Organolithium Compounds and Acetylenes. VII.[1] Effect of N,N,N′,N′-Tetramethylethylenediamine on Reactivity and Products

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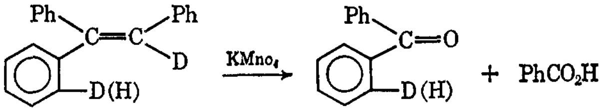
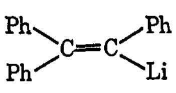
The activating effect of N,N,N′,N′-tetramethylethylenediamine (TMEDA) on addition–metalation reactions of phenyllithium and *n*-butyllithium with diphenylacetylene (DPA) is reported. Phenyllithium and *n*-butyllithium react much more rapidly with DPA—in the presence of TMEDA—to give products arising from addition plus metalation. Whereas *t*-butyllithium and DPA in hydrocarbon solvent react to the extent of 50% after 72 hr, the addition of TMEDA causes quantitative conversion to an addition product in less than 20 min. No metalation of the addition product occurs. The stereochemistry of the addition products (6:1 *cis*:*trans*) was determined by the stereospecific conversion of the carboxylic acid derivative, having a phenyl group and a carboxyl *cis*, into an indone using sulfuric acid at 0°.

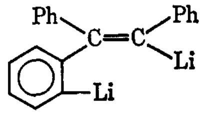
In previous papers organolithium compounds have been reported to yield various combinations of addition, metalation and electron transfer products with acetylenes.[3] A number of workers have recently reported the activating effect of N,N,N′,N′-tetramethylethylenediamine (TMEDA) on a variety of reactions of organolithium compounds.[4] We describe here the activating effect of TMEDA in organolithium and diphenylacetylene (DPA) reactions.

Phenyllithium in ethyl ether reacts slowly (24 hr) with DPA to give after carbonation an 11% yield of triphenylacrylic acid.[5,6] A mixture of 1.0 mol of DPA and 2.5 mol of a 1:1 phenyllithium–TMEDA complex in hexane was heated under reflux for 6 hr and after treatment with deuterium oxide yielded 80% (glpc) of triphenylethylene containing 1.62 D/molecule. One deuterium atom was obviously vinylic because of the absence of an nmr signal in that area, and the second deuterium atom was found by oxidation of the product with basic permanganate to benzophenone-*o*-*d* containing 0.8 D/molecule. The *ortho* position of deuterium was apparent because the nmr spectrum of the ketone revealed only 3.2 *ortho* hydrogens (which appear at τ 2.3 in contrast to the *meta* and *para* protons at a higher field). Thus in the absence of TMEDA only addition occurs to product I, whereas the use of TMEDA results not only in considerably more rapid addition but in metalation as well (II).



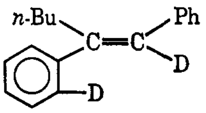


I



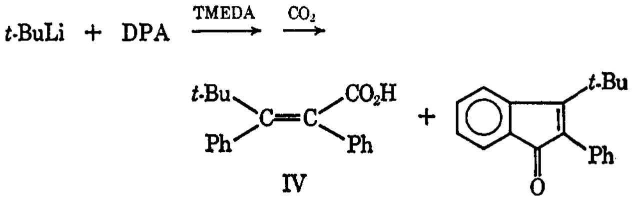
II

n-Butyllithium and DPA in pentane do not react over a period of many hours,[6] but in the presence of a 1:1 *n*-butyllithium–TMEDA complex in hexane at room temperature DPA gave a 69% yield of *trans*-α-*n*-butylstilbene containing 1.91 D/molecule (III). The position of the deuterium atoms was determined as in the case of the triphenylethylene (above) by oxidation and nmr.[6b]



III

t-Butyllithium and DPA in hydrocarbon solvents give a quite complex series of reaction products involving polyaddition, metalation and electron transfer.[7] Again, using a 1:1 TMEDA-*t*-butyllithium complex in hexane, DPA yielded after carbonation 41% (isolated) of *cis*-4,4-dimethyl-2,3-diphenyl-2-pentenoic acid (IV) and only a trace of 2-phenyl-3-*t*-butylindone (V).



