and filtered. The solid was crystallized from ethanol–water to give the adduct as pale yellow microcrystals, mp 125–129°.

Anal. Calcd for $C_{40}H_{32}$: C, 93.70; H, 6.29. Found: C, 93.96; H, 5.88.

trans-1-(2-Hydroxy-2a,3,4,5-tetrahydroacenaphthyl) *m*-Chlorobenzoate (XI).—To a cooled solution of 4.25 g of 2a,3,4,5-tetrahydroacenaphthylene in 100 ml of chloroform, 5.66 g of 83% *m*-chloroperbenzoic acid was added in portions with good stirring. The mixture was allowed to stir at room temperature for 6 hr. At that time 97% of the peracid had been consumed as determined by iodometric titration. The reaction mixture was filtered and the chloroform solution was washed with water. The solution was dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo* to give a light yellow oil. The oil solidified when rubbed with a glass rod in the presence of approximately 15 ml of Skellysolve B to give 1.73 g of a white solid. The crude solid was chromatographed on alumina (Merck, no. 71707). Elution with 250 ml of benzene gave a yellowish oil, which was not characterized. Elution with 750 ml of ethyl acetate followed by crystallization from benzene–Skellysolve B gave 1-(2-hydroxy-2a,3,4,5-tetrahydroacenaphthyl) *m*-chlorobenzoate as white needles, mp 160.5–162.5°. The substance gave a positive Beilstein test for halogen and a positive test with ferric hydroxamate for ester. An nmr spectrum of an acetone solution exhibited a singlet at δ 5.97 and a doublet at 4.13 (J = 5 cps).

Anal. Calcd for $C_{14}H_{17}O_3Cl$: C, 69.40; H, 5.21; Cl, 10.78. Found: C, 69.53; H, 5.30; Cl, 10.26.

trans-1,2-Dihydroxy-2a,3,4,5-tetrahydroacenaphthene (XII).—1-(2-Hydroxy-2a,3,4,5-tetrahydroacenaphthyl) *m*-chlorobenzoate (2.62 g) was refluxed with 100 ml of 3 *N* sodium hydroxide for 3 hr. The heterogeneous mixture was cooled, filtered, and diluted with 1 l. of cold water. The aqueous solution was extracted five times with 200-ml portions of ether. Removal of the ether *in vacuo* gave 0.76 g of *trans*-1,2-dihydroxy-2a,3,4,5-tetrahydroacenaphthene, mp 142–143.5° after crystallization from benzene. A sample in carbon tetrachloride (18 mg/15 ml) exhibited a single peak in the infrared at 3710 cm^{-1}. An nmr spectrum of the material in acetonitrile showed a singlet at δ 7.55, aromatic absorption peaks centered about 7.06, a singlet at 4.64, and a doublet at 4.28 (J = 4 cps).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.62; H, 7.44.

Registry No.—I, 16897-56-6; V, 16897-57-7; VI, 16897-58-8; VIII, 16897-59-9; IX, 16897-60-2; 1,7-trimethylenindene, 16897-56-6; tetracyclone adduct of 2a,3,4,5-tetrahydroacenaphthalene, 16897-62-4; XI, 16897-63-5; XII, 16897-64-6.

Organolithium Compounds and Acetylenes. IV.[1] Sequence of Addition–Metalation in the Reaction of Organolithium Compounds with Diphenylacetylene

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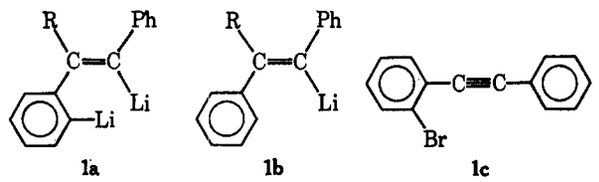
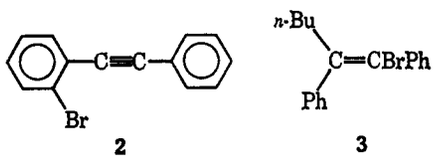
Products from the reaction of *n*-butyllithium and/or lithium metal with *o*-bromodiphenylacetylene (2) and 1-bromo-1,2-diphenyl-1-hexene (3) have been identified. The results lead to the conclusion that *n*-butyllithium reacts with diphenylacetylene by addition followed by metalation. In the course of the work the stereochemistry of the isomeric 2,3-diphenyl-2-heptenoic acids has been determined by stereoselective decarboxylation to the corresponding α-*n*-butylstilbenes.

In previous papers[1] reactions of organolithium compounds and acetylenes have been described. The reaction of diphenylacetylene (DPA) with an excess of primary organolithium compounds yields deuterolysis or carbonation products arising very largely from the dilithiated intermediate **1a**. Only very small amounts of **1b** and **1c** were present in the reaction mixture.[3] Furthermore, although the stereochemistry of **1a** was proven, the carbonation product of **1b** was not obtained in sufficient purity or quantity to allow a stereochemical assignment.



1a **1b** **1c**

To determine whether addition to DPA precedes and/or promotes metalation or *vice versa*, and to determine the stereochemistry of **1b**, *o*-bromodiphenylacetylene (2) and 1-bromo-1,2-diphenyl-1-hexene (3)

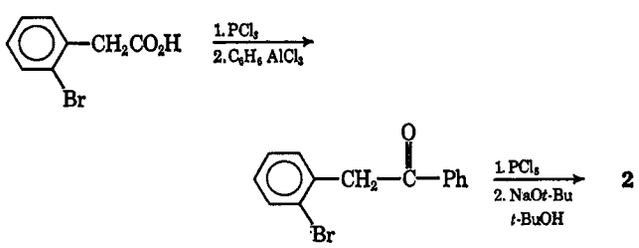


2 **3**

were synthesized, and reactions of these compounds with *n*-butyllithium and/or lithium metal were examined.

Results

o-Bromodiphenylacetylene was synthesized by a different procedure from that reported in the literature. The method used in this work is shown briefly.



