[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Chemistry of Trityllithium. Direct Preparation and Some Reactions[1,2]

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The preparation of trityllithium by the reaction of lithium with trityl chloride has been studied under a variety of conditions. The highest yield (70%) of the carbonation product, triphenylacetic acid, was obtained with 1,2-dimethoxyethane as solvent, although the reaction proceeded more readily in tetrahydrofuran. Triphenylmethane and *p*-benzhydryltetraphenylmethane are formed as side products in the preparation of trityllithium. The carbanion character of this reagent has been demonstrated by reactions with several carbonyl compounds.

Although a number of organometallic compounds containing the triphenylmethyl (trityl) group have been prepared, tritylsodium and the trityl Grignard reagent are by far the most common. Bachmann demonstrated that tritylmagnesium bromide underwent a number of reactions typical of organomagnesium compounds, such as addition to phenyl benzoate to give benzopinacolone in 46% yield.[3] Yields near 90% were obtained in coupling reactions with alkyl halides,[3,4] and carbonation gave 83% of the theoretical amount of triphenylacetic acid.[5]

A study of the reactions of tritylsodium was made by Schlenk and Bergmann in 1928, who found addition to take place with triphenylacetyl chloride and phenyl isocyanate.[6] Compounds with acidic hydrogen atoms gave triphenylmethane. The yields in these conversions, however, were not indicated. The strong basic properties of tritylsodium have found use in the catalysis of ester condensations,[7,8] and in the determination of active hydrogen atoms.[9] The nucleophilic properties of tritylsodium have been demonstrated by its reaction with diphenyl ether to give tetraphenylmethane,[10] and by conjugate addition observed with ethyl crotonate and ethyl cinnamate.[11]

The direct preparation of trityllithium was first reported in 1929 by Grosse who treated trityl chloride with lithium amalgam in ethyl ether.[12] Based on analytical data, a structure has been proposed for the orange dietherate formed in this reaction.[13] The lithium amalgam method has been reported to give a 16–20% yield of the reagent,[14] but reaction does occur with lithium metal alone in diethyl ether[15] or in tetrahydrofuran.[16] An attempt to prepare trityllithium by the action of lithium amide on triphenylmethane appeared to be successful until ether was added to replace the liquid ammonia solvent, whereupon the color of the reagent disappeared and only starting material was recovered.[17] Also, no reaction was observed when triphenylmethane was treated with lithium in tetrahydrofuran.[18] Metalation of triphenylmethane has been carried out by use of *n*-butyl- or *n*-propyllithium in ethyl ether.[19–21] Carbonation of trityllithium produced by exchange gave triphenylacetic acid in 82% yield.[19]

As a result of the present work, a number of solvents have been found suitable for the preparation of trityllithium by the action of lithium on trityl chloride. Among these are: tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), ethyl ether, benzene, and toluene. The reaction failed in cyclohexane. The ease of preparation differs markedly, however, mainly due to variations in the initiation period. The superior solvating properties of tetrahydrofuran and 1,2-dimethoxyethane in many organometallic reactions also are evidenced here. In the solvent of choice, tetrahydrofuran, consist-

$$(C_6H_5)_3CCl + 2Li \longrightarrow (C_6H_5)_3CLi + LiCl$$

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[1] Presented in part at the 133rd Meeting of the American Chemical Society, San Francisco, April 1958; Abstracts, p. 7N.

[2] This work was supported by a research grant from the University of Minnesota.

(3) W. E. Bachmann and R. F. Cockerill, *J. Am. Chem. Soc.*, **55**, 2932 (1933).

(4) W. E. Bachmann, *J. Am. Chem. Soc.*, **55**, 2135 (1933).

(5) J. Schmidlin, *Ber.*, **39**, 628 (1906).

(6) W. Schlenk and E. Bergmann, *Ann.*, **464**, 1 (1928).

(7) For a review, see C. R. Hauser and B. E. Hudson, Jr., *Org. Reactions*, **1**, 266 (1942).

(8) For a recent example, see D. F. Thompson, P. L. Bayless, and C. R. Hauser, *J. Org. Chem.*, **19**, 1490 (1954).

(9) A. H. Corwin and R. C. Ellingson, *J. Am. Chem. Soc.*, **64**, 2098 (1942).

(10) A. Lüttringhaus, G. Wagner-v. Sääf, E. Sucker, and G. Borth, *Ann.*, **557**, 46 (1945); A. Lüttringhaus and H. Schuster, *Angew. Chem.*, **70**, 438 (1958).

(11) W. D. McPhee and E. G. Lindstrom, *J. Am. Chem. Soc.*, **65**, 2177 (1943).

(12) A. von Grosse, *Ber.*, **59**, 2646 (1926).

(13) B. M. Mikhailov and N. G. Chernova, *Doklady Akad. Nauk S.S.S.R.*, **74**, 939 (1950).

(14) C. Mannerskantz and L. G. Sillen, *Acta Chem. Scand.*, **8**, 1466 (1954).

(15) G. Wittig, U. Todt, and K. Nagel, *Chem. Ber.*, **83**, 110 (1950).

