this compound was treated with acetyl chloride, a substance, mp 197–198°, having the same composition as the starting material was recovered, and the higher melting material was said to be the second diastereoisomer.

This reaction was repeated and worked up using the saturated ammonium chloride method. From ethereal solution there first crystallized an isomer of 1,2,3,4-tetraphenylbutanone, in 38% yield, having mp 197–198°. Further concentration of the mother liquor yielded the second diastereoisomer (16%), mp 128–129°. Treatment of the 128–129° melting compound with acetyl chloride caused no change. We can only conclude that the 178–179° melting compound reported earlier[1] was an impure form of the 197–198° melting compound and that the former was simply purified in the course of the acetyl chloride treatment. These results are in accord with the observation by Crawford[2] that treatment of an ester of 2,3,4-triphenylbutyric acid with phenyllithium resulted in the formation of two 1,2,3,4-tetraphenylbutanones, one melting 198–199° and the more soluble melting at 125–126°.

Continued fractional crystallization of the mother liquors yielded two more compounds. 1,2,3-triphenylpropanone (IV) was obtained in 1% yield and finally, in 2% yield, the 1,2-addition product, 1,2,3,4-tetraphenyl-3-buten-2-ol. Some earlier publications[1,3] have indicated that only 1,4-addition products were isolated from α-phenylchalcone and various Grignard reagents. We are not certain of the origin of the 1,2,3-triphenylpropanone.

The higher melting and less soluble isomer of 1,2,3,4-tetraphenylbutanone has been tentatively assigned the *erythro* configuration. If one examines the two diastereoisomers in what one would predict to be their most stable conformations, it may be seen that the *erythro* compound "comes closer" to having a center of symmetry than does the *threo* compound. In the case of 1,2,3,4-tetraphenylbutane[4] as well as 2,3-diphenylbutane,[5] the more symmetrical *meso* form has been identified as the higher melting isomer.

Experimental Section[6]

trans-α-Phenylchalcone was synthesized, according to the method of Dornow and Boberg[7] condensing benzaldehyde and desoxybenzoin in refluxing benzene with piperidine catalyst. The yield of product, melting at 102.5–104.0°, was 86% (lit.[8] mp 103–103.5°). Benzylmagnesium chloride was made according to the method of Gilman[9] and was used immediately.

Reaction of Benzylmagnesium Chloride with *trans*-α-Phenylchalcone.—To 1500 ml of an ethereal solution of 43.7 g (0.15 mole) of *trans*-α-phenylchalcone, 400 ml of an ethereal solution of benzylmagnesium chloride [prepared from 4.9 g (0.20 g-atom) of magnesium and 26.0 g (0.21 mole) of benzyl chloride] was added over a 30-min period. The reaction was carried out under nitrogen. After standing at room temperature for 2 hr, the mixture was hydrolyzed with saturated aqueous ammonium chloride. The ether layer was decanted and, after standing in the refrigerator, deposited a white solid; a smaller amount of the same solid was obtained from acetone rinsings of the glassware and the inorganic residue. The total, after recrystallization from acetone, was 21.9 g (38%) of *erythro*-1,2,3,4-tetraphenylbutanone: mp 197–198°; nuclear magnetic resonance (nmr) spectra (numbers in parentheses indicate integrated intensity) τ 2.0–3.3 (20), τ 4.85 doublet (0.8), τ 6.10 multiplet (0.9), and τ 7.25 multiplet (1.7).

The mother liquor was removed under vacuum at room temperature. The yellow solid which remained was twice recrystallized from methanol yielding 9.0 g (16%) of *threo*-1,2,3,4-tetraphenylbutanone: mp 128–129°; nmr spectra τ 2.0–3.3 (20), τ 5.12 doublet (0.9), τ 6.15 multiplet (0.8), and τ 7.10 multiplet (2.0).

The methanolic mother liquor was further concentrated and yielded two additional fractions, the first of which consisted of 0.50 g (1%) of a crystalline solid, mp 143.5–144.0°, analyzing for $C_{21}H_{20}O_2$. When this substance was treated with acetyl chloride in benzene under reflux it was quantitatively converted to 1,2,3-triphenylpropanone, mp 120–121°. The compound $C_{21}H_{20}O_2$ appears to be a hydrate of 1,2,3-triphenylpropanone. A mixture melting point with an authentic sample was not depressed (see below).