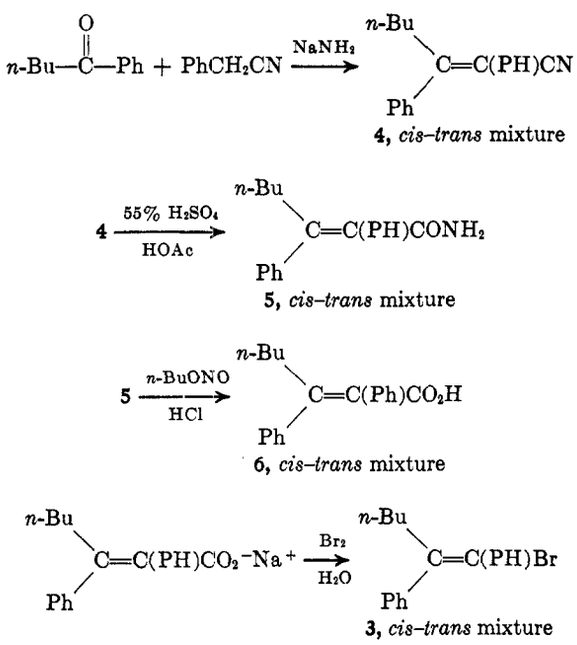
(1) Research supported by AFOSR(SRC)-OAR, U.S.A.F. Grant No 720-65 and 720-67.

(2) NASA Predoctoral Fellow, 1964–1966.

(3) J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlund, and D. J. Newton, *J. Amer. Chem., Soc.*, **88**, 476 (1966).

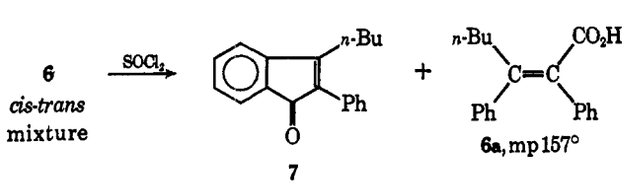
Because a number of vinylic bromides have been synthesized, although in low yields, by treating 1,1-dibromo compounds with a mixture of triphenylphosphine, potassium *t*-butoxide, and a ketone,[4] we treated valerophenone with benzal bromide–triphenylphosphine and potassium *t*-butoxide in an attempt to obtain **3** directly. However, only starting materials were recovered. The synthesis of **3** was accomplished starting with valerophenone and proceeding as shown in Scheme I.

SCHEME I



Compounds **4**, **5**, **6** and **3** were all shown to be *cis–trans* mixtures by a number of criteria, particularly the nmr spectra which in the region τ 7–8 showed two distinct multiplets for the allylic protons. Pure stereoisomers (see below) gave only one multiplet for the allylic protons.

To learn the stereochemistry of **1b** it was desirable to isolate and distinguish between the *cis* and *trans* forms of **6**. One pure geometrical isomer of **6**, mp 157° (**6a**), was obtained when the *cis–trans* mixture was treated with thionyl chloride to yield 55% of 2-phenyl-3-*n*-butylindone (**7**) and 43% of a crystalline sharp melting

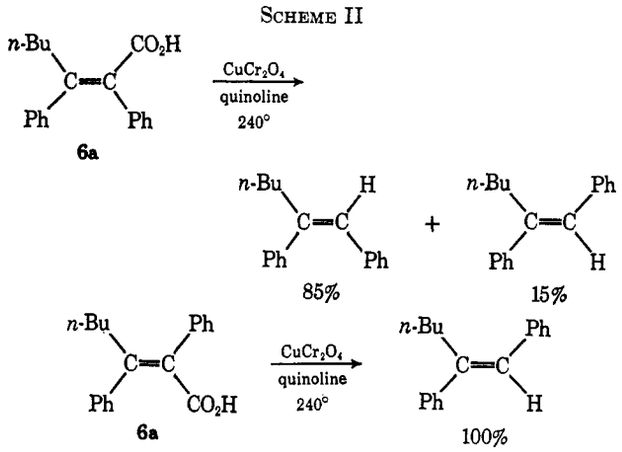


compound **6a** which showed only one allylic proton multiplet in its nmr spectrum and was assigned the *cis* structure (see below). The other stereoisomer **6b**, mp 127°, was obtained by the treatment of **3** with *n*-butyllithium as described in succeeding paragraphs.

(4) J. W olinsky and K. L. Erickson, *J. Org. Chem.*, **30**, 2208 (1965).

α,β-Unsaturated carboxylic acids are said to decarboxylate with retention of configuration to the corresponding olefins when treated with copper chromite in refluxing quinoline.[5] Isomer **6a** was decarboxylated under these conditions to give a quantitative yield of a mixture consisting of 85% *cis*-α-*n*-butylstilbene and 15% *trans*-α-*n*-butylstilbene. Under the same conditions isomer **6b** gave a quantitative yield of only *trans*-α-*n*-butylstilbene (Scheme II).

SCHEME II



It may be concluded that **6a** is *cis*-2,3-diphenyl-2-heptenoic acid and that **6b** is the *trans* isomer.

It is worth noting in passing that **6b** is converted to indone **7** in 75% yield with thionyl chloride as would be expected, but **6a** is also converted to **7** under the same conditions albeit in 25% yield. The point is that ring closure of a cinnamic acid derivative with thionyl chloride to an indone does not necessarily allow one to designate the stereochemistry of the cinnamic acid.[6]

Reactions of **2** and **3** with *n*-butyllithium in diethyl ether at room temperature for 22 hr produced the results indicated in Scheme III.

It should also be pointed out that treatment of 1.0 mol of **3** with 2.2 g-atoms of lithium in diethyl ether resulted in the formation of a 77% yield of the *trans* acid **6b**.