IV

V

The stereochemistry of IV was unequivocally determined as follows. Treatment of IV with sulfuric acid resulted only in the recovery of the starting material. However, IV could be photoisomerized to a 45:55 mixture of the *cis*–*trans* isomers, the quantities of each being determined by the integrated intensities of the different *t*-butyl groups in the nmr spectrum of the isomers. When a mixture of the isomers was treated with sulfuric acid, there was obtained 2-phenyl-

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[1] For paper VI, see J. E. Mulvaney and L. J. Carr, *J. Org. Chem.*, **34**, 1177 (1969).

[2] Research supported by AFOSR(SRC)-OAR, USAF Grant No. 720-67. From the Ph.D. Thesis of D. J. N., 1968.

[3] See ref 1 and also J. E. Mulvaney and L. J. Carr, *J. Org. Chem.*, **33**, 3286 (1968).

[4] (a) G. G. Eberhardt and W. A. Butte, *ibid.*, **29**, 2928 (1964)· (b) G. G. Eberhardt and W. R. Davis, *J. Polym. Sci., Part A*, **3**, 3753 (1965); (c) A. W. Langer, *Trans. N. Y. Acad. Sci.*, **27**, 741 (1965); (d) H. E. Ziegler and E. M. Laski, *Tetrahedron Lett.*, 3801 (1966). See also the technical literature on organometallic-amine complexes, Foote Mineral Co.

[5] J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, **84**, 1501 (1962).

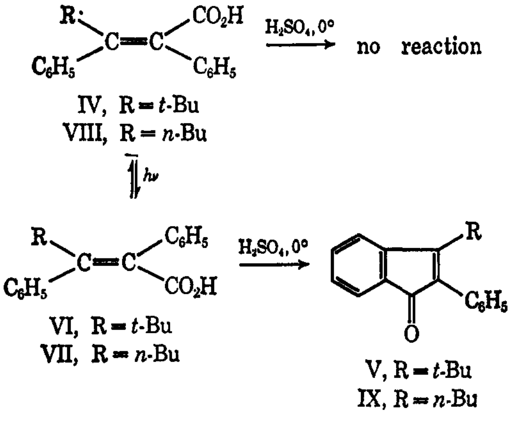
[6] (a) J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *ibid.*, **85**, 3897 (1963); (b) J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlund, and D. J. Newton *ibid.*, **88**, 476 (1966).

[7] J. E. Mulvaney, S. Groen, L. J. Carr, Z. G. Gardlund, and S. L. Gardlund, *J. Amer. Chem. Soc.*, **91**, 388 (1969).

3-*t*-butylindone. The nmr spectrum revealed that only the isomerized acid had reacted and, therefore, must have had a carboxyl group and a phenyl group *cis* to one another.

The stereospecificity of the sulfuric acid catalyzed ring closure was further demonstrated by the fact that only *trans* isomer VII of both *cis*- and *trans*-2,3-diphenyl-2-heptenoic acid[3] formed indone IX when treated with sulfuric acid[8] (Scheme I).

SCHEME I



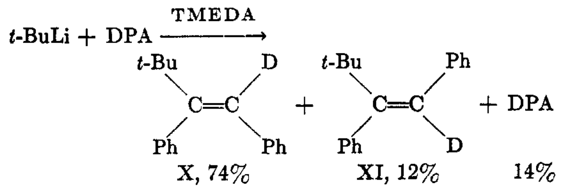
IV, R = *t*-Bu
VIII, R = *n*-Bu

VI, R = *t*-Bu
VII, R = *n*-Bu

V, R = *t*-Bu
IX, R = *n*-Bu

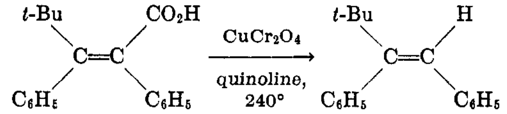
It is interesting that both IV and VIII are converted into their corresponding indones by thionyl chloride.[3,9] Therefore, sulfuric acid catalyzed cyclization of cinnamic derivatives at 0° is a very useful probe for stereochemistry, whereas, thionyl chloride is not.