(16) G. Wittig, R. Mangold, and G. Felletschin, *Ann.*, **560**, 116 (1948).

(17) C. R. Hauser, D. S. Hoffenberg, W. H. Puterbaugh, and F. C. Frostick, *J. Org. Chem.*, **20**, 1531 (1955).

(18) H. Gilman and R. D. Gorsich, *J. Org. Chem.*, **23**, 550 (1958).

(19) H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 315 (1936).

(20) A. G. Brook, H. Gilman, and L. S. Miller, *J. Am. Chem. Soc.*, **75**, 4759 (1953).

(21) H. Gilman, A. H. Haubein, and H. Hartzfeld, *J. Org. Chem.*, **19**, 1034 (1954).

ently reproducible results were obtained. In the hydrocarbon solvents, the initiation requires a considerable period and occasionally the reaction cannot be started. The course of the reaction can be followed by observing the color changes and the disappearance of the lithium. The first evidence of reaction is the appearance of the red color of the reagent on the surface of the lithium. This may be hastened by vigorous stirring with a Teflon paddle which is adjusted to scrape the surface of the metal. After a few minutes to a few hours, depending on the solvent, the yellow solution suddenly acquires a red color. This change is usually very abrupt and requires about 10 min. In tetrahydrofuran, the induction period is about 15–30 min.; in benzene, the period is about 24 hr. Once the red color appears, the mixture darkens rapidly as the concentration of the lithium reagent increases; the reaction is usually complete within 4 hr. In hydrocarbon solvents and ethyl ether, trityllithium is not very soluble and forms an orange suspension. The red or orange color, however, is not always indicative of the reagent; in several experiments which employed long reflux periods, the color was present at the time of carbonation but no acidic compounds were isolated. Apparently various by-products of the reaction are also colored but do not react with carbon dioxide.

The yields of trityllithium were determined by isolation of triphenylacetic acid following carbonation with Dry Ice. The benzyl chloride double titration method has been found unsatisfactory for this analysis.[19] The compositions of the neutral organic residues were determined by quantitative infrared methods and by chromatographic analysis. The yields obtained and the various reaction conditions are outlined in Table I.

TABLE I

Yields of Triphenylacetic Acid

Solvent	Temp.	Time, hr.	Yield, %
C_6H_6	80	24	49
C_6H_6	80	49	0
C_7H_8	110	27	16
C_6H_{12}	80	46	..[a]
Et_2O	25	23	68
DME	[b]	24	70
DME	84	18	10
DME	84	23	0
THF	25[c]	3	55
THF	−10[d]	2	57
THF	−60[d]	4	43

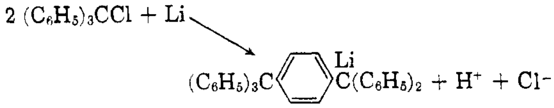
[a] Reaction could not be initiated. [b] Reflux for 5 hr.; 25° for 19 hr. [c] Reaction is exothermic; temperature depends on rate of addition of trityl chloride. [d] Bath temperature.

That all the trityl chloride reacts was demonstrated by an experiment in which hydrolysis was effected by a sodium azide solution. Because of the very strong nucleophilic character of the azide ion, any unchanged trityl chloride would react preferentially with the azide ion rather than with water[22]; however, no trace of trityl azide was observed.

The presence of small amounts of triphenylcarbinol in the reaction product may be explained by (1) contamination of the trityl chloride with about 1.5% of triphenylcarbinol (as shown by infrared analysis) or (2) reaction of trityllithium with traces of oxygen present. In an experiment in which the lithium reagent was treated with oxygen, the major product was triphenylcarbinol, with only a small amount of trityl peroxide indicated.[23] In no experiment which employed freshly distilled solvent was an appreciable amount of trityl peroxide observed. A sample of tetrahydrofuran which had been purified but allowed to stand in a partially filled bottle for three weeks gave a 63% yield of trityl peroxide when treated with trityl chloride and lithium.

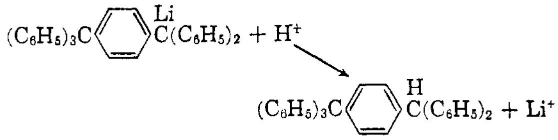
Recovery of excess lithium metal from reactions run in 1,2-dimethoxyethane and tetrahydrofuran indicated that 70–80% of the theoretical amount of lithium reacts. This is consistent with the observed quantities of triphenylacetic acid and *p*-benzhydryltetraphenylmethane.

The formation of the two hydrocarbon by-products may be explained by the equations given below.