Discussion

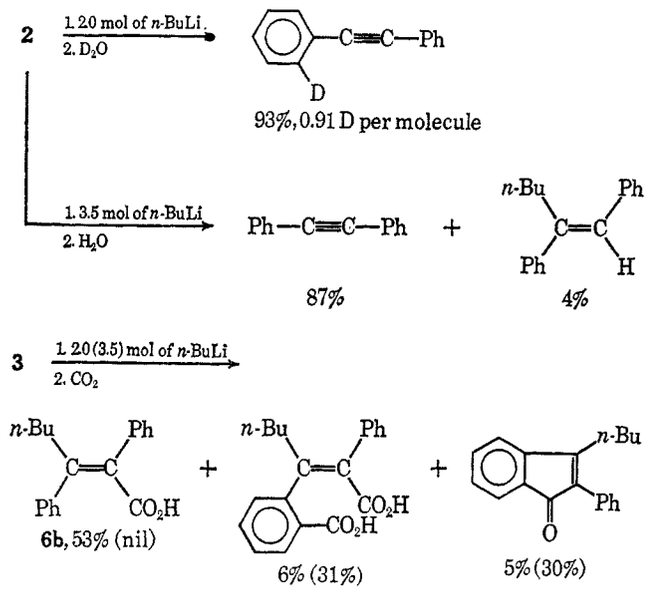
From Chart I and from ref 3 it is apparent that the reaction of *n*-butylithium with *o*-bromodiphenylacetylene (**2**) produces the *o*-lithiated intermediate **1c** in at least 90% yield and that this intermediate, in fact, reacts with *n*-butyllithium more slowly than does DPA itself. (The 4% yield of *trans*-α-*n*-butylstilbene obtained when a 3.5:1 molar ratio of RLi to **2** was used may have arisen by addition followed by metalation.) In contrast treatment of **3** (Scheme III) with *n*-butyllithium followed by carbonation indicates in the first example that approximately 20% of the product is dilithiated and that, within the limits of detection, all of the product is dilithiated at the 3.5:1 ratio of RLi to acetylene (**3**).

(5) D. Y. Curtin and E. E. Harris, *J. Amer. Chem. Soc.*, **73**, 2716 (1951), and references cited therein.

(6) (a) See also J. A. Kampmeier and R. M. Fautzier, *ibid.*, **88**, 1959 (1966); (b) J. E. Mulvaney, L. J. Carr, Z. G. Gardlund, and S. L. Gardlund, in preparation.

The course of reaction of primary organolithium compounds with DPA must proceed very largely then by addition followed by metalation. It may be pointed out that when **3** is treated with an excess of lithium metal only monolithiated product is obtained. Apparently the vinyl carbanion derived from **3** is not sufficiently basic to remove an *o*-hydrogen of a phenyl ring, but *n*-butyllithium can.

SCHEME III



A possible explanation as to why the addition product is metalated to form a dicarbanion-like intermediate is discussed in the preceding paper in this series.[1]

A few other observations seem pertinent. The addition of *n*-butylithium to the acetylenic bond of DPA is irreversible inasmuch as no DPA was obtained from reaction of **3** with *n*-butyllithium or lithium metal.

The *trans* stereochemistry of the products does not necessarily reflect the initial mode of addition across the triple bond. Treatment of **3**, which from its nmr spectrum is a 70:30 mixture of geometrical isomers, with Li metal or *n*-butyllithium gives after carbonation or hydrolysis only the *trans*-stilbenyl derivatives. This indicates that the *cis*-stilbenyllithium intermediate isomerizes to the *trans*, a result in accord with the work of Curtin and Koehl concerning the parent stilbenyllithium itself.[7a] It has been shown that carbonation of vinylic lithium compounds proceeds with retention of configuration.[7b]

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Nuclear magnetic resonance spectra were determined on a Varian Model A-60 spectrometer (at 60 MHz) using tetramethylsilane as an internal standard; ultraviolet spectra were determined in 95% ethanol on a Cary 11 recording spectrometer. A Beckman IR-4 spectrometer was used to determine infrared spectra; a polystyrene film was used to calibrate the instrument.

Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill., and by C. F. Geiger, Ontario, Calif. Deuterium analyses were made by Mr. J. Nemeth, Urbana, Ill., using the falling drop method. Vapor phase chromatography was carried out on a F & M Model 609 flame ionization instrument. For analytical glpc determinations, correction factors for weight ratio–area ratio data were determined with standards containing the same compounds as in the unknown mixture.

Ligroin (bp 30–60°) was purified by stirring overnight with 95% sulfuric acid, washing with distilled water, drying over magnesium sulfate, and refluxing for 24 hr over sodium prior to final distillation.

n-Butyllithium was synthesized in the usual manner[8] and its concentration determined by the double titration method.[9] All organolithium reactions were run under a helium atmosphere in a flame-dried apparatus protected by drying tubes.

α-(*o*-Bromophenyl)acetophenone was prepared according to a procedure used in the synthesis of α-(*p*-nitrophenyl)acetophenone.[10] A stirred solution containing phosphorus trichloride (65.0 ml) and *o*-bromophenylacetic acid[11] (116.5 g, 0.542 mol) was heated at 90° for 2 hr, followed by addition of 150 ml of thiophene-free benzene. The solution was decanted from the yellow phosphorus acid and added slowly to anhydrous aluminum chloride (95.2 g, 0.712 mol) in 250 ml of benzene. After refluxing for 2.5 hr, the solution was poured into a 4-l. beaker containing 2 kg of ice and 350 ml of 12 *M* hydrochloric acid.

The benzene solution was separated and extracted with 200 ml of 10% sodium hydroxide. After drying over anhydrous sodium sulfate, benzene was removed under reduced pressure. There remained 158.3 g of yellow oil which solidified on standing. Recrystallization from 95% ethanol yielded 129.0 g (86.5%) of colorless needles: mp 69.5–70.0°; nmr (10% in $CDCl_3$), τ 1.83–2.00 (2, multiplet), 2.19–3.06 (7, multiplet), 5.56 (2, singlet); $\nu_{max}^{CHCl_3}$ 1695 cm^{-1}.

Anal. Calcd for $C_{14}H_{11}OBr$: C, 61.11; H, 4.03; Br, 29.04. Found: C, 61.32; H, 4.04; Br, 28.92.