Deuterolysis of a reaction mixture containing 1.0 mol of DPA, 2.5 mol of TMEDA, and 2.5 mol of *t*-butyllithium enabled us to make a quantitative determination of the product composition by glpc. There was obtained 14% DPA, 74% *cis*-α-*t*-butylstilbene (X), and 12% *trans*-α-*t*-butylstilbene (XI). This reaction is complete in less than 20 min at room temperature. This is in sharp contrast to the same reaction in the absence of TMEDA under which conditions only about 50% of the reactants are consumed after 74 hr. Each of the three components was isolated and identified by comparison of glpc retention times, nmr spectra, and/or mixture melting points with authentic samples.[7] Deuterium analyses of the products revealed that DPA contained 1.79 D/molecule, *cis*-α-*t*-butylstilbene contained 0.99 D/molecule, and *trans*-α-*t*-butylstilbene contained 1.05 D/molecule. Control experiments showed that the products did not exchange hydrogen under the work-up conditions.

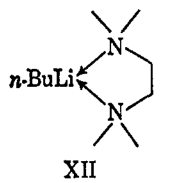


X, 74% — 0.99 D/molecule
XI, 12% — 1.05 D/molecule
14% — 1.79 D/molecule

The stereochemistry of the α-*t*-butylstilbenes was assigned on the basis of the following arguments. As was just pointed out, carbonation of the *t*-butyllithium–DPA–TMEDA reaction mixture resulted in the isolation of 41% yield (pure) of *cis* carboxylic acid IV. *trans*-Carboxylic acid was surely present in the reaction mixture, but the products were too high boiling for a glpc analysis. When the same reaction mixture was terminated by deuteriolysis, two α-*t*-butylstilbenes were shown by glpc to be present in the ratio of 6:1. Because carbonation and hydrolysis of vinylic lithium compounds proceed with retention of configuration,[10] *cis*-carboxylic acid IV must have been the major product of the carbonation. Because IV was the major carbonation product, the major deuteriolysis product must also have had *cis* stereochemistry. Furthermore, IV was decarboxylated with quinoline and copper chromite to a quantitative yield of α-*t*-butylstilbene identical with the major component of *t*-butyllithium–DPA deuteriolysis product. This decarboxylation reaction has been shown to proceed with a high degree of stereospecificity.[3,11]

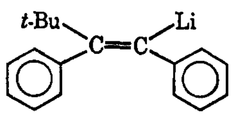


In the case of all other organolithium compounds and DPA which have been discussed in this paper, addition plus ring metalation occurs predominantly, if not exclusively, but with *t*-butyllithium no addition metalation occurs. However, when no TMEDA is present metalation does occur even in the *t*-butyllithium case.[7] This probably represents simply a steric effect. The isolation of a 1:1 butyllithium–TMEDA complex having structure XII has been reported.[4c]



XII

If *t*-butyllithium has the same structure, nucleophilic attack on a hydrogen atom of the benzene ring in XIII or XIV should be difficult, especially if one considers



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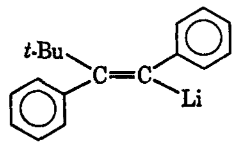

XIII

XIV

that the vinyllic lithium atoms in XIII or XIV are also probably coordinated with TMEDA.

The *t*-butyllithium–DPA–TMEDA reaction is complete in less than 20 min at room temperature and gives the composition indicated above. This composition remains constant for at least 24 hr after mixing. In view of the lack of configurational stability of organo-

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[8] In the case of the isomers of α,β-dimethylcinnamic acids, only the isomer with phenyl and carboxyl *cis* to one another undergoes sulfuric acid catalyzed indone formation at 0°: L. M. Jackman and J. W. Lown, *J. Chem. Soc.*, 3776 (1962).

[9] No stereospecificity was observed in the case of thionyl chloride cyclization of the isomeric α,β-dimethylcinnamic acids: J. A. Kampmeier and R. M. Fantazier, *J. Amer. Chem. Soc.*, **88**, 1959 (1966).

[10] D. Seyferth and L. G. Vaughan, *ibid.*, **86**, 883 (1964).