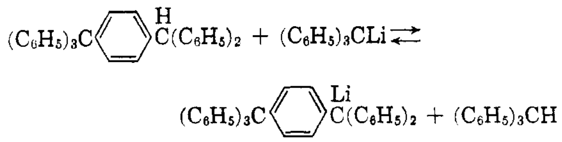


(1)

$$(C_6H_5)_3CLi + H^+ \rightarrow (C_6H_5)_3CH + Li^+ \qquad (2)$$



(3)



(4)

Equation (1) represents the "dimerization" of trityl chloride, probably a Friedel-Crafts type reaction. A similar type of coupling has been observed by several workers who treated acetic acid solutions of trityl chloride with zinc and silver.[24] The hydrogen ion produced may react with trityllithium (Equation 2) or with the lithium derivative of *p*-benzhydryltetraphenylmethane (Equation 3). In the trityllithium reaction mixture, the equilibrium (4) lies to the right (see below). During

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(22) C. G. Swain, C. B. Scott, and K. H. Lohmann, *J. Am. Chem. Soc.*, **75**, 136 (1953).

(23) Bachmann and Cockerill (ref. 3) reported a similar behavior when the trityl Grignard reagent was treated with oxygen. They reported a 54% yield of triphenylcarbinol and a 10% yield of trityl peroxide.

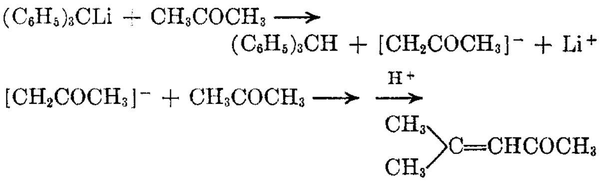
(24) (a) F. Ullman and W. Borsum, *Ber.*, **35**, 2877 (1902); (b) M. Gomberg, *Ber.*, **35**, 3915 (1902).

carbonation, however, this equilibrium is shifted to the left since the tritryllithium reacts with carbon dioxide, whereas the lithium derivative of *p*-benzhydryltetraphenylmethane apparently does not react, since no acid corresponding to this anion was isolated.

Other sources of triphenylmethane may be from the reaction of trityllithium with: (1) triphenylcarbinol, (2) traces of hydrochloric acid occluded in the trityl chloride, and (3) the solvent. Reaction with the solvent is probably responsible for the low yields observed in the experiments with high reaction temperatures or long reaction periods.

Information on the equation (4) was obtained from the reaction of trityllithium with deuterium oxide. Assuming equation (4) to be a rapid reversible equilibrium and assuming that no loss of deuterium occurred during the work-up, then the total "labile" hydrogen in the system was either in the triphenylmethane (39.8%) or the *p*-benzhydryltetraphenylmethane (7.4%). This hydrogen came from reaction (1) and from the other sources listed above. The results of the deuteration analyses give the relative amounts of the two lithium derivatives prior to reaction with deuterium oxide: 60.2% triphenylmethane and 92.6% *p*-benzhydryltetraphenylmethane. Thus, the equilibrium constant for (4) is approximately 8, which indicates that the more stable lithium reagent is that derived from *p*-benzhydryltetraphenylmethane. This stability may result from the inductive effect of the *p*-trityl group.

The reaction of trityllithium with acetone demonstrates the strong basic nature of the reagent.[25]



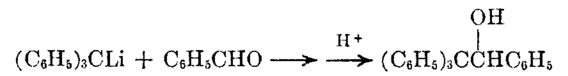
$$(C_6H_5)_3CLi + CH_3COCH_3 \longrightarrow (C_6H_5)_3CH + [CH_2COCH_3]^- + Li^+$$

$$[CH_2COCH_3]^- + CH_3COCH_3 \longrightarrow \xrightarrow{H^+} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}CHCOCH_3$$

The reagent is decomposed rapidly to triphenylmethane; the acetone enolate condenses with another mole of acetone to give (after acidification) mesityl oxide, which was isolated as the 2,4-dinitrophenylhydrazone.

Similar results were observed in the reaction of trityllithium with cyclohexanone. No adduct was obtained and the products were not investigated further.

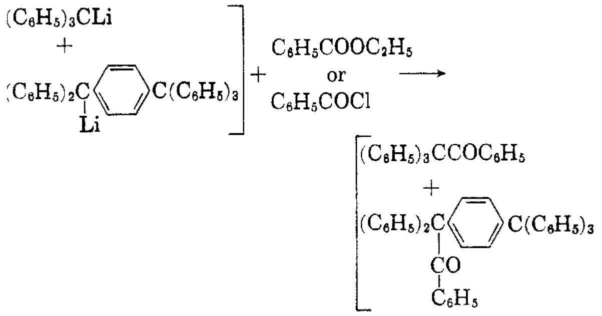
The action of trityllithium on benzaldehyde did yield the expected adduct, 1,2,2,2-tetraphenylethanol, in 12.5% yield. Difficulty in isolation of the alcohol was partly responsible for the low yield.