α-(*o*-Bromophenyl)acetophenone forms a 2,4-dinitrophenylhydrazone derivative having mp 202.5–203.0° after two recrystallizations from 95% ethanol–benzene.

o-Bromodiphenylacetylene (2).—α-(*o*-Bromophenyl)acetophenone (129.0 g, 0.472 mol) and phosphorus pentachloride (107.0 g, 0.600 mol) were mixed and ground into a fine powder. After heating at 75–80° for 0.5 hr, the mixture liquefied with rapid evolution of hydrogen chloride. The yellow melt was stirred for an additional 2 hr at 85°. Distillation yielded 120.3 g of light yellow oil, bp 167–171° (1.6 mm). This oil was added immediately to a rapidly stirred solution of 313 g (3.26 mol) of sodium *t*-butoxide in 1800 ml of *t*-butyl alcohol and refluxed for 17 hr. The resulting orange solution was diluted with 4 l. of water and extracted with two 250-ml portions of diethyl ether. After drying over anhydrous sodium sulfate, solvent was removed under reduced pressure. There remained 87.8 g of red oil. Distillation gave 75.3 g (62.1%) of pale yellow *o*-bromodiphenylacetylene, bp 129–130° (0.40 mm) [lit.[12] bp 155–160° (0.70 mm)], $n^{26.5}D$ 1.6684.

2,3-Diphenyl-2-heptenenitrile (4).—2,3-Diphenyl-2-heptenenitrile was prepared by the procedure used in the synthesis of 2,3-diphenyl-2-pentenenitrile.[13] To a stirred suspension of 39.0 g (1.00 mol) of commercial sodamide in 500 ml of xylene was added one-fifth of a total of 117 g (1.00 mol) of commercial phenylacetonitrile. The mixture was heated to reflux, and the remainder of the phenylacetonitrile was added as rapidly as the exothermic reaction permitted. To this α-sodiophenylacetonitrile, an insoluble green sludge, 162.0 g (1.00 mol) of commercial valerophenone was added rapidly. The mixture turned deep red and pasty. After refluxing for 4 hr, the solution was cooled to room temperature. Glacial acetic acid (60 ml) in 200 ml of water was added slowly and the mixture stirred for 2 hr. Diethyl ether (600 ml) and 50 ml of 12 *M* hydrochloric acid in 150 ml of water were added and the layers separated. After drying the organic layer over anhydrous sodium sulfate, the solvents and starting materials were removed by heating to 100° under reduced pressure

(7) (a) D. Y. Curtin and W. J. Koehl, *J. Amer. Chem. Soc.*, **84**, 1967 (1962); (b) D. Seyferth and L. G. Vaughn, *ibid.*, **86**, 883 (1964).

(8) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 352 (1951).

(9) H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, **66**, 1515 (1944).

(10) E. J. Corey and J. P. Schaefer, *ibid.*, **82**, 918 (1960).

(11) H. Gilman and O. L. Marrs, *J. Org. Chem.*, **30**, 325 (1965), and references cited therein.

(12) R. L. Letsinger, T. J. Saveriede, and J. R. Nazy, *ibid.*, **26**, 1273 (1961).

(13) K. Rorig, *J. Amer. Chem. Soc.*, **73**, 1290 (1951).

(0.50 mm). The remaining dark semisolid was added to 300 ml of rapidly stirred pentane at 0° and filtered; the crude solid phenylacetamide (15 g) was discarded.

Distillation of the pentane solubles gave 163 g (62.5%) of a pale yellow mixture of *cis*- and *trans*-2,3-diphenyl-2-heptenenitrile (**4**): bp 152–159° (0.70 mm); $\nu_{max}^{CHCl_3}$ 2225 cm^{-1}; nmr (10% in CCl_4), τ 2.55 and 2.89 (10), 7.07 (1.3, triplet), 7.42 (0.7, triplet), 8.40–8.83 (4, multiplet) and 9.09 (3, triplet, J = 5 cps).

Anal. Calcd for $C_{19}H_{19}N$: C, 87.33; H, 7.33; N, 5.36. Found: C, 87.61; H, 7.03; N, 5.33.

In 15 ml of pentane was dissolved 2.0 g of this mixture of *cis*- and *trans*-2,3-diphenyl-2-heptenenitrile. After cooling at −18° for 1 week, filtration gave 1.59 g of white solid, mp 34–37°. The nitrile had mp 50.5–51.0° after three recrystallizations from pentane at −18°. This solid is presumed to be *trans*-2,3-diphenyl-2-heptenenitrile: nmr (10% in CCl_4), τ 2.89 (10, singlet), 7.07 (2, triplet, J = 8 cps), 8.40–8.83 (4, multiplet), and 9.09 (3, triplet, J = 5 cps).

2,3-Diphenyl-2-heptenamide (**5**).—A mixture of *cis*- and *trans*-2,3-diphenyl-2-heptenenitrile (50.0 g, 0.192 mol), 250 ml of 55% sulfuric acid, and 700 ml of glacial acetic acid were stirred at 100° for 40 hr. The reaction mixture was cooled to 20°; diluted with 2 l. of water, and filtered. The tan solid was triturated in 150 ml of warm 10% sodium hydroxide; this process was repeated until the basic filtrate was colorless. The tan solid was washed with water and dried in a vacuum oven to give 62.3% of a crude mixture of *cis*- and *trans*-2,3-diphenyl-2-heptenamide (**5**). After two recrystallizations from acetonitrile, the white powdery amide had mp 135–136°; $\nu_{max}^{CHCl_3}$ 3550, 3400, and 1685 cm^{-1}; nmr (5% in $CDCl_3$), τ 2.30 and 2.60 (10), 7.12 (1.6, triplet, J = 8 cps), 7.56 (0.4, triplet, J = 7 cps), 8.37–8.89 (4, multiplet) and 9.12 (3, triplet, J = 7 cps).

Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.49; H, 7.68; N, 4.88.

2,3-Diphenyl-2-heptenoic Acid (**6a, b**).—The following procedure was based on a method reported by Sperber, Papa, and Schwenk for the synthesis of tri-*n*-butylacetic acid.[14] Anhydrous hydrogen chloride was bubbled slowly for 30 min into a stirred solution of 27.9 g (0.1000 mol) of 2,3-diphenyl-2-heptenamide in 265 ml of dioxane. Freshly distilled *n*-butylnitrite[15] (28.3 g, 0.275 mol) was added dropwise over a period of 2 hr. After the addition of *n*-butylnitrite was completed, the deep red solution was stirred at room temperature for 17 hr and then on a steam bath for an additional 3 hr. The solvent was removed under reduced pressure, and the residual oil was dissolved in 100 ml of diethyl ether. The ether solution was extracted with three 50-ml portions of 2% sodium hydroxide. The combined basic extracts were acidified wih 6 *N* hydrochloric acid and extracted with diethyl ether. After drying over anhydrous sodium sulfate, the ether was removed under reduced pressure, leaving 16.1 g of crude 2,3-diphenyl-2-heptenoic acid (**6a, b**).