[11] D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716 (1951).

lithium compounds under these conditions[12] the deuteriolysis products most likely arise from the thermodynamically more stable vinyllic lithium compound which in this case is the *cis* isomer.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus or a Mel-Temp and are uncorrected. Nuclear magnetic resonance spectra were determined using a Varian Model A-60 (60 MHz) spectrometer, with tetramethylsilane as an internal standard. Either a Perkin-Elmer Infracord or a Beckman IR-4 spectrophotometer was used to determine infrared spectra; a polystyrene film was used to calibrate the instruments.

Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill. Deuterium analyses reported as "atom % excess deuterium" were performed by Joseph Nemeth, Urbana, Ill., using the falling drop method; those reported as "deuterium atom per molecule" were calculated from mass spectral data. Gas–liquid partition chromatography (glpc) was carried out on a F & M Model 609 flame ionization instrument using columns packed with GE-SE-30 on Chromosorb W. For analytical glpc determinations, correction factors for mole ratio/area ratio data were determined with standards containing the same compounds as in the unknown mixture. For irradiation experiments a quartz jacketed, Hanovia Type L mercury arc lamp was used.

Solvents and reagents were purified as described previously.[3,6b] Eastman Grade N,N,N′,N′-tetramethylethylenediamine (TMEDA) was purified by distilling from calcium hydride and storing over potassium hydroxide. Deuterium oxide was obtained from Stohler Isotope Chemicals and contained 99.8 atom % deuterium. Lithium wire and *t*-butyllithium in pentane were obtained from the Lithium Corp. of America. *n*-Butyllithium in hexane was obtained from Foote Mineral Co. *n*-Butyllithium in ethyl ether was synthesized from *n*-butyl bromide and lithium. All organolithium reactions were run under a nitrogen atmosphere in a flame-dried apparatus protected by calcium chloride drying tubes.

Phenyllithium, TMEDA, and DPA.—*n*-Butyllithium (0.35 mol) in 220 ml of hexane was added slowly to a stirred solution of benzene (78.0 g, 1.00 mol) and TMEDA (40.6 g, 0.35 mol) followed by 6 hr of reflux (65°). After allowing the dark red solution to cool to room temperature, DPA (25.0 g, 0.14 mol) in 50 ml of anhydrous ethyl ether was added and the solution refluxed (65°) for an additional 12 hr. Termination of the reaction was accomplished with deuterium oxide (14.0 g, 0.70 mol) while maintaining a temperature of 5° by external cooling. Water (100 ml) was added and the layers were separated. The organic layer was dried (Na_2SO_4) and concentrated to yield 38.4 g of a dark red oil, which was shown by glpc to contain $\sim$80% triphenylethylene. A spinning-band distillation of the oil afforded 22.7 g (63%) of glpc pure yellow product, bp 152–156° (0.15 mm). After two recrystallizations from 95% ethanol, the deuterated triphenylethylene had mp 68.5–69.5°; the mixture melting point with authentic sample was undepressed.

Anal. Calcd for $C_{20}H_{14}D_2$: D, 12.50 atom % excess deuterium. Found: D, 10.15 atom % excess deuterium.

A portion of the deuterated triphenylethylene (5.0 g, 0.019 mol) was oxidized with basic potassium permanganate[13] to give 1.6 g (68%) of benzoic acid and 1.2 g (34%) of benzophenone-*o*-*d*. The nmr spectrum of the benzophenone-*o*-*d* indicated the presence of 3.2 lowfield *ortho* protons.

Anal. Calcd for $C_{13}H_9DO$: D, 10.00 atom % excess deuterium. Found: D, 8.02 atom % excess deuterium.

***n*-Butyllithium, DPA and TMEDA.**—*n*-Butyllithium (0.25 mol) in 150 ml of hexane was added slowly to a stirred solution of DPA (17.8 g, 0.10 mol) and TMEDA (29.0 g, 0.25 mol) at −20°. The solution was allowed to warm to room temperature and stirred for 16 hr. The dark red reaction mixture, containing a considerable amount of yellow precipitate, was cooled to 5° and deuterium oxide (10.0 g, 0.50 mol) was added slowly. The mixture was stirred for an additional 4 hr at room temperature, 100 ml of water was added and the layers were separated. The organic layer was dried (Na_2SO_4) and concentrated to give 22.1 g of a dark red oil. Distillation through a small Vigreux column yielded 16.4 g (69%) of glpc pure deuterated *trans*-*α*-*n*-butylstilbene, bp 113–115° (0.25 mm). The nmr spectrum and the glpc retention time of the product were identical with those of *trans*-*α*-*n*-butylstilbene prepared in ether.[6]

Anal. Calcd for $C_{18}H_{18}D_2$: D, 10.00 atom % excess deuterium. Found: D, 9.55 atom % excess deuterium.