The second fraction from the methanolic mother liquor 1.0 g (2%) was 1,2,3,4-tetraphenyl-3-buten-2-ol: mp 144.5–146°; nmr spectra τ 2.3–3.3 (21) (vinylic proton not resolved from phenyls), τ 6.50 (2.0), and τ 7.86 (0.9).

Anal. Calcd for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.59; H, 6.72.

Preparation of 1,2,3-Triphenylpropanone.—This compound was prepared according to the method of Cragoe and Pietruszkiewicz[10] by treating 9.5 g (0.075 mole) of benzyl chloride with 9.8 g (0.050 mole) of desoxybenzoin in the presence of 4.4 g (0.11 mole) of sodium hydroxide suspended in 50 ml of toluene. The mixture was heated on a steam bath and yielded 10.5 g (73%) of 1,2,3-triphenylpropanone, mp 120–121° (lit.[11] mp 121°).

Registry No.—I, 10126-56-4; II, 10126-57-5; III, 10126-58-6; IV, 4842-45-9; benzylmagnesium chloride, 6921-34-2; *trans*-α-phenylchalcone, 7512-67-6.

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Polylithiated Species from 1-Phenylpropyne and Organolithium Reagents[1]

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It has previously been shown that primary organolithium compounds react with diphenylacetylene to give a dilithium compound whereas under some conditions *t*-butyllithium gives products arising from electron transfer.[2]

This report is prompted by the recent observation by West, Carney, and Mineo[3] that terminal alkynes re-

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[2] J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963); J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlund, and D. J. Newton, *ibid.*, **88**, 476 (1966).

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act with n-butyllithium to produce remarkable polylithiated species such as C_3Li_4 in the case of propyne.

In the course of extending our work we have examined the reaction of organolithium reagents with 1-phenylpropyne. No addition or electron transfer was observed with this compound with either n-butyllithium in ether or hexane, or t-butyllithium in pentane, but rather the alkyne was isomerized to 3-phenylpropyne in 50–75% yield.

$$C_6H_5C{\equiv}CCH_3 \xrightarrow[\text{ether or hydrocarbon}]{\text{RLi}} \xrightarrow{H_2O} C_6H_5CH_2C{\equiv}CH$$

$$R = n\text{-Bu or } t\text{-Bu}$$

When 1 mole of 1-phenylpropyne was treated with 6 moles of n-butyllithium in hexane for 16 hr under reflux followed by addition of deuterium oxide to the reaction mixture, deuterated 3-phenylpropyne was obtained. The nuclear magnetic resonance (nmr) spectra of the product showed no aliphatic protons, and deuterium analysis revealed the presence of 3.22 atoms of deuterium/molecule. The product is, therefore, essentially I probably admixed with a small amount of II

$C_6H_5CD_2C{\equiv}CD$ I

$C_6H_4DCD_2C{\equiv}CD$ II

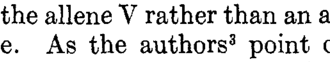
which must in turn have arisen from the polylithiated species III and IV.

$C_6H_5C_3Li_3$ III

$C_6H_4LiC_3Li_3$ IV

Under the conditions of the hydrolysis (1-phenylpropyne or 3-phenylpropyne in the presence of LiOD–D_2O) no deuterium was found to be incorporated into either of the above-mentioned alkynes.

In the case of n-butyllithium and propyne[3] the tetralithiated product (C_3Li_4) reacts with trimethylchlorosilane to give the allene V rather than an acetylene such as we observe. As the authors[3] point out, however, this is very likely a steric effect and in fact the trilithiated product from propyne when treated with trimethylchlorosilane gives VI.