The crude neutral material, predominantly *n*-butyl 2,3-diphenyl-2-heptenoate, was hydrolyzed by refluxing for 4 hr in a solution containing 10 ml of 50% aqueous sodium hydroxide and 40 ml of absolute alcohol. Acidification gave 9.60 g of crude **6a, b**.

The acidic fractions (25.7 g) were combined, triturated in 50 ml of cold pentane (0°), and filtered to give 20.40 g (73.0%) of a mixture of *cis*- and *trans*-2,3-diphenyl-2-heptenoic acid (**6a, b**): mp 115–118° after two recrystallizations from hexane (the two isomers were not separable by fractional recrystallization from hexane); $\nu_{max}^{CHCl_3}$ 1695 cm^{-1}; nmr (10% in CCl_4), τ 2.68 and 2.98 (10, doublet and singlet), 7.22 (1.1, triplet, J = 8 cps), 7.69 (0.9, triplet, J = 7 cps), 8.41–9.33 (7, multiplet).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19; neut equiv, 280. Found: C, 81.31; H, 7.24; neut equiv, 279.

Refluxing a solution of commercial valerophenone (16.2 g, 0.10 mol), phenylmalonic acid (36.0 g, 0.20 mol), piperidine (17.0 g, 0.20 mol), and pyridine (125 ml) under nitrogen for 24 hr yielded no 2,3-diphenyl-2-heptenoic acid.

The reaction of 2,3-diphenyl-2-heptenoic acid with thionyl chloride was run according to the method of Koelsh.[16] A mixture of *cis*- and *trans*-2,3-diphenyl-2-heptenoic acid (2.0 g, 7.1 × 10^{-3} mol) was dissolved in 20 ml of anhydrous carbon tetrachloride. Thionyl chloride (1.28 ml, 1.78 × 10^{-2} mol) was added in one portion and the mixture refluxed for 6 hr. The yellow reaction mixture was allowed to cool to room temperature and poured into a solution of 10 ml of concentrated hydrochloric acid in 125 ml of water. The stirred mixture was boiled on a steam bath for 1 hr and then cooled to 15°. Diethyl ether was added and the layers were separated. The ether solution was extracted with two 50-ml portions of 2% aqueous sodium hydroxide. The neutral solution was dried and solvent was removed under reduced pressure to yield 1.03 g (55.3%) of red 2-phenyl-3-*n*-butylindone (**7**). After two recrystallizations from ethyl acetate–95% ethanol, the 2,4-dinitrophenylhydrazone derivative of the indone had mp 178.0–179.0° (lit.[3] mp 176–178°). An infrared spectrum of the indone was identical with that of an authentic sample.[3]

The combined basic extracts were acidified with 10% hydrochloric acid and extracted with diethyl ether. Evaporation of the dried ether solution yielded 0.69 g (42.5%) of a solid acid, mp 154–155°. After two recrystallizations from hexane, the acid had mp 7157.0–157.5°; $\nu_{max}^{CHCl_3}$ 1695 cm^{-1}; λ_{max} 254 mμ (ϵ 8950) 223 (12,700); nmr (10% in $CDCl_3$), τ 2.53 (1),0, singlet 7.00, (2, triplet, J = 8 cps), 8.34–8.83 (4, multiplet), and 9.12 (3, triplet, J = 6 cps). This isomer of 2,3-diphenyl-2-heptenoic acid has been assigned the *cis* configuration (see Results).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19; neut equiv, 280. Found: C, 81.20; H, 7.28; neut equiv, 279.

Treatment of *cis*-2,3-diphenyl-2-heptenoic acid with thionyl chloride under the above reaction conditions yielded 2-phenyl-3-*n*-butylindone in 25% yield.

Preparation of 1-Bromo-1,2-diphenyl-1-hexene (**3**).—The procedure used is similar to the one reported by Price and Berman for the preparation of *cis*- and *trans*-α-bromostilbenes from the corresponding isomeric α-phenylcinnamic acids.[17] A mixture of *cis*- and *trans*-2,3-diphenyl-2-heptenoic acid (16.10 g, 0.0575 mol) was dissolved in a solution of 2.36 g (0.0625 mol) of sodium hydroxide in 90 ml of water. Bromine (10.0 g, 0.0625 mol) was added dropwise to the rapidly stirring solution at 58–60°. The yellow heterogeneous solution was stirred for 1 hr at 60° before cooling to room temperature and extracting with diethyl ether. The ether solution was extracted twice with 50-ml portions of 2% sodium hydroxide and dried over anhydrous sodium sulfate. After removal of the ether under reduced pressure, the remaining viscous yellow oil (20.37 g) was distilled to give 14.30 g (79.1%) of a mixture of straw-yellow *cis*- and *trans*-1-bromo-1,2-diphenyl-1-hexene (**3**): bp 142–144° (0.80 mm); $n^{27.0}$D 1.5888; nmr (10% in CCl_4), τ 2.63–2.95 (10), 7.19 (1.4, triplet, J = 7 cps), 7.78 (0.6, triplet, J = 6 cps), 8.33–8.89 (4, multiplet), and 9.05 (3, triplet, J = 6 cps).

Anal. Calcd for $C_{18}H_{19}Br$: C, 68.57; H, 6.03. Found: C, 68.18; H, 5.98.

Both *trans*-2,3-diphenyl-2-heptenoic acid and *cis*-2,3-diphenyl-2-heptenoic acid, when treated with bromine under the above conditions, gave an inseparable mixture of the isomeric bromides.

The following procedure was attempted in order to prepare the desired bromide (**3**) directly from valerophenone. To a stirred solution of triphenylphosphine (30.0 g, 0.111 mol), potassium *t*-butoxide (30.6 g, 0.111 mol) and 250 ml of heptane at 0° were added over a period of 30 min to freshly distilled commercial benzal bromide (27.7 g, 0.111 mol) in 200 ml of heptane. The resulting yellow suspension was concentrated to *ca.* 100 ml under reduced pressure. Valerophenone (16.2 g, 0.100 mol) in 100 ml of heptane was added and the mixture heated at 50° for 3 hr. Distillation under reduced pressure gave 15.8 g of valerophenone (97.8% recovered).

