[2.2]Metacyclophane-4,14-dicarboxylic Acid (**9**). **A.**—A mixture of 250 mg (1.1 mmol) of **4**, 900 mg (5.7 mmol) of potassium permanganate, and 10 ml of water containing 1 ml of sulfuric acid was heated under reflux for 1 hr. The reflux was further continued for 30 min by adding additional 500 mg of potassium permanganate. After being made acidic with hydrochloric acid, the mixture was extracted continuously with benzene. A small amount of **9**, which did not melt below 300°, was obtained by extraction with a sodium hydroxde solution, $\nu_{\max}^{\mathrm{KBr}}$ 1680 cm^{-1}.

B.—To a solution of 200 mg (0.76 mmol) of **10** in 7.5 ml of acetone, 8 ml of 3.2% potassium permanganate solution was added with stirring during the course of 1 hr at 50–80°. After filtration, the filtrate was made acidic and 192 mg (86% yield) of a crystalline material was collected. It was recrystallized from acetic acid as colorless plates: mp >300°; $\lambda_{\max}^{\mathrm{EtOH}}$ 250 mμ (sh), 286 (ϵ 2330), and 355 (43); $\nu_{\max}^{\mathrm{KBr}}$ 1680 cm^{-1}.

Registry No.—**1,** 2319-97-3; **4,** 16620-99-8; **6,** 10125-36-7; **7,** 16621-01-5; **8,** 16621-02-6; **9,** 16621-03-7; **10,** 16621-04-8; **12,** 16621-05-9.

Acenaphthene Chemistry. IX.[1,2] The Synthesis and Epoxidation of 2a,3,4,5-Tetrahydroacenaphthylene

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2a,3,4,5-Tetrahydroacenaphthylene (I) was synthesized. This compound, when treated with *m*-chloroperbenzoic acid, formed *trans*-1-(2-hydroxy-2a,3,4,5-tetrahydroacenaphthyl) *m*-chlorobenzoate, *via* the intermediate epoxide. Hydrolysis of the ester formed *trans*-1,2-dihydroxy-2a,3,4,5-tetrahydroacenaphthene.

Only two attempts to epoxidize an acenaphthylene are described in the literature. In 1939, Wittig and Henkel[4] treated 1,2-diphenylacenaphthylene with perbenzoic acid in chloroform but were only able to isolate 1,8-dibenzoylnaphthalene. Bartlett and Brown[5] found the reaction to lead to the formation of a complex mixture from which they isolated 1,2-diphenylacenaphthylene glycol, 1,2-diphenyl-1,2-dichloroacenaphthene, 1,1-diphenylacenaphthenone, and 1,8-dibenzoylnaphthalene.

It is possible that, in acenaphthylene, delocalization of the electrons of the double bond is sufficient to reduce its nucleophilic character such that the molecule is sensitive to gross oxidative effects such as radical attack, but insensitive toward less electrophilic systems. This is reasonable in view of the fact that Bartlett and Brown found, among their products, 1,2-dichloro-1,2-diphenylacenaphthene which could arise from radical breakdown of the solvent chloroform.

We treated acenaphthylene with the nitrile–hydrogen peroxide system described by Payne,[6] but the starting material was recovered nearly quantitatively. 1,2-Diphenylacenaphthylene was similarly unreactive.

Base-catalyzed elimination of HX from *trans* halohydrins offers another possible route to epoxides. Even though the halohydrin formed by addition of hypohalite to acenaphthylene could not assume a *trans* coplanar arrangement, since the bridge substituents are in an eclipsed conformation, the possibility that HX elimination would proceed to give an epoxide could not be excluded. The treatment of acenaphthylene with a solution of "hypochlorous acid"[7] resulted in no change.

The properties of acenaphthylene[8] suggest that the double bond is not epoxidized since it is part of an essentially aromatic system. The 2a,3,4,5-tetrahydroacenaphthylene ring system, however, resembles the readily epoxidized indene and thus we visualized a synthesis of acenaphthylene oxide through its tetrahydro derivative.

