at the reflux temperature over 5–8 days, the yield of triphenylacetic acid ranged from 59–72% and that of recovered triphenyl methane dropped to 15%.

The triphenylacetic acid melted in the range 269–272° and the recovered triphenylmethane melted above 93°.

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(14) All melting and boiling points are uncorrected. Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. The tetrahydrofuran was dried and purified by refluxing over sodium, distilling into lithium aluminum hydride, refluxing over this reagent, then distilling immediately before use under dry nitrogen.