***n*-Butyllithium and 1-Bromo-1,2-diphenyl-1-hexene** (**3**). **1. Reaction with *n*-Butyllithium (2 Mol).**—To a stirred solution of a freshly distilled mixture of *cis*- and *trans*-1-bromo-1,2-diphenyl-1-hexene (6.30 g, 0.020 mol) in 8 ml of anhydrous diethyl ether at −78° was added rapidly 0.020 mol of *n*-butyllithium in 14 ml of diethyl ether. The solution was stirred for 15 min at −78° before an additional 0.020 mol of *n*-butyllithium in 14 ml of diethyl ether was added. The yellow solution was allowed to warm to room temperature and stirred for 22 hr. The solution, which contained a small amount of yellow precipitate, was cooled to −50° and decanted onto a large excess of powdered Dry Ice. After standing for 9 hr, the product was acidified with

(14) N. Sperber, D. Papa, and E. Schwenk, *J. Amer. Chem. Soc.*, **70**, 3091 (1948).

(15) W. A. Noyes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 108.

(16) C. F. Koelsh, *J. Amer. Chem. Soc.*, **54**, 2487 (1932).

(17) C. C. Price and J. D. Berman, *ibid.*, **79**, 5474 (1957).

10% hydrochloric acid and the organic layer separated. The ether solution was extracted with two 50-ml portions of 2% sodium hydroxide. The combined basic extracts were acidified with hydrochloric acid and extracted with several portions of ether. After drying over sodium sulfate, the ether was removed under reduced pressure leaving 4.07 g of yellow solid. Trituration with cold (0°) pentane removed 0.74 g of valeric acid. The remaining 3.33 g of white solid, mp 120–121°, was added to 250 ml of boiling hexane. After stirring for 15 min, the hot hexane solution was filtered to yield 0.27 g (5.7%) of insoluble *trans*-2-phenyl-3-(*o*-carboxyphenyl)-2-heptenoic acid, mp 170–175°. Two recrystallizations from acetonitrile afforded white needles, mp 177.5–178.5° (lit.[3] mp 176–177°). A mixture melting point with an authentic sample showed no depression, and the infrared spectra were identical.

The hexane filtrate was concentrated to give 2.96 g (52.9%) of *trans*-2,3-diphenyl-2-heptenoic acid (**6b**), mp 123–124°. Two recrystallizations from hexane produced a pure product: mp 126.5–127.0°; $\nu_{max}^{CHCl_3}$ 1695 and 1625 cm^{-1}; λ_{max} 242 mμ (ε 11,000); nmr (10% in $CDCl_3$), τ 2.41 and 2.50 (10), 6.37 (2, triplet, J = 8 cps), 8.60–9.09 (4, multiplet) and 9.30 (3, triplet, J = 7 cps).

Anal. Calcd for $C_{15}H_{19}COOH$: C, 81.40; H, 7.19; neut equiv, 280. Found: C, 81.08; H, 7.19; neut equiv, 276.

2-Phenyl-3-*n*-butylindone (7) was prepared in 80% yield by refluxing for 6 hr a solution containing 0.50 g (1.78×10^{-3} mol) of *trans*-2,3-diphenyl-2-heptenoic acid, 0.32 ml (4.45×10^{-3} mol) of thionyl chloride, and 5.0 ml of anhydrous carbon tetrachloride.

The neutral layer from the carbonation reaction of **3** with *n*-butyllithium was dried over sodium sulfate. Removal of the ether under reduced pressure left 2.61 g of red oil. The crude neutral oil produced a solid 2,4-dinitrophenylhydrazone derivative which had mp 176–178° after one recrystallization from ethyl acetate–95% ethanol. A mixture melting point with the 2,4-dinitrophenylhydrazone derivative of 2-phenyl-3-*n*-butylindone showed no depression.

2. Reaction with *n*-Butyllithium (3.5 Mol).—To a stirred solution of 0.070 mol of *n*-butyllithium in 39 ml of diethyl ether at −10° was added dropwise 6.03 g (0.020 mol) of a mixture of *cis*- and *trans*-1-bromo-1,2-diphenyl-1-hexene in 6 ml of anhydrous diethyl ether. After allowing the solution to warm to room temperature, an exothermic reaction occurred, followed by the precipitation of a yellow solid. The solution was stirred for 22 hr at room temperature, then cooled to −78° and decanted onto a large excess of powdered Dry Ice. After standing overnight, 250 ml of 5% hydrochloric acid and 200 ml of ether were added to the orange carbonation mixture; the mixture was stirred to dissolve the solids. The ether layer was separated and extracted with two 100-ml portions of 5% sodium hydroxide. The combined basic extracts were acidified with 6 *N* hydrochloric acid and extracted with two 50-ml portions of ether. After drying over sodium sulfate, the ether was removed under reduced pressure, leaving 3.94 g of yellow semisolid. Trituration with 5 ml of cold (0°) pentane removed 1.92 g of valeric acid. There remained 2.02 g (31.2%) of solid *trans*-2-phenyl-3-(*o*-carboxyphenyl)-2-heptenoic acid, mp 170–171°. After two recrystallizations from acetonitrile, the acid had mp 178.5–179.5° (lit.[3] mp 176–177°). A mixture melting point with an authentic sample showed no depression.

The neutral ether solution was dried and the ether removed under reduced pressure. There remained 4.01 g of orange red oil. Distillation yielded 30.5% of 2-phenyl-3-*n*-butylindone, bp 170–180° (0.30 mm) [lit.[3] bp 170° (0.30 mm)]. The indone formed a 2,4-dinitrophenylhydrazone derivative, mp 177–178° after one recrystallization from ethyl acetate–95% ethanol. A mixture melting point with an authentic sample showed no depression.