Only one example of a 2a,3,4,5-tetrahydroacenaphthene ring system is reported in the literature. Buchta and Maar[9] described the synthesis of the 1,2-diphenyl-2a,3,4,5-tetrahydroacenaphthylene (II). We find that, when this compound was treated with benzonitrile–50% hydrogen peroxide, buffered with solid potassium bicarbonate, for 142 hr, 90% of the starting material was recovered. When II was treated with *m*-chloroperbenzoic acid, a yellowish oil was recovered. Chromatography of this oil gave a yellow glass. An infrared (ir) spectrum of the glass indicated that the tetrahydro ring was still intact, but no chemical entity could be isolated.

Attention was then directed toward the synthesis of an unsubstituted tetrahydroacenaphthylene. Utilizing a procedure similar to that of Buchta and Maar, we prepared 1,2,3,4-tetrahydronaphthyl-1-acetic acid (III) by the condensation of α-tetryl chloride and diethyl sodiomalonate, followed by hydrolysis and decarboxylation. Ring closure was effected in high yield by briefly heating the acid in polyphosphoric acid. The resulting 1-oxo-2a,3,4,5-tetrahydroacenaphthene (IV) was reduced with sodium borohydride to the alcohol V and then treated with phosphorous tribromide to form 1-bromo-2a,3,4,5-tetrahydroacenaphthene (VI). The bromide was found to be unstable as a marked discoloration appeared after 3 days at room temperature.

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[1] Paper VIII: H. J. Richter, R. L. Dressler, and S. F. Silver, *J. Org. Chem.*, **30**, 4078 (1965).

[2] This work was supported by U. S. Public Health Service Research Grant CA 02997-8,9 from the National Cancer Institute, National Institutes of Health.

[3] Taken from a portion of the dissertation submitted to the Graduate School of the University of Colorado in partial fulfillment of the requirements for the Ph.D. degree, 1966.

[4] G. Wittig and K. Henkel, *Ann.*, **542**, 130 (1939).

[5] P. D. Bartlett and R. F. Brown, *J. Amer. Chem. Soc.*, **62**, 2927 (1940).

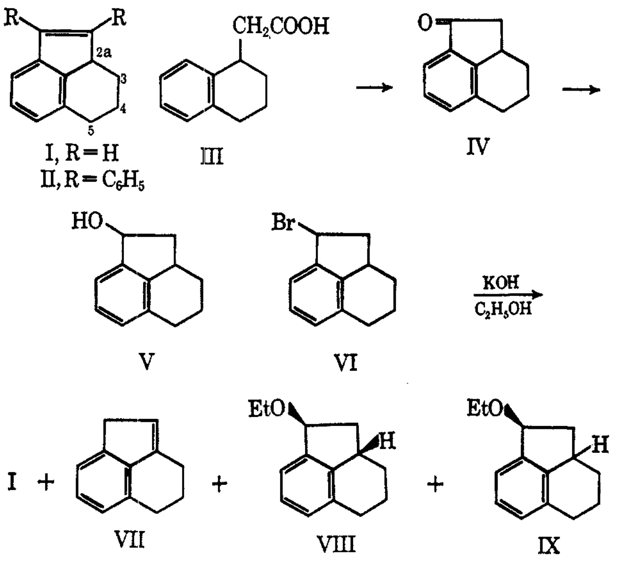
[6] G. B. Payne, P. H. Deming, and P. H. Williams, *J. Org. Chem.*, **26**, 659 (1961); G. B. Payne, *Tetrahedron*, **18**, 763 (1962).

[7] G. H. Coleman and H. J. Johnstone, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 158.

[8] R. H. Boyd, R. L. Christensen, and R. Pua, *J. Amer. Chem. Soc.*, **87**, 3554 (1965).

[9] E. Buchta and H. Maar, *Ber.*, **95**, 1826 (1962); E. Buchta and H. Maar, *Ann.*, **674**, 129 (1964).

Base-catalyzed dehydrohalogenation in refluxing alcoholic potassium hydroxide and extraction with benzene yielded a residue which distilled between 94 and 110° at 0.8-mm pressure. A vpc analysis of the distillate indicated four components in approximately equal amounts. The first two components were shown to be the isomeric hydrocarbons I and VII. The latter two components were separated as one fraction by preparative vpc. An elemental analysis required $C_{14}H_{18}O$. The nmr spectrum of the mixture was very complex but was consistent with $C_{14}H_{18}O$ and the isomeric ether structures VIII and IX.