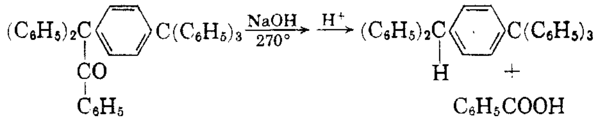
$$(C_6H_5)_3CLi + C_6H_5CHO \longrightarrow \xrightarrow{H^+} (C_6H_5)_3C\overset{\overset{OH}{|}}{C}HC_6H_5$$

When benzaldehyde was added to a solution of the reagent containing excess lithium, tetraphenylethanol was not formed. Instead, a complex mixture of substances was obtained which could not be separated by any of the usual procedures. The presence of lithium apparently was responsible for the formation of the mixture of compounds.[26]

The action of the trityllithium reaction mixture on benzoyl chloride was also investigated. A chromatographic separation of the reaction products furnished a 27% yield of benzopinacolone and a small amount of a ketone whose structure was shown to be α-benzoyl-$\alpha,\alpha,\alpha',\alpha',\alpha'$-pentaphenyl-*p*-xylene. Reaction of ethyl benzoate with the trityllithium reaction mixture gave essentially the same results. The formation of these two adducts again demonstrates the presence of the two lithium derivatives in the mixture formed by the reaction of trityl chloride with lithium.



The structure of α-benzoyl-$\alpha,\alpha,\alpha',\alpha',\alpha'$-pentaphenyl-*p*-xylene was established by base catalyzed cleavage of the ketone to form *p*-benzhydryltetraphenylmethane and benzoic acid.



EXPERIMENTAL[27]

Trityl chloride was prepared[28] from triphenylcarbinol or obtained from commercial sources. Crystallization from ether or an acetyl chloride–hexane mixture, followed by heating the sample at 70° and 0.3 mm. pressure for several hours, furnished large pale yellow prisms, m.p. 112–114° after sintering near 109°. The commercial samples of triphenylcarbinol yielded products with slightly lower melting points, presumably due to traces of dichlorodiphenylmethane present. Analysis for triphenylcarbinol in the trityl chloride was accomplished by quantitative infrared methods. Under actual working conditions, the amount of triphenylcarbinol was found to be 1.5–2.0%. The presence of greater amounts

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[25] Tritylmagnesium chloride is reported to be completely "passive" toward acetone, acetaldehyde, and acetyl chloride; J. Schmidlin and H. H. Hodgson, *Ber.*, **41**, 430 (1908).

[26] The action of trityl Grignard reagent on benzaldehyde is reported to give a mixture of 1,2,2,2-tetraphenylethanol and *p*-benzhydrylbenzhydrol; A. E. Tschitschibabin, *Ber.*, **42**, 3469 (1909), and J. Schmidlin and A. Garcia-Banus, *Ber.*, **45**, 3193 (1912).

[27] All melting points are corrected. The microanalyses were performed by Mrs. Olga Hamerston.

[28] W. E. Bachmann, *Org. Syntheses*, Coll. Vol. III, 841 (1955).

of triphenylcarbinol seemed to have no effect on the course of the reaction. Hydrolysis of the trityl chloride gave triphenylcarbinol free from any detectable contaminant.

Solvents. The hydrocarbon solvents used were dried over sodium and distilled before use. The ethers were dried over potassium hydroxide and/or sodium and distilled from lithium aluminum hydride directly into the reaction system. Tetrahydrofuran and 1,2-dimethoxyethane rapidly form peroxides or hydroperoxides which react with trityllithium.

Atmosphere. The use of an inert oxygen-free atmosphere was necessary in order to obtain consistent results and prevent formation of triphenylcarbinol. For this purpose, argon purified by passage through Fieser's solution and dried with magnesium perchlorate was employed. In reactions employing freshly purified solvents and an argon atmosphere, no trityl peroxide was found; triphenylcarbinol was usually present in about the same amount as in the trityl chloride (1.5–2.0%).

Lithium wire or lithium sand was equally effective in the reaction, although the wire was more convenient to use and permitted easy removal of excess lithium. Also, initiation by exposure of a fresh metal surface of the wire was easy to accomplish by means of a Teflon stirring paddle.

Infrared analyses were performed by standard techniques. The spectra were usually measured in carbon disulfide solution in 0.5-mm. thick cells at concentrations of about 5%. Solvent compensation was made by use of a 0.5-mm. cell containing the solvent in the reference beam. The spectra were obtained from a Perkin-Elmer model 21 spectrophotometer equipped with sodium chloride optics. The following absorption bands were used in the quantitative analysis of mixtures: triphenylmethane—2880, 1076, 725 cm.$^{-1}$; deuterotriphenylmethane (carbon tetrachloride solution)—2110, 985, 902 cm.$^{-1}$; *p*-benzhydryltetraphenylmethane—1020, 725 cm.$^{-1}$; triphenylcarbinol—3610, 1325, 1158, 1030, 1010, 887 cm.$^{-1}$; trityl peroxide—975, 758 cm.$^{-1}$ The analyses were checked against known mixtures and the relative error in the determination of any component was found to be less than 20%.

Techniques for the transferral of trityllithium. The following methods were found satisfactory: (1) a pipet flushed with argon, (2) a glass tube inserted below the surface of the reagent and leading to another flask, and (3) an inverse Grignard flask (a flask fitted with a stopcock on the bottom). The reagent reacts very rapidly with air, as evidenced by disappearance of the deep red color.