Decarboxylation of *trans*-2,3-Diphenyl-2-heptenoic Acid (6b).—*trans*-2,3-Diphenyl-2-heptenoic acid (0.50 g, 1.8×10^{-3} mol) was added to a suspension of 0.075 g of copper chromite in 1.0 ml of quinoline. The black mixture was heated at 240° for 10 min. After the addition of diethyl ether and filtration extraction with acid and base there remained 0.42 g (100%) of a dark neutral oil. Vapor phase chromatography (5-ft GE-SE-30; 190°) and nuclear magnetic resonance spectroscopy indicated that this oil was *trans*-α-*n*-butylstilbene:[3] nmr (10% in CCl_4), τ 2.69 (10), 3.36 (1), 7.33 (2), 8.41–8.91 (4), and 9.19 (3).

Decarboxylation of *cis*-2,3-Diphenyl-2-heptenoic Acid (6a).—*cis*-2,3-Diphenyl-2-heptenoic acid (0.50 g) was decarboxylated under the same conditions described above for *trans*-2,3-diphenyl-2-heptenoic acid. A dark oil (0.42 g) was obtained which contained 85% *cis*-α-*n*-butylstilbene[3] and 15% *trans*-α-*n*-butylstilbene as shown by vapor phase chromatography and nuclear magnetic resonance spectroscopy: nmr (10% in CCl_4), τ 2.78 and 3.02 (10), 3.36 (0.15), 3.61 (0.85), 7.53 (2), 8.64 (4), and 9.11 (3).

Lithium Metal and 1-Bromo-1,2-diphenyl-1-hexene (3).—To a suspension of small freshly cut lithium metal pieces (0.29 g, 0.0418 mol) in 10 ml of anhydrous diethyl ether under helium, there was added dropwise over a period of 15 min a mixture of *cis*- and *trans*-1-bromo-1,2-diphenyl-1-hexene (6.0 g, 0.019 mol) in 5 ml of diethyl ether. Occasional external cooling (ice bath) was necessary to maintain the reaction temperature at 31–33°. After stirring at room temperature for 23 hr, the black solution was cooled to −30° and decanted onto a large excess of powdered Dry Ice.

After standing overnight, 100 ml of 6 *N* hydrochloric acid and 50 ml of diethyl ether were added. The ether layer was separated and extracted with two 30-ml portions of 2% sodium hydroxide. The combined basic extracts were acidified and extracted with diethyl ether. The ethereal solution was separated, dried, and the solvent removed under reduced pressure. There remained 4.10 g (77.0%) of *trans*-2,3-diphenyl-2-heptenoic acid, mp 124–125°.

***n*-Butyllithium and *o*-Bromodiphenylacetylene (2). 1. Reaction with *n*-Butyllithium (2 Mol). A. Termination of Reaction by Deuteriolysis.**—To a stirred solution of *o*-bromodiphenylacetylene (2.86 g, 0.015 mol) in 8 ml of anhydrous diethyl ether at −20° was added 0.0150 mol of *n*-butyllithium in 10.5 ml of diethyl ether. After stirring at −20° for 15 min, the yellow solution was warmed to 0°. An additional 0.0150 mol of *n*-butyllithium was added, and the mixture was allowed to warm to room temperature. After stirring for 22 hr the mixture was cooled to 0° and 5 ml of deuterium oxide was added slowly. The solution was stirred at room temperature for 2 hr, followed by the addition of 20 ml of water. The ether layer was separated, dried, and concentrated to yield 2.91 g of yellow oil, which solidified on standing. Two recrystallizations from 95% ethanol gave white needles of deuterated diphenylacetylene in 93% yield, mp 58.5–59.0°.

Anal. Calcd for $C_{14}H_9D$: D, 10.0 atom %. Found: D, 9.10 atom %.

Glpc indicated no *trans*-α-*n*-butylstilbene.

B. Termination of Reaction by Carbonation.—To a solution of *o*-bromodiphenylacetylene (10.3 g, 0.040 mol) in 15 ml of anhydrous diethyl ether at −78° was added 0.040 mol of *n*-butyllithium in 28 ml of diethyl ether. After stirring at −78° for 15 min, the solution was warmed to room temperature. An additional 0.040 mol of *n*-butyllithium in 28 ml of diethyl ether was added, and the yellow reaction mixture stirred for 22 hr. After cooling to −78°, the reaction mixture was decanted onto a large excess of powdered Dry Ice and let stand overnight. The product was acidified with 10% hydrochloric acid and the ether layer separated. The ethereal solution was extracted with two 100-ml portions of 2% aqueous sodium hydroxide. The combined basic extracts were acidified and extracted with ether. After drying over sodium sulfate, the ether was removed under reduced pressure, leaving 4.64 g (52.3%) of crude *o*-carboxydiphenylacetylene, mp 127–129°. Two recrystallizations from heptane afforded pure product: mp 128.0–129.0° (lit.[18] mp 126° from acetic acid–heptane).

The neutral ether solution from the basic extractions was dried and the ether removed under reduced pressure. There remained 4.60 g of a dark red oil. Elution chromatography gave 46% by weight of diphenylacetylene (over-all yield, 30%). Vapor phase chromatography of the crude neutral product gave four peaks corresponding to *n*-butyl bromide, *n*-octane, diphenylacetylene, and *o*-bromodiphenylacetylene.

2. Reaction with *n*-Butyllithium (3.5 Mol).—To a stirred ethereal solution of 22.5 ml of 1.96 *M* (0.0441 mol) of *n*-butyllithium at −20° was added rapidly 3.23 g (0.0126 mol) of *o*-bromodiphenylacetylene in 5 ml of anhydrous diethyl ether. A yellow precipitate formed after 1 min of stirring. The solution was stirred for an additional 15 min at −20° and then allowed to warm to room temperature. After stirring for 22 hr, the yellow mixture was cooled to −40°, and 20 ml of water was added

(18) R. L. Letsinger, E. N. Offedahl, and J. R. Nazy, *J. Amer. Chem. Soc.*, **87**, 742 (1965).

slowly. The ether solution was separated, dried, and concentrated to yield 2.57 g of yellow oil. Heating the oil to 100° under reduced pressure (35 mm) removed 0.80 g of *n*-butyl bromide. The residual oil, which solidified on standing, was dissolved in 5 ml of pentane and cooled to −18° for 3 hr. Filtration gave white needles of diphenylacetylene (61.5%), mp 57–58°.