***t*-Butyllithium, TMEDA, and DPA. Termination of Reaction by Carbonation.**—*t*-Butyllithium (0.35 mol) in 250 ml of pentane was added slowly to a stirred solution of DPA (25.0 g, 0.14 mol) and TMEDA (40.6 g, 0.35 mol) while maintaining a temperature of 5° by external cooling. After stirring for 22 hr under reflux (43°), the dark red reaction mixture was carbonated by decantation onto powdered Dry Ice. The mixture was allowed to stand overnight before 1 l. of water was added. The resulting basic solution was extracted with ether and the layers were separated. The neutral ether layer was dried (Na_2SO_4) and concentrated to give 9.3 g of a dark red oil. Distillation of the oil yielded 2.1 g (6%) of *cis*-*α*-*t*-butylstilbene, mp 49.5–50°; the mixture melting point with an authentic sample was undepressed. There was also obtained 2.6 g of an orange oil [bp 120–150° (0.1 mm)] which glpc analysis showed to contain *cis*-*α*-*t*-butylstilbene and about 20% 2-*t*-butyl-3-phenylindone.[7] This corresponds to a 1.3% yield of the indone based on DPA. The remaining 4.6 g was undistillable.

The basic aqueous solution was acidified with 6 *M* hydrochloric acid and extracted with ethyl ether. The organic layer was dried (Na_2SO_4) and concentrated to yield 42.0 g of yellow acidic material. Two recrystallizations from hexane gave 16.2 g (41%) of *cis*-4,4-dimethyl-2,3-diphenyl-2-pentenoic acid IV: mp 189–190° (lit.[7] mp 186.5–187.0°); there was no melting point depression with authentic sample.

Proof of Stereochemistry of *cis*-4,4-Dimethyl-2,3-diphenyl-2-pentenoic Acid (IV). A. Photoisomerization of IV.—A solution of *cis*-4,4-dimethyl-2,3-diphenyl-2-pentenoic acid (7.2 g) in 1600 ml of benzene was irradiated under nitrogen with a Hanovia uv lamp for 49 hr. The benzene layer was concentrated to 300 ml and extracted with saturated aqueous sodium carbonate. Upon acidification of the basic layer, extraction with ether, drying (Na_2SO_4) and removal of the ether there remained 6.7 g (93%) of a 45% *cis*–55% *trans* mixture of 4,4-dimethyl-2,3-diphenyl-2-pentenoic acid: nmr (8% $CDCl_3$) τ 2.4–3.0 (m, 10.0, aromatic), 8.8 [s, 4.5, *cis*-$(CH_3)_3C$], 9.1 [s, 5.5, *trans*-$(CH_3)_3C$].[7]

B. Reaction of a *cis*-*trans* Mixture of 4,4-Dimethyl-2,3-diphenyl-2-pentenoic Acid with Thionyl Chloride.—The reaction was run according to the method of Koelsh.[14] A mixture of 52% *cis*- and 48% *trans*-4,4-dimethyl-2,3-diphenyl-2-pentenoic acid (0.87 g, 3.1 mmol) was dissolved in 4.35 ml of carbon tetrachloride with heating. Thionyl chloride (0.87 ml, 8.7 mmol) was added, and the solution was heated under reflux for 6 hr. The yellow reaction mixture was allowed to cool and poured into 100 ml of ice water. The mixture was heated under reflux for 0.5 hr before cooling. Ether was added and the layers were separated. The ether solution was extracted with two 20-ml portions of saturated aqueous sodium carbonate. The neutral organic layer was dried (Na_2SO_4) and concentrated to yield 0.74 g (91%) of yellow 2-phenyl-3-*t*-butylindone. Recrystallization from 80% ethanol gave 0.60 g (74%) of pure indone, mp 133–134° (lit.[7] mp 131.5–132°). The nmr spectrum of the indone was identical with that of an authentic sample.

