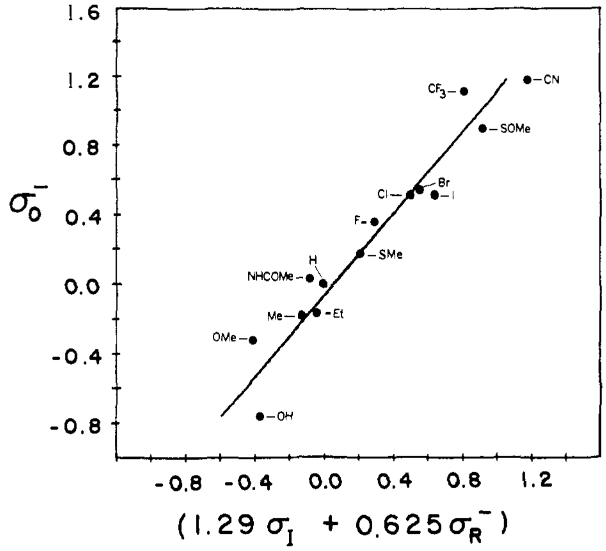

Figure 5. Correlation of $(1.29\sigma_I + 0.625\sigma_R^-)$ with σ_o^- ($r = 0.966$, $s = 0.127$).

Experimental Section

Nmr data were obtained with a Varian Associates A-60A spectrometer equipped with a V-6040 variable-temperature controller. Dimethyl sulfoxide (Crown Zellerbach) was dried over barium oxide, distilled (10 mm) over calcium hydride, and stored over Linde Type 4A activated Molecular Sieve. All of the phenols used are well-characterized compounds. Most were acquired commercially, but some were synthesized according to descriptions in the literature.[50] Samples used met the usual melting point and/or gas chromatographic criteria for purity.

Phenol solutions were prepared in concentrations up to ~10% (w/v). The O*H* absorption was demonstrated to be independent of concentration for all phenols studied by a minimum of four separate runs of each compound at various concentrations at a constant temperature of 40 ± 1°. The chemical shifts of all phenols investigated were found to be temperature dependent, and extreme care was exercised to equilibrate every sample in the nmr spectrometer before the hydroxyl chemical shift was recorded. All resonances are reported in parts per million (ppm) downfield from the internal standard, tetramethylsilane.

Dual parameter statistical analysis was performed with a linear least-squares program on an IBM 7040 computer. All correlations of this type were plotted on a Calcomp 563 incremental plotter coupled to a Calcomp 570 magnetic tape unit. Multiple parameter analysis was performed with a linear iterative least-squares program (Louisiana State University Computer Center code: NLLSCF).

Acknowledgment. We gratefully acknowledge partial support of this research by a grant from the National Science Foundation (Grant No. 5749) and financial assistance from the Dr. Charles E. Coates Memorial Fund of the LSU Foundation donated by George H. Coates for the preparation of the Ph.D. dissertation of M. T. T.

(50) The Ph.D. dissertation of M. T. T. may be consulted for detail

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Organolithium Compounds and Acetylenes. V. Electron Transfer Plus Addition–Metalation in the Case of a Tertiary Organolithium Compound[1]

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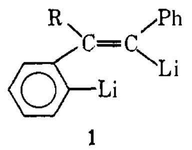
Abstract: The reaction of *t*-butyllithium with diphenylacetylene at 70° results in products arising from electron transfer, *cis,cis*-1,2,3,4-tetraphenylbutadiene and *trans*-stilbene. At lower temperature, products arising from addition and metalation are obtained, namely **7**, **8**, and **9**. Factors affecting the kinds of products and their stereochemistry are discussed.

We have previously reported[4] that primary organolithium compounds react with diphenylacetylene (DPA) in ethyl ether to give a product resulting from *o*-metalation as well as addition to the triple bond. The dilithiated product was shown to have the *trans* configuration and may be stoichiometrically represented as **1**, although the degree of association or dissociation to ions or ion pairs is not known.[5]



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In contrast, either primary or tertiary organolithium compounds react with an alkylphenylacetylene such as methylphenylacetylene by abstracting protons to produce polylithiated species.[1b]

We report here reactions of DPA with *t*-butyllithium, a system in which either addition–metalation or reductive dimerization may occur.

Results and Discussion

Reactions of *t*-butyllithium with DPA were carried out in ligroin. That reaction occurred at all is a manifestation of the greater reactivity of the tertiary

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(1) (a) Research supported by AFOSR(SRC)-OAR, USAF Grant No. 720-65. (b) For paper IV, see J. E. Mulvaney and L. J. Carr, *J. Org. Chem.*, **33**, 3286 (1968).

(2) (a) Postdoctoral fellow supported by the University of Arizona "Science Development Program." (b) NASA Predoctoral Fellow, 1964–1966.

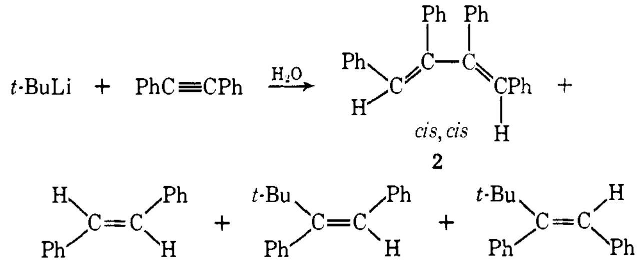
(3) Socony Mobil Predoctoral Fellow, 1962–1964.

(4) (a) J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963); (b) J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlung, and D. J. Newton, *ibid.*, **88**, 476 (1966).