Work-up of carbonation mixtures. After the reagent had been added to Dry Ice and sufficient time had been allowed for complete reaction, methylene chloride and 5% sodium carbonate solution were added. The layers were shaken well and the aqueous layer was separated. Extraction with base was repeated until no more precipitate was observed when a portion of the extract was acidified. The basic extracts were combined, filtered, and acidified. The precipitated triphenylacetic acid was collected on a filter, washed with water, and dried; the melting point (with decomposition) was 264–267°. A mixture with an authentic sample melted at 265–268°, with decomposition. The infrared spectrum was identical with that of a known sample of triphenylacetic acid. The neutralization equivalent was 293 (theoretical 288). All the experiments gave acid of essentially this purity. The organic layer from the basic extraction was filtered to remove any insoluble material and then the solvent was evaporated under reduced pressure. Repeated attempts to crystallize the residue did not effect a satisfactory fractionation of the neutral components.

Each of the procedures below describes one experiment taken usually from a group of three to eight similar experiments which all gave essentially the same results. Some of the data mentioned in the discussion were taken from experiments which are not included.

Preparation of trityllithium in benzene; (A) *24-hour reaction period.* In a 100-ml. flask, 3.33 g. (0.0120 mole) of trityl chloride, 0.44 g. (0.063 g. atom) of lithium sand, and 30 ml. of benzene were stirred at the reflux temperature. The mixture gradually turned to an opaque brown. After 22 hr., the dark mixture suddenly assumed a pasty consistency and the color changed to orange. Two hours after this change occurred, the contents of the flask were cooled and transferred to a Dry Ice–ether slurry. The color of the mixture changed immediately to grey-green. After the work-up, 1.69 g. (49% yield) of triphenylacetic acid was isolated. One tenth of a gram of neutral organic solid was obtained by filtration of the basic extracts. This material had no definite melting point. Evaporation of the solvent from the neutral organic fraction left 0.97 g. of orange-brown semisolid. An infrared analysis of this mixture indicated the following components: triphenylcarbinol (27%), triphenylmethane (35%), *p*-benzhydryltetraphenylmethane (20%), and unidentified material (10%).

Preparation of trityllithium in benzene; (B) *49-hour reaction period.* Trityl chloride (3.45 g., 0.0124 mole) and lithium (0.49 g., 0.071 g. atom) were placed in a flask containing about 30 ml. of benzene. The mixture was stirred under reflux. The orange color of trityllithium was noted after about 25 hr. The color deepened slightly during the next 8 hr. After a total of 49 hr., 60 ml. of ether was added, and the reaction mixture was poured into a Dry Ice–ether slurry. The orange color persisted even after hydrolysis. No acid was obtained; the infrared spectrum showed the red-brown semisolid product to be a complex mixture of compounds including triphenylcarbinol, triphenylmethane, *p*-benzhydryltetraphenylmethane, and several alcoholic components. No separation was attempted.

Preparation of trityllithium in toluene. A mixture of 3.76 g. (0.0135 mole) of trityl chloride, 0.43 g. (0.062 g. atom) of lithium sand and 35 ml. of toluene was stirred under gentle reflux. After 21 hr., the solution was clear red. During the next 6 hr., the color deepened gradually and the mixture became opaque. One third of the reaction mixture then was added to Dry Ice and allowed to stand. Following the usual work-up, 0.21 g. (16%) of triphenylacetic acid was isolated. Infrared analysis of the neutral fraction of the product indicated the presence of 15% triphenylcarbinol, 40% triphenylmethane, and 35% *p*-benzhydryltetraphenylmethane.

Attempted preparation of trityllithium in cyclohexane. A mixture of 2.04 g. (0.0073 mole) of trityl chloride, 0.24 g. (0.035 g. atom) of lithium sand, and 35 ml. of cyclohexane was stirred under reflux. The grey-green color of the initial mixture was unchanged after 46 hr., when the attempt was stopped. Attempts to initiate the reaction by extensive crushing of the lithium particles had no effect.

Preparation of trityllithium in ether. A mixture of 0.99 g. (0.143 g. atom) of lithium wire, 4.35 g. (0.0156 mole) of trityl chloride, and 30 ml. of ethyl ether was stirred at room temperature. After 5 hrs. the pasty yellow mixture began to darken; the solution was red and the precipitate (probably the lithium reagent) was orange. Eighteen hr. later, the mixture was poured onto Dry Ice. After the usual work-up, 3.08 g. (68%) of triphenylacetic acid was found. The neutral organic residue weighed 0.73 g.

Preparation of trityllithium in 1,2-dimethoxyethane; (A) *24-hour reaction period.* To 0.42 g. (0.061 g. atom) of finely cut lithium wire in 20 ml. of 1,2-dimethoxyethane, 3.23 g. (0.0116 mole) of trityl chloride was added. The red color of the lithium reagent soon appeared on the surface of the lithium, and then gradually in the solution. After being stirred for 5 hr. under gentle reflux, the mixture was stirred for an additional 19 hr. at room temperature before carbonation. The deep red color faded immediately to a pale pink when the reagent came in contact with carbon dioxide. Hydrolysis was effected with 20 ml. of an aqueous solution containing 3.2 g. (0.049 mole) of sodium azide and 0.4 g. of ammonium chloride. The *p*H of this solution was about 6. After addition of the organic mixture, the *p*H was 7–8. A total of 2.34 g. (70%) of triphenylacetic acid was obtained. By infrared analysis the neutral fraction of the product (0.57 g.) was found to contain: 30% triphenylmethane, 57% *p*-benzhydryltetraphenylmethane, and 7% triphenylcarbinol. The characteristic absorption band of the azide group (2130 cm.$^{-1}$) was absent.