The combined basic extracts were acidified with 6 *M* hydrochloric acid and extracted with ether. Evaporation of the dried (Na_2SO_4) ether solution yielded an unweighable trace of acid.

C. Cyclodehydration of Butylstilbenecarboxylic Acids with Sulfuric Acid.—The procedure used was that of Jackman and Lown.[8] The powdered acid was added in portions to an excess of stirred concentrated sulfuric acid at 0°. The solution was stirred for 5 min, poured on crushed ice, and extracted with ether. The ether layer was extracted with saturated aqueous sodium carbonate solution and the layers were separated. The neutral ether layer was dried (Na_2SO_4) and concentrated to give the indone.

The basic aqueous layer was acidified with 6 *M* hydrochloric acid and extracted with ether. The ethereal extract was dried (Na_2SO_4) and concentrated to recover unreacted acid.

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[12] D. Y. Curtin and W. J. Koehl, Jr., *ibid.*, **84**, 1967 (1962).

[13] R. L. Shriner, R.C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1962, p 250.

[14] C. F. Koelsh, *J. Amer. Chem. Soc.*, **54**, 2487 (1932).

1. **Reaction with *cis*-2,3-Diphenyl-2-heptenoic Acid.**—Treatment of 0.05 g (0.18 mmol) of *cis*-2,3-diphenyl-2-heptenoic acid[8] with 1 ml of sulfuric acid gave a yellow solution. Work-up afforded the starting *cis* acid in quantitative yield; no 2-phenyl-3-*n*-butylindone was obtained.

2. **Reaction with *trans*-2,3-Diphenyl-2-heptenoic Acid.**—Treatment of 0.05 g (0.18 mmol) of *trans*-2,3-diphenyl-2-heptenoic acid[3] with 1 ml of sulfuric acid gave a dark green solution. Work-up afforded 0.041 g (86%) of crude 2-phenyl-3-*n*-butyl indone; no acid was obtained.[6]

3. **Reaction with *cis*-4,4-Dimethyl-2,3-diphenyl-2-pentenoic Acid (IV).**—Treatment of *cis*-4,4-dimethyl-2,3-diphenyl-2-pentenoic acid (1.0 g, 3.6 mmol) with 20 ml of sulfuric acid gave a yellow solution. Work-up afforded 0.97 g (97%) of the starting *cis* acid; no 2-phenyl-3-*t*-butylindone was obtained.

4. **Reaction with a *cis-trans* Mixture of 4,4-Dimethyl-2,3-diphenyl-2-pentenoic Acid.**—Treatment of a 40% *cis*–60% *trans* mixture of 4,4-dimethyl-2,3-diphenyl-2-pentenoic acid (0.454 g, 1.62 mmol) with 20 ml of sulfuric acid gave a dark green solution. After work-up followed by sublimation there was obtained 0.185 g (44%) of 2-phenyl-3-*t*-butylindone, mp 133–134°; the mixture melting point with authentic sample[7] was undepressed. The nmr spectrum was identical with that of an authentic sample.

Sublimation of the recovered acid gave 0.154 g (34%) of a 60% *cis*–40% *trans* mixture of 4,4-dimethyl-2,3-diphenyl-2-pentenoic acid by nmr analysis.

Conversion of *cis*-4,4-Dimethyl-2,3-diphenyl-2-pentenoic Acid (IV) to *cis*-α-*t*-Butylstilbene.[15a]—The following procedure was based on a method described by Fieser[15b] for the stereospecific decarboxylation of *cis*-α-phenylcinnamic acid. *cis*-4,4-Dimethyl-2,3-diphenyl-2-pentenoic acid (0.060 g, 0.21 mmol) was added to a suspension of 0.010 g of copper chromite in 0.50 ml of quinoline. After heating at 240° for 10 min, the mixture was cooled and 10 ml of ethyl ether was added. After filtration the dark ethyl ether solution was extracted with two 10-ml portions of 10% hydrochloric acid and two 10-ml portions of 10% sodium hydroxide. The solution was dried over sodium sulfate and the ether was removed under reduced pressure. A nmr spectrum of the crude product (0.049 g, 100%) was identical with the 49° melting isomer of α-*t*-butylstilbene. In particular, the nmr spectrum revealed no *t*-butyl signal due to the 35° melting isomer. This evidence, in combination with what has been said in the discussion, proves that the 50° melting isomer is the *cis*-α-*t*-butylstilbene.[7]