(5) For a report concerning intramolecular addition of organolithium compounds to acetylenes, see S. A. Kandil and R. E. Dessy, *ibid.*, **88**, 3027 (1966).

organolithium compound compared to primary organolithium reagents which do not react under such circumstances in hydrocarbon solvent at moderate temperatures.[4]

Initial experiments were carried out at 90–95° for 24 hr. The products obtained after hydrolysis were



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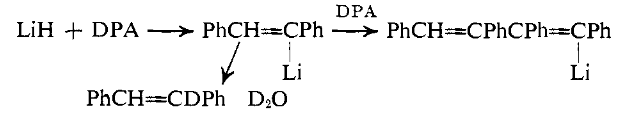
cis,cis-1,2,3,4-tetraphenylbutadiene, *trans*-stilbene, and both *cis*- and *trans*-α-*t*-butylstilbenes.[6a] The gross structure and stereochemistry of the butadiene derivative was proven by comparison with an authentic sample.[6b,7]

The formation of *trans*-stilbene and *cis,cis*-tetraphenylbutadiene as reduction products we believe arises from electron transfer from *t*-butyllithium. The formation of radical ions, or the existence of radical intermediates from organolithium compounds has recently been reported.[8] From the standpoint that *t*-butyllithium has some carbanion character one would expect it to be a better electron donor than *n*-butyllithium (which yields no reduction products), the conversion tertiary carbanion → tertiary radical being energetically more favorable than primary carbanion → primary radical.

t-Butyllithium decomposes at elevated temperatures to lithium hydride and isobutylene. One could argue that **2** arises by the addition of lithium hydride to DPA followed by the addition of a second mole of DPA.



$$\mathrm{LiH} + \mathrm{DPA} \longrightarrow \mathrm{PhCH{=}}\underset{\mathrm{Li}}{\mathrm{CPh}} \xrightarrow{\mathrm{DPA}} \mathrm{PhCH{=}CPhCPh{=}}\underset{\mathrm{Li}}{\mathrm{CPh}}$$

$$\downarrow \mathrm{D_2O}\quad \mathrm{PhCH{=}CDPh}$$

However, treatment of DPA with lithium hydride under the reaction conditions resulted only in the recovery of unreacted DPA. In addition, treatment of the *t*-butyllithium DPA reaction mixture with deuterium oxide yields 1,4-dideuterio-1,2,3,4-tetraphenylbutadiene (1.94 D/molecule) and α,β-dideuteriostilbene (1.7 D/molecule) [PhCD=CPhCPh=CDPh, PhCD=CD(H)Ph]. The small amount of vinylic hydrogen in the stilbene is discussed below.

While this work was being carried out, we learned from Professor P. D. Bartlett of some similar unpublished work from his laboratory.[9] Bartlett and Tauber studied the reaction between *t*-butyllithium and DPA in ethyl ether at −30°. After carbonation they obtained an 11% yield of β-*t*-butyldiphenylacrylic acid, an addition product, but the principal product was a neutral solid (43%) which proved to be the lactol **5**. The lactol is also a product which must arise from electron transfer from *t*-butyllithium to DPA. A comparison of Bartlett and Tauber's work with ours ties together a number of observations and allows the formulation of some reasonable pathways by which the reaction products may arise (Chart I).

The small amount of vinylic hydrogen in the stilbene obtained after treatment of the reaction mixture with D_2O could arise from transfer of a hydrogen atom from the *t*-butyl radical to the DPA radical anion (upper right, Chart I).

Electron transfer and dimerization occurs between lithium metal and DPA, a reaction which also results in the formation of *cis,cis*-1,2,3,4-tetraphenylbutadiene (**2**).[6b,7]

In contrast, *t*-butyllithium and DPA, when allowed to react in ligroin at 40° for 22 hr, give products similar to the *n*-alkyllithium cases (Chart II).

After carbonation, there was obtained *trans*-2-phenyl-3-(*o*-carboxyphenyl)-4,4-dimethyl-2-pentenoic acid (**7**, 8–12%), 4,4-dimethyl-2,3-diphenyl-2-pentenoic acid (**8**, 5–15%), and 2-phenyl-3-*t*-butylindone (**9**, 4%). DPA was recovered to the extent of 50–70%.

The gross structures of the products as represented were in accord with analytical and spectral data with the exception of the dicarboxylic acid **7** which by potentiometric titration gave an apparent neutralization equivalent twice the theoretical. It was considered that **7** might in fact be the lactone carboxylic acid **10**. However, a number of data proved that the compound was indeed a dicarboxylic acid rather than **10**. The nmr spectrum showed no methinyl hydrogen, but did show a low-field signal at τ 0.10 which integrated for the two carboxylic protons. The infrared spectrum (KBr) had two carbonyl maxima at 1718 and 1675 $\mathrm{cm^{-1}}$ and nothing in the range of 1760–1740 $\mathrm{cm^{-1}}$ which might be expected for a lactone such as **10**. The compound **7** was treated with diazomethane to give an ester containing *two* singlet methyl peaks of equal intensity at τ 6.09 and 6.36, and **7** was also converted to its anhydride (**7a**) (see below). Finally, an examination of the ultraviolet spectrum of **7** added conclusive evidence for the indicated structure. The acid (**7**) (H_2A) had a molar absorptivity of 1000 in ethanol at 282 mμ. The molar absorptivity decreased to 670 after the addition of 1 equiv of sodium hydroxide (formation of HA^-) and rose again to 770 after the addition of the second equivalent of base (formation of A^{2-}) and remained constant as more base was added.