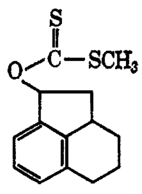


When a solution of the bromide VI was refluxed in pyridine, only one product could be isolated in low yield. An elemental analysis indicated the formula $C_{12}H_{12}$. An nmr spectrum of the compound exhibited a quintet at δ 5.82 (J = 2.0 cps, 1 H) and a quartet at 3.15 (J = 2.0 cps, 2 H). Over-all integration was consistent with the formula $C_{12}H_{12}$. Structure VII, 3,4-trimethyleneindene, provides the most reasonable interpretation of the observed splitting patterns and the proton integration values. A pyrolytic method such as xanthate pyrolysis appeared attractive.

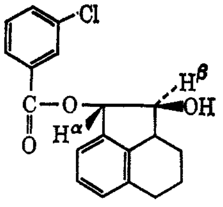
The sodium salt of V was prepared by refluxing a solution of V in ether with powdered sodium. The xanthate X was prepared by the addition of carbon disulfide followed by methyl iodide. It was not isolated but decomposed directly to give a pale yellow oil which distilled at 59–61° at 0.18-mm pressure. The nmr spectrum was characteristic of compound I. Vinyl proton absorption occurred as an AB quartet at δ 6.57 (J = 5 cps), that had been split into an octet (J = 2 cps) by the proton at the 2a position. Over-all integration of the proton absorption peaks was consistent with the formula $C_{12}H_{12}$. A great deal of difficulty was experienced in removing small amounts of sulfur from the distillate. The normal procedure involving storage over sodium wire could not be used because of the acidity of the hydrocarbon. When a solution of the xanthate decomposition product in ether was vigorously stirred with mercury, all but trace amounts of sulfur were removed. Satisfactory elemental analysis could not be obtained owing in part to residual sulfur but chiefly because the material readily decomposed at room temperature. Both olefins I and VII were readily convertible into acenaphthylene by the action of 2,3-dichloro-5,6-dicyanobenzoquinone. When a mixture of 2a,3,4,5-tetrahydroacenaphthylene (I) and tetraphenylcyclopentadienone was strongly heated, an adduct was formed.

When a solution of I in chloroform was treated with *m*-chloroperbenzoic acid at room temperature, a yellow oil was formed. Trituration with petroleum ether produced a white solid which was purified by chromatography on alumina to afford white needles melting at 160.5–162.5°. The substance gave a positive test for halogen and elemental analysis required $C_{19}H_{17}O_3Cl$. Its ir spectrum exhibited hydroxyl and doublet carbonyl absorption. The position of the ester moiety was established by a comparison of nmr chemical shifts[10] observed for the benzylic proton (H^{α}) in XI (δ 5.97), the diol XII (4.64), benzyl benzoate (5.34),[11a] and benzyl alcohol (4.58).[11b]

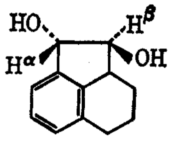
The similarity in the chemical shifts of H^{α} in both XI and benzyl benzoate, and again the correspondence in the hydrolysis products, XII and benzyl alcohol, allow the conclusion that the ester moiety exists at position 1 as shown in XI. The additional downfield shift in both XI and XII can be attributed to both ring strain and a shielding effect from the vicinal hydroxyl group.



X



XI



XII

Hydrolysis of the hydroxy ester XI gave colorless needles of *trans*-1,2-dihydroxy-2a,3,4,5-tetrahydroacenaphthene (XII), mp 142–143.5°. A solution of 18 mg of XII in 15 ml of carbon tetrachloride exhibited a single peak at 3710 cm^{-1}. Since intramolecular hydrogen-bonding peaks are present even in very dilute solutions of *cis*-diols the possibility of a *cis*-diol is eliminated since no intramolecular hydrogen-bonding peak was observed.