Preparation of trityllithium in 1,2-dimethoxyethane; (B) *23-hour reaction period at reflux temperature.* A solution of trityllithium was prepared by treating 0.54 g. (0.078 g. atom) of lithium sand with 2.23 g. (0.0080 mole) of trityl chloride in 20 ml. of refluxing 1,2-dimethoxyethane. Within 1 hr. the mixture became a deep opaque red. At the end of 3 hr., the color had deepened to red-purple. After a total reflux period of 23 hr., the reaction mixture, which was then an orange-red, was poured onto Dry Ice. The color remained until dilute hydrochloric acid was added, whereupon the mixture turned yellow. No acid was obtained from base extraction of the reddish oily product, which contained at least five compounds according to spectral analysis.

Preparation of trityllithium in tetrahydrofuran; (A) *3-hour reaction period at room temperature.* To a well stirred mixture of 0.252 g. (0.0364 g. atom) of finely cut lithium wire in 5 ml. of tetrahydrofuran, a solution of 3.05 g. (0.0110 mole) of trityl chloride in 40 ml. of tetrahydrofuran was added during 40 min. The reaction began almost as soon as a fresh surface of lithium was exposed by the stirrer blade. The red color of trityllithium appeared on the metal and the solution darkened rapidly. The mildly exothermic reaction subsided after all the trityl chloride had been added. After two more hours of stirring at room temperature, the mixture was carbonated with Dry Ice. After the work-up, 1.72 g. (55%) of triphenylacetic acid was obtained. The organic residue (0.97 g.) was shown by infrared analysis to contain: 30% triphenylmethane, 50% *p*-benzhydryltetraphenylmethane, 8% triphenylcarbinol, and an unidentified alcoholic component.

Preparation of trityllithium in tetrahydrofuran; (B) *4-hour reaction period at −60°.* A solution of trityllithium was prepared by addition of 5.20 g. (0.0187 mole) of trityl chloride in 30 ml. of tetrahydrofuran to 0.96 g. (0.138 g. atom) of lithium wire. The reaction flask was kept in a Dry Ice–chloroform bath at −60 ± 5°. The addition required 1 hr. and the mixture was stirred for an additional 3 hr. The normal color changes were observed. After carbonation and workup, a 43% yield (2.31 g.) of triphenylacetic acid was isolated. The neutral residue amounted to 2.36 g. No trityl peroxide was found.

Preparation of trityllithium in three-week-old tetrahydrofuran; (C). To 0.399 g. (0.058 g. atom) of lithium in a flask cooled in a Dry Ice–chloroform bath at −60 ±5°, a solution of 6.43 g. (0.0232 mole) of trityl chloride in 50 ml. of *three-week-old* tetrahydrofuran was added during 90 min. After an additional 90 min. of stirring, the mixture was carbonated. After hydrolysis, the organic layer was filtered to remove the insoluble trityl peroxide. A total of 3.80 g. (63% yield) of trityl peroxide (m.p. with decomposition 179–181°) was obtained. By basic extraction of the organic layer, 0.36 g. (5.4% yield) of triphenylacetic acid was obtained.

Reaction of trityllithium with oxygen. A solution of trityllithium was prepared from 0.33 g. (0.048 g. atom) of lithium wire and 3.07 g. (0.0110 mole) of trityl chloride in 30 ml. of 1,2-dimethoxyethane. The mixture was stirred at the reflux temperature for 5 hr. before a stream of dry oxygen was passed through the solution. The red-purple color changed to a yellow-orange. After hydrolysis, a partial separation of the reaction products was effected by chromatography on alumina[29] since fractional crystallization was not effective in separating the components. From 2.64 g. of crude product, 0.56 g. (21%) of triphenylmethane and 0.30 g. (11%) of *p*-benzhydryltetraphenylmethane were obtained. By infrared analyses, the other components were found to be: triphenylcarbinol (55%) and trityl peroxide (15%).