A possible explanation of the failure of the potentiometric titration to give the correct neutralization equivalent is that the carboxyl groups are very close to one another (models indicate this to be so) and that because of hydrogen bonding in the anion HA^- between the ionized and un-ionized carboxyl groups, the pK_a of the second carboxyl group is so high as to give no noticeable inflection point in a potentiometric titration. The fact that the carboxyl group is in the *ortho* position of the benzene ring was suggested by analogy to the primary organolithium reactions[4] and confirmed by the nmr spectrum (see Experimental Section) as well as conversion of **7** to the anhydride **7a** (see below).

When the *t*-butyllithium–DPA reaction mixture (heated at 30–40°) was terminated by hydrolysis, glpc

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(6) (a) Isobutylene was also isolated, but *t*-butyllithium alone under the reaction conditions decomposes to a small amount of isobutylene. (b) L. H. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941).

(7) H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *ibid.*, **87**, 3019 (1965).

(8) (a) H. W. Brown and R. C. Jones, *J. Chem. Phys.*, **36**, 2809 (1962); (b) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964); (c) H. R. Ward, *ibid.*, **89**, 5517 (1967); H. R. Ward and R. G. Lawler, *ibid.*, **89**, 5518 (1967).

(9) Ph.D. Thesis of S. J. Tauber, Harvard University, 1958.

Chart I

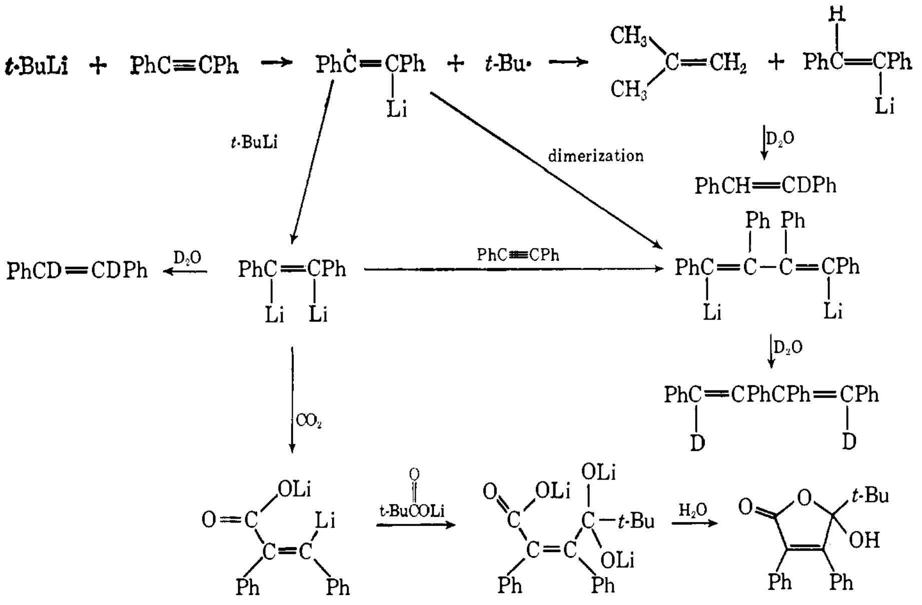

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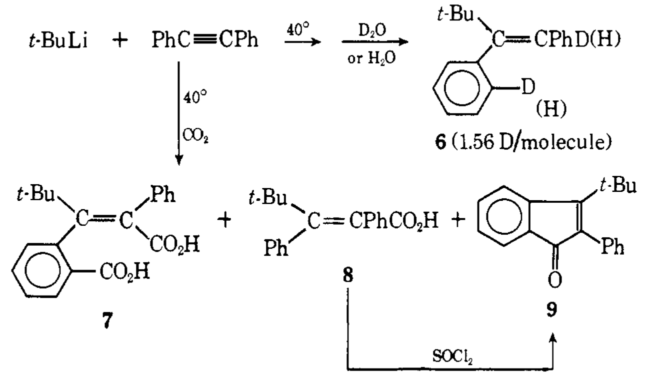
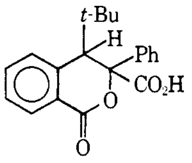
Chart II



revealed the presence of 36% unreacted diphenylacetylene, 11% *cis*-α-*t*-butylstilbene, 3% *trans*-α-*t*-butylstilbene, and 30% of a mixture consisting of α-*t*-butylstilbene containing one and two additional *t*-butyl groups on the aromatic rings.[10a] No tetraphenylbutadiene was detectable by glpc. The 11% component was separable using a preparative glpc column and shown to be *cis*-α-*t*-butylstilbene (**6a**, mp 48°). The remaining compound could not be isolated using the preparative apparatus, but was shown to be the second isomer of α-*t*-butylstilbene by independent synthesis of both isomers as outlined in the following paragraphs.



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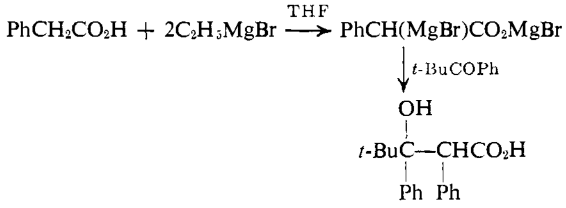
There is only one reference to *t*-butylstilbene in the literature. Some 55 years ago Ramart-Lucas reported that the dehydration of 3,3-dimethyl-1,2-diphenyl-2-butanol results in the formation of *t*-butylstilbene of unspecified stereochemistry.[10b] In our hands, this reaction produced a complex and inseparable mixture containing not only *cis*- and *trans*-α-*t*-butylstilbenes, but other products arising from rearrangement of the carbon skeleton as well.