Vapor phase chromatography (2-ft GE-SE-30; 190°) showed that the crude product contained by weight 59% diphenylacetylene, 3.3% of *trans*-α-*n*-butylstilbene, 1.2% starting material, 28.4% *n*-butyl bromide, 5.3% *n*-octane, and 3.4% *n*-butyl alcohol. This corresponds to an over-all yield of 89.3% diphenylacetylene, 3.8% *trans*-α-*n*-butylstilbene, and 1.2% *o*-bromodiphenylacetylene.

Registry No.—Diphenylacetylene, 501-65-5; *cis* **3**, 16897-91-9; *trans* **3**, 16915-88-1; *cis* **4**, 16897-92-0; *trans* **4**, 16915-89-2; *cis* **5**, 16897-93-1; *trans* **5**, 16897-94-2; **6a**, 16897-95-3; **6b**, 16897-96-4; α-(*o*-bromophenyl)acetophenone, 16897-97-5; 2,4-dinitrophenylhydrazone of α-(*o*-bromophenyl)acetophenone, 16915-90-5; deuterated diphenylacetylene, 16897-98-6.

Small-Ring Epoxides. II. 2,2,6,6,7,7-Hexamethyl-1,5-dioxadispiro[2.0.2.1]heptane[1a]

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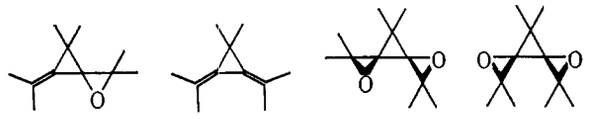
2,2,6,6,7,7-Hexamethyl-1,5-dioxadispiro[2.0.2.1]heptane (**3**) has been prepared by epoxidation of its dimethylenecyclopropane precursor **2**. Thermolysis of the diepoxide gives two ketones, 2,2,5,5,6,6-hexamethyl-4-oxo-1-oxaspirohexane (**5**) and a compound tentatively assigned as 3,5,5-trimethyl-2-(1-hydroxy-1-methylethyl)cyclopent-2-enone (**6**). Acid-catalyzed rearrangement yields 2,2,4,4,5,5-hexamethylcyclopentane-1,3-dione (**14**) and 3,3,4,4,5,5-hexamethylcyclopentane-1,2-dione (**15**), probably by way of **5** as an intermediate. The rearrangement of **3** with diethylamide produces 2,5-dimethyl-4-isopropylidene-5-hydroxyhex-2-en-3-one (**17**). The mechanistic details of these transformations are discussed.

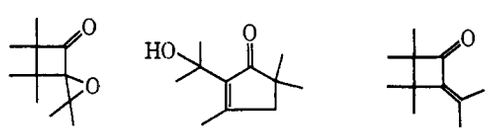
We have recently reported on the preparation and some of the reactions of the interesting oxaspiropentane derivative **1**.[2] Reaction of the precursor dimethylenecyclopropane **2** with an excess of peracetic acid leads, as expected, to the diepoxidation product, 2,2,6,6,7,7-hexamethyl-1,5-dioxadispiro[2.0.2.1]heptane (**3**), in good yield. The present paper is concerned with some of the properties of diepoxide **3**.

The assignment of the *anti* structure **3** as opposed to *syn* structure **4** is based on a 100-MHz spectrum of the homogeneous epoxidation product which shows three equivalent sharp methyl peaks rather than the four types of methyls expected for **4**. The predominance of epoxide **3** can probably be attributed to unfavorable dipole–dipole interactions in the transitions state leading to the *syn* diepoxide.[3]



1 **2** **3** **4**

Pyrolysis of **3** in a vacuum pyrolysis system at 400° gave two major compounds. The predominant product (75%) was identified as 2,2,5,5,6,6-hexamethyl-4-oxo-1-oxaspirohexane (**5**), and the minor product (13%) is tentatively assigned as 3,5,5-trimethyl-2-(1-hydroxy-1-methylethyl)cyclopent-2-enone (**6**).



5 **6** **7**

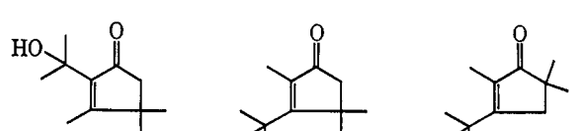
(1) (a) Supported by Research Grant GP-6610 from the National Science Foundation. (b) National Institutes of Health Predoctoral Fellow 1966–1968.

(2) J. K. Crandall and D. R. Paulson, *J. Org. Chem.*, **33**, 991 (1968).

(3) See, for example, N. S. Crossley, A. C. Darby, H. B. Henbest, J. J. McCullough, B. Nicholls, and M. F. Stewart, *Tetrahedron Lett.*, 398 (1961), and references cited therein.

Compound **5** displays a strong band at 5.63 μ indicative of a cyclobutanone carbonyl,[4] and its 100-MHz nmr spectrum shows six different methyl groups. Confirmation of structure **5** was effected by alternate preparation from the *m*-chloroperbenzoic acid epoxidation of ketone **7**.[2]

The structure of compound **6** is assigned on the basis of its spectroscopic properties. The infrared spectrum of **6** displays carbonyl absorption (5.95 μ), a conjugated double bond (6.13 μ), and an alcohol group (2.92 μ). These data, along with ultraviolet absorption at 232 mμ, are in agreement with other examples of 2-cyclopentenones.[5] The nmr spectrum of **6** shows a two-proton quartet (J = 1.0 Hz) at τ 7.68 and a three-proton triplet (J = 1.0 Hz) at 7.83. The chemical shift of the olefinic methyl is as expected for a methyl β to the carbonyl group.[6] Possible alternate structures **8**, **9**, and **10** are therefore not compatible with the observed coupling patterns and chemical shifts.[7] The remainder of the spectrum shows six-proton singlets



8 **9** **10**

(4) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, p 141.

(5) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," The Macmillan Co., New York, N. Y., 1966, p 66.

(6) The methyl resonance of 3-methylcyclopent-2-enone appears at τ 7.9.

(7) The methyl group in the 2 position of i appears at τ 8.30 while the methyl group in the 2 position of ii appears at τ 8.28: W. E. Doering, M. R. Wilcott, and M. Jones, *J. Amer. Chem. Soc.*, **84**, 1224 (1962).

i ii