Reaction of trityllithium with deuterium oxide. To a stirred mixture of 0.99 g. (0.143 g. atom) of lithium wire and 5 ml. of tetrahydrofuran was added a solution of 5.93 g. (0.0213 mole) of trityl chloride in 45 ml. of tetrahydrofuran during 90 min. The reagent was stirred for an additional 30 min. before it was added to 3 ml. of Stuart 99.5^{+}% deuterium oxide in 15 ml. of tetrahydrofuran. This mixture was stirred for 30 min., then allowed to stand overnight. After addition of dilute hydrochloric acid and benzene, the organic layer was removed, dried, and the solvent was distilled to yield 4.92 g. of yellow semisolid. This crude product was subjected to chromatography on a column packed with freshly activated alumina. Elution with a benzene-hexane mixture (1:19) furnished 3.34 g. (64.5% yield) of triphenylmethane and elution with a 3:7 mixture afforded 1.36 g. (24% yield) of *p*-benzhydryltetraphenylmethane. The deuterium content[30] of these two hydrocarbons was determined by (1) combustion of the samples, (2) followed by reduction to hydrogen, deuterium, and hydrogen deuteride, and (3) determination of the DH/H$_2$ ratio by mass spectrometry. The observed DH/H$_2$ ratios were: triphenylmethane, 0.0782; *p*-benzhydryltetraphenylmethane, 0.0622. This is equivalent to 58.7% and 90.3% deuteration, respectively. After correction for the water in the deuterium oxide, the numbers of millimoles of the various products are: triphenylmethane, 5.44; deuterotriphenylmethane, 8.23; *p*-benzhydryltetraphenylmethane, 0.21; and deutero-*p*-benzhydryltetraphenylmethane, 2.58.

A sample of the partially deuterated triphenylmethane was allowed to stand for 3 hr. in a tetrahydrofuran-water mixture containing lithium hydroxide. Infrared analysis of the recovered triphenylmethane indicated no appreciable loss of deuterium.

Action of trityllithium on acetone. A solution containing about 0.015 mole of trityllithium was added through a filter to an excess (3.5 g., 0.060 mole) of acetone in 20 ml. of tetrahydrofuran. The deep red color of the reagent was discharged immediately, leaving a pink solution. After 30 min. of stirring, the contents of the reaction flask were added to a mixture of 50 ml. of saturated sodium bisulfite solution and 50 ml. of methylene chloride. After the organic layer had been shaken well with the bisulfite solution, the aqueous layer was removed and the extraction was repeated three times. (This method was found to be the most convenient for removing the acetone from the organic layer.) The last aqueous extract gave no precipitate when treated with the 2,4-dinitrophenylhydrazine reagent. The organic layer then was stirred overnight with 1200 ml. of a saturated solution of 2,4-dinitrophenylhydrazine (about 4 g.) in 3*N* hydrochloric acid. The deep red organic layer was then removed and the solvent was evaporated. The semisolid red residue was washed well with hot hexane, and then crystallized twice from a benzene-ethanol mixture. The 2,4-dinitrophenylhydrazine derivative melted with decomposition at 201–203° and the mixture melting point with an authentic sample of mesityl oxide 2,4-dinitrophenylhydrazone was also 201–203°. The hexane washes were concentrated to yield mainly triphenylmethane. An infrared analysis indicated the absence of any carbonyl or alcohol compounds other than a small amount of triphenylcarbinol.

Action of trityllithium on cyclohexanone. To the lithium reagent prepared from 4.11 g. (0.0148 mole) of trityl chloride, 2.0 g. (0.020 mole) of cyclohexanone was added. The color of the reagent disappeared immediately. Following hydrolysis, the volatile components of the mixture were removed by vacuum distillation leaving 4.11 g. of a yellow semisolid oil which was subjected to chromatography on alumina. Only triphenylmethane (2.33 g.) and *p*-benzhydryltetraphenylmethane (about 1.0 g.) were isolated as crystalline com-

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(29) Alcoa F-20 Grade alumina was used for most of the chromatograms. A more active adsorbent could be made by heating the alumina at 200° for 5 hr. under reduced pressure. Matheson Reagent Grade aluminum oxide which had been treated similarly was employed when an adsorbent less active than Alcoa alumina was required.

(30) Deuterium analyses were performed by Dr. C. B. Koons.

pounds. No evidence for any adduct was observed and no attempt was made to isolate the cyclohexanone self-condensation product.

Action of trityllithium on benzaldehyde in the absence of lithium. Trityllithium was prepared from 3.05 g. (0.0110 mole) of trityl chloride, 0.297 g. (0.0428 g. atom) of lithium wire, and 30 ml. of tetrahydrofuran. After a total reaction period of 5 hr., the lithium was removed and 0.85 g. (0.0080 mole) of benzaldehyde in 9 ml. of tetrahydrofuran was added. The color faded to amber and did not change during the next 5 hr., after which time the reaction mixture was added to Dry Ice. Following hydrolysis and work-up, a yellow semisolid was obtained. No triphenylacetic acid was isolated. The infrared spectrum of the crude product exhibited bands characteristic of 1,2,2,2-tetraphenylethanol (778, 1182, 1380, 3620 cm.$^{-1}$) as well as absorption assigned to triphenylmethane and a weak carbonyl band at 1700 cm.$^{-1}$ (probably benzaldehyde). The mixture was subjected to chromatography on alumina. By combination and crystallization of various fractions, the following compounds were obtained: triphenylmethane (0.55 g.), *p*-benzhydryltetraphenylmethane (0.25 g.) and 1,2,2,2-tetraphenylethanol (0.48 g., 12.5%). Most of the later fractions did not yield crystalline material. The tetraphenylethanol melted at 152–153° and did not depress the melting point of a mixture with an authentic sample.