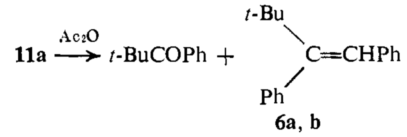
Pure *cis*- and *trans*-α-*t*-butylstilbenes were obtained by the reaction sequence shown below, starting with an Ivanoff reaction to give a mixture of the diastereoisomeric β-hydroxy acids **11**. One diastereoisomer **11a**, mp 222–223°, was separated by fractional crystallization, and in the nmr spectrum showed a singlet for the *t*-butyl group at τ 9.33. The other isomer (**11b**) could not be separated from **11a**, and the nmr spectrum of the mixture before separation showed two singlets for the *t*-butyl group at τ 9.33 and 9.06 in a two to one ratio.



$$PhCH_2CO_2H + 2C_2H_5MgBr \xrightarrow{THF} PhCH(MgBr)CO_2MgBr \xrightarrow{t\text{-BuCOPh}} t\text{-BuC(OH)(Ph)}\text{—CH(Ph)CO}_2\text{H}$$

11a,b (47%)

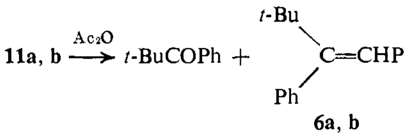
Treatment of **11a** with acetic anhydride at 140° yielded 50% pivalophenone and 50% of a mixture of *cis*- and *trans*-α-*t*-butylstilbenes as indicated by glpc.



$$\mathbf{11a} \xrightarrow{Ac_2O} t\text{-BuCOPh} + (t\text{-Bu})(Ph)C{=}CHPh$$

6a, b

6b, stereoisomer separated by fractional recrystallization, mp 39.5–40.5°, τ (olefinic proton) 3.60, shoulder at 233 mμ (log ε 4.14)



$$\mathbf{11a, b} \xrightarrow{Ac_2O} t\text{-BuCOPh} + (t\text{-Bu})(Ph)C{=}CHPh$$

6a, b

6a, stereoisomer separated by fractional recrystallization, mp 47.0–48.0°, τ (olefinic proton) 3.43, λ_{max} 255 mμ (log ε 4.22)

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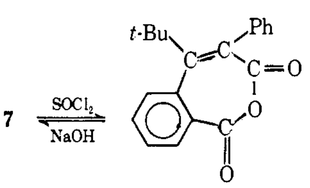
(10) (a) It has not yet been possible to obtain this mixture or its components in sufficient quantity to determine where in the rings the additional *t*-butyl groups are located. (b) P. Lucas, *Compt. Rend.*, **150**, 1060 (1910); P. Ramart-Lucas, *Ann. Chim. Phys.*, (8), **30**, 349 (1910).

Fractional crystallization of the stilbene mixture yielded a pure geometrical isomer (**6b**, mp 39.5–40.5°) which was not the same as the compound isolated from the hydrolysis of the *t*-butyllithium–DPA reaction mixture.

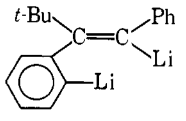
Treatment of a 2:1 mixture of **11a**–**11b** with acetic anhydride yielded 13% pivalophenone and 66% of the isomeric α-*t*-butylstilbenes from which pure **6a** was obtained by fractional crystallization and shown to be identical with the product isolated from *t*-butyllithium and DPA. Both **6a** and **6b** were shown to be configurationally stable under the work-up conditions of the *t*-butyllithium–DPA reaction mixture.

In an independent study[11] the 47–48° melting compound (**6a**) was shown to be the *cis* isomer and the *trans* (**6b**).

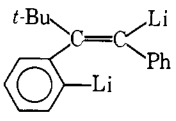
An unequivocal configurational assignment of the dicarboxylic acid **7** was made by conversion to the anhydride **7a** (another example of an unusual seven-membered ring anhydride[4b]) which in turn could be hydrolyzed with dilute sodium hydroxide to the same dicarboxylic acid **7**, thus proving the *trans* arrangement of the phenyl groups. In order to obtain 2-phenyl-3-*t*-butylindone (**9**) and the dicarboxylic acid **7**, the *trans*-phenyl intermediate **13a** must have been present in the reaction mixture, because it has been shown that carbonation or hydrolysis[12] of vinylic lithium compounds occurs with retention of configuration.



7a

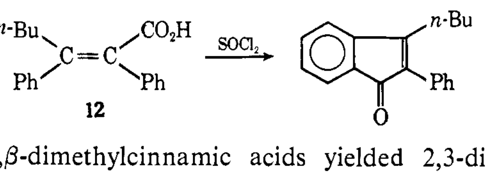


13a



13b

The monocarboxylic acid **8** was converted into 2-phenyl-3-*t*-butylindone (**9**) in 50% yield upon treatment with thionyl chloride. This, however, cannot be taken as unequivocal proof of the *trans* stereochemistry of **8**. We have observed, for example, that *cis*-2,3-diphenyl-2-heptenoic acid (**12**) can be converted to the corresponding indone in 25% yield when treated with thionyl chloride.[13] Similarly, Kampmeier and Fautazier[14] have recently reported that both *cis*- and *trans*-α,β-dimethylcinnamic acids yielded 2,3-dimethylindone when treated with thionyl chloride. Clearly *cis*-α-phenylcinnamic acids can isomerize to the *trans* form under these reaction conditions.