***t*-Butyllithium-DPA-TMEDA. Termination by Deuteriolysis.**—*t*-Butyllithium (0.35 mol) in 227 ml of pentane was added slowly to a stirred solution of DPA (25.0 g, 0.14 mol) and TMEDA (40.6 g, 0.35 mol). After stirring under reflux (43°) for 6 hr the reaction mixture was treated slowly with deuterium oxide (20.0 g, 1.0 mol) while maintaining a temperature of approximately 5° by external cooling. The mixture was stirred for an additional 12 hr at room temperature, 100 ml of water added and the layers were separated. The organic layer was dried (Na_2SO_4) and concentrated to give 34.2 g of a dark red oil, which was shown by glpc to contain 14% DPA, 74% *cis*-α-*t*-butylstilbene, and 12% *trans*-α-*t*-butylstilbene. The addition of a seed crystal of *cis*-α-*t*-butylstilbene caused solidification of the oil. The solid was filtered, recrystallized twice from 95% ethanol and sublimed to give 16.2 g (49%) of glpc pure deuterated *cis*-α-*t*-butylstilbene: mp 50.5°; mixture melting point with authentic sample[7] was undepressed; nmr (30% $CDCl_3$) τ 2.65–3.45 (m, 10.0, aromatic), 8.83 (s, 9.0, *t*-Bu).

Anal. Calcd for $C_{18}H_{19}D$: D, 5.00 atom % excess deuterium. Found: D, 4.95 atom % excess deuterium.

A portion of the filtrate was fractionated through a preparative scale gas-liquid partition chromatograph. The first and third components were collected to give deuterated DPA and deuterated *trans*-α-*t*-butylstilbene.

The deuterated DPA was recrystallized twice from 95% ethanol to yield glpc pure product, mp 59–60°; the mixture melting point with authentic sample was undepressed.

Anal. Calcd for $C_{14}H_8D_2$: D, 2.00 atom per molecule. Found: D, 1.79 atom per molecule.

The deuterated *trans*-α-*t*-butylstilbene was recrystallized from 95% ethanol and sublimed to yield glpc pure product: mp 41°; the mixture melting point with authentic sample[7] was undepressed; nmr (30% CCl_4) τ 2.80 (s, 9.7, aromatic), 9.00 (9.0, *t*-Bu).

Anal. Calcd for $C_{18}H_{19}D$: D, 5.00 atom % excess deuterium. Found: D, 5.25 and 5.06 atom % excess deuterium.

Osmium Tetroxide Periodate Oxidative Cleavage of Deuterated *o*-*n*-Butylstilbene.—The procedure was similar to that used by Pappo, *et al.*,[16] to cleave oxidatively *trans*-stilbene. *trans*-α-*n*-Butylstilbene (9.0 g, 0.038 mol), prepared by deuteriolysis of an *n*-butyllithium DPA reaction mixture, was oxidatively cleaved according to the method previously described.[6b] There was obtained 3.0 g (74%) of benzaldehyde-α-*d* and 3.2 g (52%) of valerophenone-*o*-*d*. The benzaldehyde contained 0.91 D per molecule and the valerophenone contained 1.03 D per molecule. The *ortho* position of the deuterium was determined by nmr.[6b]

Registry No.—TMEDA, 19289-58-8; DPA, 501-65-6; phenyllithium, 591-51-5; *n*-butyllithium, 109-72-8; *t*-butyllithium, 594-19-4; *trans*-α-*n*-butylstilbene, 5041-39-4; IV, 19289-60-2.

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(15) (a) We are grateful to Dr. L. J. Carr for this experiment. (b) L. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass, 1957, p 186.

(16) R. Pappo, O. S. Allen, R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).