Action of trityllithium on benzaldehyde in the presence of lithium. A solution of trityllithium was prepared from 3.60 g. (0.0130 mole) of trityl chloride, 0.291 g. (0.042 g. atom) of lithium, and 40 ml. of tetrahydrofuran. After a total reaction period of 5 hr., 1.3 g. (0.013 mole) of benzaldehyde in 8 ml. of tetrahydrofuran was added. The deep red color of the reagent faded to amber, then gradually the deep red color returned during the next 6 hr. The mixture was hydrolyzed with water, and acid was added until the *p*H reached 7. The organic layer was separated and the solvent was evaporated to yield 4.38 g. of yellow oil. The infrared spectrum of this material showed absorption bands assignable to triphenylmethane, *p*-benzhydryltetraphenylmethane, and a hydrogen-bonded alcohol. The only carbonyl absorption was a weak band at 1677 cm.$^{-1}$ None of the characteristic bands of 1,2,2,2-tetraphenylethanol was present. Fractional crystallization of this mixture was unsuccessful. Chromatography of the mixture on alumina yielded the following results: 1.78 g. triphenylmethane, 0.79 g. of *p*-benzhydryltetraphenylmethane, several fractions which had melting point ranges from 145–200°, and a number of fractions which did not crystallize. Attempted crystallization of these fractions also did not yield any discrete compounds.

Action of trityllithium on benzoyl chloride. The trityllithium reagent was prepared in the usual manner from 6.19 g. (0.0222 mole) of trityl chloride and 0.901 g. (0.130 g. atom) of lithium in 50 ml. of tetrahydrofuran. The reagent was added through a filter to 2.3 g. (0.017 mole) of benzoyl chloride in 10 ml. of tetrahydrofuran. The deep opaque red-purple mixture turned to a clear red-amber within a few seconds. This reaction mixture was stirred for 3 hr. before hydrolysis. After removal of the solvent from the organic layer, the yellow solid (7.31 g.) was subjected to chromatography on a deactivated alumina column. A total of 6.38 g. of solid was obtained; elution with benzene and chloroform gave 0.73 g. of yellow oil which did not crystallize and was discarded. A second chromatographic separation on activated alumina yielded: 1.15 g. of triphenylmethane, 0.25 g. of impure *p*-benzhydryltetraphenylmethane, and a number of fractions with wide melting point ranges. Some of these fractions were combined and subjected to a third chromatographic separation. By combination and crystallization of fractions from the second and third chromatographic analyses, 2.09 g. (27% yield) of benzopinacolone and 0.69 g. of α-benzoyl-$\alpha,\alpha,\alpha',\alpha',\alpha'$-pentaphenyl-*p*-xylene (m.p. 239–245°) were obtained. The benzopinacolone was identified by its infrared spectrum, melting point (180–182°), and mixture melting point with an authentic sample (181–183°).

The *α-benzoyl-$\alpha,\alpha,\alpha',\alpha',\alpha'$-pentaphenyl-p-xylene* was identified as follows: Three crystallizations from a benzene-hexane mixture furnished an analytical sample; m.p. 246–247°.

Anal. Calcd. for $C_{45}H_{34}O$: C, 91.49; H, 5.80. Found: C, 91.16; H, 5.91.

The infrared spectrum was very similar to that of benzopinacolone. Conjugated ketone bands occur at 1675 and 1212 cm.$^{-1}$; absorption assigned to a *para*-disubstituted benzene ring occurs at 808 cm.$^{-1}$ Fusion of 180 mg. of this ketone with 400 mg. of sodium hydroxide at 270° for one hour gave 31 mg. of benzoic acid (m.p. 122–122.5°) and 180 mg. of impure *p*-benzhydryltetraphenylmethane (m.p. 212–220°). The hydrocarbon was purified by chromatography; 155 mg. of reasonably pure hydrocarbon was obtained. Identity with an authentic sample was proved by comparison of infrared spectra and by the fact that no melting point depression was observed upon admixture of the two. A purified sample melted at 226–229°.

Action of trityllithium on ethyl benzoate. A mixture of 6.02 g. (0.0216 mole) of trityl chloride, 0.933 g. (0.134 g. atom) of lithium wire, and 50 ml. of tetrahydrofuran were used to prepare the lithium reagent, which was then added to 2.6 g. (0.0175 mole) of ethyl benzoate. The color changed to a clear red-brown. After being stirred for 20 hr. at room temperature, the reaction mixture was hydrolyzed. The 6.55 g. of organic material obtained was subjected to chromatography on alumina. From the early fractions, 1.20 g. of triphenylmethane and about 0.20 g. of *p*-benzhydryltetraphenylmethane were obtained. Some of the later fractions were combined and a second chromatographic separation was attempted. By combination and crystallization of various fractions from the first and second separations, 2.44 g. (32% yield) of benzopinacolone (m.p. 180–182°) and 0.61 g. of α-benzoyl-$\alpha,\alpha,\alpha',\alpha',\alpha'$-pentaphenyl-*p*-xylene (m.p. 243–246°) were obtained.

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