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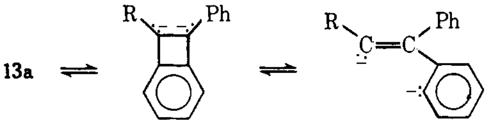
It is apparent from this work as well as that of Bartlett and Tauber[9] that both electron transfer and addition–metalation are competitive processes in this system. In fact there has been recent evidence which suggests that even addition[8b,c,15] reactions of organolithium compounds proceed *via* electron transfer to give a radical, radical-anion pair which collapses to product. Such a precursor may also arise in the addition to DPA of organolithium compounds. One might speculate that collapse of the alkyl radical–DPA anion radical pair is the lower activation energy process leading to the observed addition products and that higher temperatures favor processes which occur after diffusion out of the solvent cage such as addition of the DPA anion radical to a molecule of DPA or even dimerization of two DPA anion radicals (see Chart I). Further work is required to clarify this point.

The properties or existence of the cyclobutadiene dianion is a subject of current interest because of the possible aromatic character of this species. We considered the possibility that the dicarbanion-like species **13a** formed because of stabilization by cyclization to give a benzocyclobutadiene dianion.



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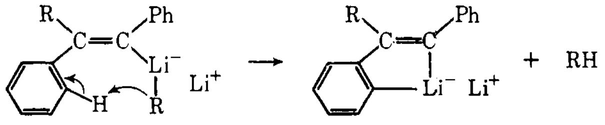
However, no benzocyclobutene derivatives were obtained either with *t*-butyllithium or the previously reported primary alkyllithiums. Inasmuch as 1,2-diphenylbenzocyclobutene can be recovered from refluxing solvents and is stable to acid or base[16] there is no compelling reason to believe that a benzocyclobutene was the initial product, and even if it was one would not expect it to rearrange to the stilbene derivatives which are actually obtained.[16] The presence of a small equilibrium concentration of the dianion would be expected to result in a (probably small) equilibrium concentration of **15**, but we do not detect products which might arise from **15**. There is no evidence in this system of the existence of a benzocyclobutadiene dianion.

The formation and stereochemistry of the dilithium compound **13a** deserves comment. In the case of *n*-butyllithium and DPA we have evidence which indicates that addition precedes metalation. Evidence that this is true in the case of *t*-butyllithium is afforded by the observation that DPA recovered after treatment of the reaction mixture with deuterium oxide contains no deuterium, and that furthermore an unmetalated addition product **8** is obtained upon carbonation of the reaction mixture. It is recognized that the structure of organolithium compounds in solution is complex, but it is suggested that at least a partial structural feature of the addition product is complexation with a molecule of unreacted RLi as shown in **16**.



16 **17**

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[11] J. E. Mulvaney and D. J. Newton, *J. Org. Chem.*, in press.

[12] D. Seyferth and L. C. Vaughan, *J. Am. Chem. Soc.*, **86**, 883 (1964).

[13] L. J. Carr and J. E. Mulvaney, submitted for publication.

[14] J. A. Kampmeier and R. M. Fautazier, *J. Am. Chem. Soc.*, **88**, 1959 (1966).

[15] C. S. Screttas and J. F. Eastham, *ibid.*, **88**, 5668 (1966); see also M. A. Doran and R. Waack, *J. Organometal. Chem.*, **3**, 94 (1965).

[16] (a) F. R. Jensen and W. E. Coleman, *J. Am. Chem. Soc.*, **80**, 6149 (1958); (b) W. Baker, J. F. W. McOmie, and D. R. Preston, *J. Chem. Soc.*, 2971 (1961); (c) L. A. Carpino, *J. Am. Chem. Soc.*, **84**, 2196 (1962).

The complex **16** could then provide a path for the formation of the addition–metalation product. If one of the lithium atoms is chelated as shown in **17** this would force the large *t*-butyl group and the phenyl group into a *cis* relationship, and thus provide an explanation for the stereochemistry of the dicarboxylic acid **7**. There is some analogy here to the explanation offered by Jones, Vauex, and Hauser for the reactivity of N,N-dimethylbenzylamine toward *o*-lithiation with *n*-butyllithium.[17]

Experimental Section

Melting points are uncorrected. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as an internal standard; ultraviolet spectra were determined in 95% ethanol on a Cary 11 recording spectrometer, and a Beckman IR-4 instrument was used to obtain infrared spectra.

Gas–liquid partition chromatography was carried out with a F & M Model 609 flame ionization instrument. For analytical determinations correction factors for weight ratio/area ratio data were determined with standards containing the same compounds as were in the unknown mixture.

Ligroin was purified by stirring overnight with 95% sulfuric acid, washing with distilled water, drying over magnesium sulfate, and 24-hr reflux over sodium prior to final distillation.

Lithium wire and *t*-butyllithium in pentane were obtained from the Lithium Corporation of America.

All organolithium reactions were run under a helium atmosphere in a flame-dried apparatus protected by a drying tube. When nmr data are presented, numbers in parentheses represent relative integrated areas.