V

$(CH_3)_3SiCHC{\equiv}CSi(CH_3)_3$

VI

It is of interest to note that phenylacetonitrile and acetomesitylene form dilithio salts with n-butyllithium in tetrahydrofuran–hexane.[4]

Experimental Section

Nmr spectra were obtained using a Varian Associates A-60 spectrometer with tetramethylsilane as internal standard. Deuterium analyses were determined by J. Nemeth, Urbana, Ill. Hydrocarbon solvents were purified by washing with sulfuric acid, then water, drying over sodium sulfate, and distillation from sodium. Melting points are uncorrected.

n-Butyllithium in ether was prepared according to the method of Gilman[5] and filtered through a glass-wool plug prior to use. The concentration of organolithium reagent was determined by the double-titration method.[6]

n-Butyllithium in hexane was obtained from Foote Mineral Co., and t-butyllithium in pentane from Lithium Corp. of America.

1-Phenylpropyne.—The procedure of Hurd and Tockman[7] was used starting with phenylacetone. It was found that sodium t-butoxide is more effective than potassium hydroxide in the dehydrohalogenation step.

Reaction of n-Butyllithium with 1-Phenylpropyne in Ether.—To 0.39 mole of n-butyllithium in 425 ml of ether held at ice-bath temperature and under helium atmosphere, there was added rapidly 20 g (0.175 mole) of 1-phenylpropyne. An almost immediate color change to yellow was observed. The color turned to red when the solution reached room temperature. After 16 hr of stirring at room temperature the reaction mixture was slowly treated with 125 ml of water (external cooling). The ether layer was separated and dried over magnesium sulfate. Distillation yielded 14 g (70%) of 3-phenylpropyne, bp 55–56° (4 mm), $n^{25.2}\text{D}$ 1.5259 [lit.[8] bp 71–73° (17 mm), $n^{23}\text{D}$ 1.53481] The nmr spectrum showed five protons centered at τ 2.70, two protons at τ 6.47, and one proton at τ 7.95. The bis-3-phenylpropynylmercury derivative was prepared, mp 105–106.5°, and the melting point was not depressed when it was mixed with an authentic sample.[9]

Reaction of n-Butyllithium with 1-Phenylpropyne in Hexane.—Under a nitrogen atmosphere a solution of 1.00 mole of n-butyllithium and 19.3 g (0.167 mole) of 1-phenylpropyne in 625 ml of n-hexane was heated under reflux for 16 hr. At the end of this time 40 g (2.0 moles) of deuterium oxide was slowly added with external cooling. Work-up was the same as in the case above, and there was obtained 9.7 g (50%) of deuterated 3-phenylpropyne, pure by vapor phase chromatography (vpc). Only aromatic protons appeared in the nmr spectrum.

Anal. Calcd for $C_9H_5D_3$: D, 37.5 atom % excess. Found: D, 40.3 atom % excess.

t-Butyllithium and 1-Phenylpropyne Deuterolysis.—To 0.26 mole of t-butyllithium in 230 ml of pentane at room temperature under a nitrogen atmosphere, there was added 13.0 g (0.112 mole) of 1-phenylpropyne in 160 ml of ligroin (bp 100–115°). The color of the solution changed almost immediately to a deep red and a precipitate was later formed. The solution was allowed to react at room temperature for 22 hr. At the end of this time 13.4 g (0.67 mole) of deuterium oxide was added very slowly to the cooled solution. After reacting for 2 hr the organic layer was separated, and the solvent was removed under reduced pressure. Flame-ionization gas chromatography showed three components: 3-phenylpropyne (85%), 1-phenylpropyne (5%), and a higher boiling component (10%). This was a 55% yield of 3-phenylpropyne (7.1 g).

Registry No.—I, 10147-10-1; 1-phenylpropane, 673-32-5; 3-phenylpropane, 10147-11-2.

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The Catalytic Fluorination of Perfluorocarbon Nitriles and Imines

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The reaction of fluorine with unsaturated carbon–nitrogen compounds has been the subject of numerous investigations. Most of these studies have been carried out in flow systems employing halogenated nitriles. Under mild conditions trifluoroacetonitrile or pentafluoropropionitrile were converted to the corresponding azo compounds whereas under more vigorous conditions the saturated perfluoro compounds $C_2F_5NF_2$ and C_3F_7-