***t*-Butyllithium and DPA at 90–95°. Hydrolysis.** Ligroin (50 ml, bp 95–97°) was added to a solution of *t*-butyllithium (0.14 mol) in 90 ml of pentane and the pentane was removed by distillation. To this was added 16.0 g (0.09 mol) of DPA in 60 ml of ligroin (bp 95–97°). The solution became dark red and was heated for 17 hr at 90–95°. Water was added slowly and after separation of the layers, the organic material was dried over magnesium sulfate. After removal of the solvent under vacuum the residue was separated by glpc using a 2.4-m column ("GE-SE 30," 20% on Chromosorb W at 240°). Yields were determined by comparison of areas with those of the authentic compounds. Approximately 50% of the reaction mixture could be accounted for by glpc analysis which is in accord with the observation that only about 50% of the reaction products are distillable, the remainder consisting of intractable tar. Yields were: recovered DPA, 12%; *cis*-α-*t*-butylsilbene + *trans*-stilbene 9–12% (these components were not separable on this column but were isolated by fractional distillation and recrystallization as described below); *trans*-α-*t*-butylstilbene, 3%; *cis,cis*-1,2,3,4-tetraphenylbutadiene, 4–7%; a mixture of di- and tri-*t*-butylstilbenes (10%); and five minor components with a higher retention time (10%).

cis,cis-1,2,3,4-Tetraphenylbutadiene was isolated by filtering the original reaction mixture and recrystallizing the collected solid from ethyl acetate, mp 183.5–184°. A mixture melting point with an authentic sample[6,7] showed no depression. When the reaction was carried out as above but terminated with deuterium oxide, the *cis,cis*-1,2,3,4-tetraphenylbutadiene was found to contain 1.94 D/molecule. The nmr spectrum showed no olefinic hydrogens.

trans-Stilbene was isolated by repeated distillation of the reaction mixture to give a semisolid fraction, bp 105–130° (0.2 mm), which showed a peak at τ 8.83 in the nmr spectrum corresponding to the *t*-butyl group of *cis*-α-*t*-butylstilbene (see below). Repeated recrystallization of this solid yielded *trans*-stilbene (mp 123–125°), undepressed by mixing with an authentic sample. The *trans*-stilbene which was isolated after the reaction mixture was terminated by deuterium oxide contained 1.7 D/molecule.

When *t*-butyllithium (0.300 mol) and DPA (45.0 g, 0.252 mol) in 400 ml of ligroin were stirred at 80–85°, an esr signal with no fine structure was obtained. The esr signal which was observed after 0.5 hr of reaction was 250% larger after 5 hr total reaction time and had decreased only slightly after 23.5 hr. Neither DPA alone in ligroin nor *t*-butyllithium alone in ligroin under these conditions gave a measurable esr signal.

***t*-Butyllithium and DPA at 40°. Termination of Reaction by Carbonation.** A solution of *t*-butyllithium (0.356 mol) in 196 ml of pentane was added within a few minutes to a rapidly stirred solution of DPA (45.0 g, 0.254 mol) in 414 ml of ligroin. The solution immediately became cherry red. The ligroin solution was stirred at 34–45° for 22 hr. The solution became dark red after 12 hr and red brown after 22 hr. Carbonation of the reaction mixture by decantation gave a large amount of acidic yellow oil. Trituration of the oil with hexane gave 5–12% of solid 2-phenyl-3-(*o*-carboxyphenyl)-4,4-dimethyl-2-pentenoic acid (**7**), mp 216–220°. After four recrystallizations from ethyl acetate the acid had mp 228.5–229.5°; nmr (20% in NaOD–D_2O) τ 2.76–3.18 (9.1) and 8.73 (8.9); nmr (10% in hexadeuterioacetone, corrected for external reference), τ 2.70 and 3.00 (7.9) and 8.76 (9.0); nmr (20% in acetone) τ 0.10 (2.1), 2.32 (1.0), and 2.72 and 3.00 (7.9); ν_{max}^{KBr} 1718 and 1675 cm^{-1}; λ_{max} 282 (3.03), 225 (3.92), and 207 mμ (log ϵ 4.40).

Anal. Calcd for $C_{15}H_{18}(COOH)_2$: C, 74.05; H, 6.22; neut equiv, 162. Found: C, 74.19; H, 6.39; neut equiv, 332 by potentiometric titration, 162 by ultraviolet examination (see Results and Discussion).

Distillation of the hexane-soluble acidic material gave 8–15% of 2,3-diphenyl-4,4-dimethyl-2-pentenoic acid (**8**), bp 175–185° (0.77 mm), mp 184.5–185.5°. After recrystallization from hexane the acid had mp 186.5–187.0°; nmr (15% in $CDCl_3$) τ 2.98 (9.7) and 8.75 (9.3); $\nu_{max}^{CHCl_3}$ 1704 cm^{-1}.

Anal. Calcd for $C_{15}H_{19}(COOH)$: C, 81.40; H, 7.19; neut equiv, 280. Found: C, 81.73; H, 7.26; neut equiv, 282.

The neutral fraction gave 50–70% DPA and 4% 2-phenyl-3-*t*-butylindone (9), bp 145–155° (0.25 mm); $\nu_{max}^{CHCl_3}$ 1710 cm^{-1} (lit.[9] λ_{max} 1710 cm^{-1}); λ_{max} 245 (3.95) and 240 mμ (log ϵ 3.88) (shoulder), plus impurity maxima due mainly to diphenylacetylene.

After four recrystallizations from ethanol, the 2,4-dinitrodiphenylhydrazone derivative of the indone had mp 229–232° (lit.[9] mp 236–240°), mixture melting point with an authentic sample, 234–237°. The infrared spectrum was identical with that of an authentic sample.

***t*-Butyllithium and DPA at 35–40°. Termination by Hydrolysis.** A solution of *t*-butyllithium (0.07 mol) and 6.8 g (0.04 mol) of DPA in 45 ml of pentane and 50 ml of ligroin was stirred for 27 hr at 35–40° and thereafter for 3 days at room temperature. Water was added slowly, and after separation of layers the organic material was dried over magnesium sulfate. In contrast to the 90–95° reaction reported above, greater than 90% of the reaction mixture was vacuum distillable. Yields were determined by glpc as described above by comparison with authentic samples.

There was obtained 36% recovered DPA, 11% *cis*-α-*t*-butylstilbene, 3% *trans*-α-*t*-butylstilbene, 30% a mixture of di- and tri-*t*-butylstilbenes,[10a] and 10% two minor components which were not identified. No *cis,cis*-1,2,3,4-tetraphenylbutadiene could be detected.

The *cis*-α-*t*-butylstilbene was isolated by collecting the fraction boiling at 102–116° (0.2 mm) and passing this material through a preparative glpc apparatus with a Carbowax column. *cis*-α-*t*-Butylstilbene (**6a**) was obtained, mp 48.5–49.5° after two recrystallizations from hexane [lit.[10] mp 48–49°, bp 164–165° (11 mm)]; nmr (10% in $CDCl_3$), τ 2.64–3.27 (10.0), 3.52 (1.0), and 8.82 (9.0); λ_{max} 264 (4.03) (shoulder), 255 (4.14), and 228 mμ (log ϵ 3.90).

When the reaction mixture was terminated with deuterium oxide the isolated *cis*-α-*t*-butylstilbene contained 1.56 D/molecule and the recovered DPA contained 0.00 D/molecule.

Preparation of 3-Hydroxy-4,4-dimethyl-2,3-diphenylpentenoic Acid (11a, b). This synthesis is based on that described by Ivanoff[18] for the preparation of β-hydroxy-α-arylcarboxylic acids. Phenylacetic acid (68.0 g, 0.500 mol) in 200 ml of purified tetrahydrofuran was added dropwise to a rapidly stirred solution at 0° of 2.41 *M* (350 ml, 0.840 mol) ethylmagnesium bromide in tetrahydrofuran. On completing the addition, the clear green solution was heated under reflux for 1 hr.

Pivalophenone[19] (61.0 g, 0.410 mol) in 50 ml of tetrahydrofuran was added and the solution heated under reflux for 19 hr. After cooling to 0°, the reaction mixture was hydrolyzed with a solution containing 500 ml of saturated aqueous ammonium chloride and

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(18) D. Ivanoff and A. Spassoff, *Bull. Soc. Chim. France*, **49**, 337 (1931).

(19) C. S. Marvel, J. H. Ford, and C. D. Thompson, *J. Am. Chem. Soc.*, **57**, 2619 (1935).

10 ml of 10% hydrochloric acid. A precipitate formed immediately. Filtration yielded a white solid and filtrate consisting of two immiscible liquids. The solid was triturated in 200 ml of ethyl ether, and the ethyl ether extract was combined with the upper organic layer of the filtrate. The ether–tetrahydrofuran solution was washed twice with 100-ml portions of water and extracted twice with 250-ml portions of 10% aqueous sodium carbonate.

The neutral fraction was dried, and the solvents were removed under reduced pressure. There remained 26.4 g of crude pivalophenone (44% recovered).

The combined basic extracts were acidified with glacial acetic acid. The precipitate was filtered and dried to give 96.8 g of crude acidic material. Trituration in 500 ml of hot hexane removed 26.4 g of phenylacetic acid. The hexane-insoluble acids (70.7 g, 46.6%) were dissolved in 700 ml of hot benzene and allowed to stand overnight at room temperature. Filtration yielded 29.2 g of white powder (**11a**), mp 222–223°. An nmr spectrum showed one singlet in the *t*-butyl region, suggesting that the acid is a pure diastereoisomer of 3-hydroxy-4,4-dimethyl-2,3-diphenylpentanoic acid (**8**): ν_{max}^{Nujol} 3540 and 1684 cm^{-1}; nmr (10% in $CDCl_3$), τ 2.52–2.86 (10), 5.38 (1, singlet), and 9.33 (9, singlet).

Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.51; H, 7.38; neut equiv, 298. *Found*: C, 76.25; H, 7.22; neut equiv, 296.

The filtrate from the recrystallization of (**11a**) was concentrated to 250 ml and cooled. After filtering, 25.3 g of white powder, mp 215°, remained. The nmr spectrum showed two singlets in the aliphatic region in a 2:1 ratio suggesting a 2:1 mixture of (**11a**) and its diastereoisomer (**11b**); nmr (10% in $CDCl_3$), τ 2.20–3.11 (10, multiplet), 6.38 (0.66, singlet), 5.59 (0.34, singlet), 9.06 (3, singlet), and 9.33 (6, singlet). Further recrystallizations from benzene were unsuccessful in separating the diastereoisomers.

Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.51; H, 7.38; neut equiv, 298. Found: C, 76.67; 7.54; neut equiv, 299.

Preparation of *α-t*-Butylstilbene (6b). This reaction was run according to a general procedure of Ivanoff, *et al.*[20] To 27.0 ml of acetic anhydride was added a pure diastereoisomer (**11a**), mp 222–223°, of 3-hydroxy-4,4-dimethyl-2,3-diphenylpentanoic acid (10.0 g, 0.335 mol). The solution was stirred at 140° for 18 hr, and 50 ml of water was added slowly. When the solution cooled to room temperature, 50 ml of ether was added. The ether was washed with two portions of water and extracted with two 15-ml portions of 10% aqueous sodium carbonate.

The neutral ethyl ether solution was dried over anhydrous sodium sulfate. Removal of the ethyl ether left 6.02 g of yellow oil. Distillation yielded 2.71 g of pivalophenone (50.0%), bp 55–60° (1.5 mm) and 2.73 g (50%) of an oily mixture of *cis*- and *trans-α-t*-butylstilbenes, bp 126–127° (1.5 mm). This mixture was dissolved in 15 ml of 95% ethanol and cooled to −20° for 5 hr. Filtration yielded 1.22 g (15.4%) of crude *α-t*-butylstilbene (**6b**), mp 35–36°. Glpc (5-ft QF-1 column; 200°) of the product from two additional recrystallizations from ethanol showed one peak, mp 39.5–40.5°; nmr (10% in CCl_4), τ 2.79 (10, singlet), 3.60 (1, singlet), and 9.00 (9, singlet); $\lambda_{shoulder}$ 233 mμ (ϵ 13,700).

Anal. Calcd for $C_{18}H_{20}$: C, 91.52; H, 8.49. Found: C, 91.76; H, 8.53.

Preparation of *cis-α-t*-Butylstilbene (6a). To 27.0 ml of acetic anhydride was added 10.0 g (0.335 mol) of a mixture of the diastereoisomeric 3-hydroxy-4,4-dimethyl-2,3-diphenylpentanoic acid (**11a, b**). After stirring for 12 hr at 110°, 50 ml of water was added slowly. When the solution cooled to room temperature, 50 ml of ethyl ether was added. The aqueous layer was separated and discarded. The ethyl ether solution was washed with water and extracted with two 15-ml portions of 10% aqueous sodium carbonate. Acidification of the combined basic extracts gave 1.91 g (19%) of starting material. The neutral ethyl ether solution was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. A yellow oil (6.03 g) remained. Distillation yielded 0.70 g (13%) of pivalophenone, bp 55–59° (1.5 mm), and 5.20 g (66%) of the isomeric *α-t*-butylstilbenes, bp 127–128° (1.5 mm). Dissolving the stilbenes in 8 ml of pentane and cooling to −80° for 15 min produced a white solid which was filtered rapidly. One recrystallization from ethanol at −20° gave 1.18 g (15.0%) of glpc-pure *α-t*-butylstilbene (**6a**), mp 48.0–49.0°. This compound was identical with that obtained from hydrolysis of the *t*-butyllithium–DPA reaction mixture.

Treatment of 2-hydroxy-3,3-dimethyl-1,2-diphenylbutane[10] with an acetyl chloride–acetic anhydride solution at 70° produced the isomeric *α-t*-butylstilbenes and a third compound, presumably 2,3-dimethyl-3,4-diphenyl-1-butene in 92% yield. Attempts at separating the three isomers by either distillation, elution chromatography, or preparative vapor phase chromatography were unsuccessful. No solid material could be obtained by cooling a pentane solution of the three isomers to −80°.

Anhydride 7a of 2-Phenyl-3-(*o*-carboxyphenyl)-4,4-dimethyl-2-pentenoic Acid (7). 2-Phenyl-3-(*o*-carboxyphenyl)-4,4-dimethyl-2-pentenoic acid (**7**) (1.90 g, 5.86 × 10^{-3} mol) was suspended in 125 ml of anhydrous carbon tetrachloride. Thionyl chloride (11.70 g, 0.0984 mol) was added in one portion and the mixture refluxed for 23 hr. The clear yellow solution was allowed to cool to room temperature, poured into 300 ml of water, and stirred for 30 min. Ethyl ether (300 ml) was added, and the organic layer was extracted with two 50-ml portions of saturated aqueous sodium carbonate solution and dried over anhydrous sodium sulfate. After removal of ethyl ether and carbon tetrachloride under reduced pressure, 1.62 g, (90.5%) of crude anhydride with mp 162–163° remained. Four recrystallizations from hexane produced white prisms with mp 168.0–168.5°; $\nu_{max}^{CHCl_3}$ 1797, 1757, 1275, and 1245 cm^{-1}; λ_{max} 238 (12,000), 273 (7100), and 315 mμ (ϵ 4400); nmr (10% in $CDCl_3$), τ 1.90 (1, doublet, J = 8 cps), 2.44–3.06 (7, multiplet), 3.44 (1, doublet, J = 7 cps), and 8.66 (9, singlet).

Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92; mol wt, 306. Found: C, 78.10; H, 6.07; mol wt, 313.

The pure anhydride (0.050 g) remained unchanged after being suspended in either 10 ml of water at 70° for 48 hr or in 10 ml of 5% aqueous sodium bicarbonate at 25–30° for 48 hr. Heating the pure anhydride (0.100 g, 0.33 × 10^{-4} mol) in 3 ml of 10% sodium hydroxide and 8 ml of water at 70–75° for 40 min gave a homogeneous solution. After cooling to room temperature, the basic solution was acidified and extracted with two 10-ml portions of ethyl ether. The solid was filtered and dried to give 0.104 g, (98%) of 2-phenyl-3-(*o*-carboxy-phenyl)-4,4-dimethyl-2-pentenoic acid (**7**), mp 228.0–228.5°. A mixture melting point with a pure sample of the acid showed no depression.

Reaction of 4,4-Dimethyl-2,3-diphenyl-2-pentenoic Acid (8) with Thionyl Chloride. Compound **8** (200 mg, 7.1 × 10^{-4} mol) in 1.0 ml of carbon tetrachloride was treated with 0.2 ml (2.0 × 10^{-3} mol) of thionyl chloride. The solution was heated under reflux for 6 hr after which time it was poured into 15 ml of water. The aqueous suspension was heated on a water bath for 1 hr. Upon cooling to 0°, 2-phenyl-3-*t*-butylindone (**9**) precipitated and was obtained in 50% yield after recrystallization from ethanol. The compound was identical with the earlier described 2-phenyl-3-*t*-butylindone.

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(20) D. Ivanoff, N. Marecoff, and B. Amidjine, *Bull. Soc. Chim. France*, 1214 (1963).