The intermediacy of an epoxide is confirmed since only a *trans*-diol could be isolated upon hydrolysis of the hydroxy ester. Since hydrolysis of esters with a strong base results in acyl–oxygen cleavage, the configuration about the carbon bearing the ester moiety is retained and thus the configuration of XII is *trans*. Therefore an epoxide is an intermediate in the hydroxybenzoylation of 2a,3,4,5-tetrahydroacenaphthene.

Experimental Section

All melting points were taken in capillary tubes on a Thomas-Hoover apparatus. The ir spectra were recorded by a Beckman

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[10] Because of the lack of solubility of the compounds XI and XII in solvents amenable to nmr, no discrete splitting patterns were observed.

[11] (a) Varian Nmr Spectra Catalog, Varian Associates, Palo Alto, Calif., no. 627; (b) no. 181.

Model IR-5 spectrophotometer and the details are given in ref 3. The nmr spectra were determined on a Varian A-60 spectrometer.

1-Keto-2a,3,4,5-tetrahydroacenaphthene (IV).—1-(Diethylmalonyl)-1,2,3,4-tetrahydronaphthalene[12] (186.7 g) was hydrolyzed on being refluxed with a solution of 160 g of potassium hydroxide in 1 l. of methanol for 1 hr. The separated solid was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The combined solids from above were dissolved in 1 l. of water and the solution was filtered and extracted with ether to remove unreacted ester. The aqueous layer was heated on a steam bath to remove dissolved ether, cooled to room temperature, and acidified with 15% hydrochloric acid with vigorous stirring. The precipitated solid was extracted with ether and, upon removal of the ether *in vacuo*, 165 g of solid material was obtained.

The solid material was not purified but was heated in an oil bath at 200–220° until gas evolution stopped. There was obtained 114 g of crude 1,2,3,4-tetrahydronaphthyl-1-acetic acid (III).

The acid III was heated with stirring on a steam bath with 780 g of polyphosphoric acid to an internal temperature of 85°. The dark green mixture was hydrolyzed with 2 l. of ice water, the separated solid was dissolved in benzene, and the aqueous portion was extracted four times with benzene. The combined benzene extracts were washed successively with water, 5% sodium hydroxide solution, water, 3% acetic acid solution, 10% sodium bicarbonate solution, and water. The benzene extracts were dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* yielded 88.0 g of crude solid (91% of the theoretical yield). Crystallization from ethanol–water gave white crystals, mp 101.5–103.5° (lit.[13] mp 100–101.5°).

1-Hydroxy-2a,3,4,5-tetrahydroacenaphthene (V).—To a cooled solution of 88.0 g of 1-keto-2a,3,4,5-tetrahydroacenaphthene in 900 ml of 95% ethanol, 10.0 g of sodium borohydride was added portionwise with good stirring. The reaction mixture was allowed to stand overnight. The heterogeneous mixture was then heated to boiling, water was added to incipient cloudiness, and the mixture was allowed to cool to room temperature. The solid that separated was removed by filtration and crystallized from 2 l. of Skellysolve B (bp 60–70°) to give 83 g (93%) of white crytals, mp 97.5–98.5°. A portion was sublimed *in vacuo* at 110° and used as an analytical sample. An nmr spectrum of the alcohol in acetonitrile exhibited a singlet at δ 7.32, a complex multiplet between 7.66 and 6.82, a multiplet centered at 5.17, and a doublet at 3.35.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.63; H, 8.00.

1-Bromo-2a,3,4,5-tetrahydroacenaphthene (VI).—To a solution of 6.0 g of V in 50 ml of anhydrous ether, cooled in an ice bath, was added 1.23 ml of phosphorous tribromide. The mixture was allowed to stand for 0.5 hr. The mixture was then hydrolyzed with ice–water, the layers were separated, and the benzene layer was washed successively with water, 10% sodium bicarbonate solution, and water. The benzene solution was dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* resulted in a crude solid which was digested with 20 ml of Skellysolve B and filtered, yield 6.95 g (86%) of white crystals, mp 73–75°. Recrystallization from Skellysolve B gave white crystals, mp 77.5–79.5°.

Anal. Calcd for $C_{12}H_{13}Br$: C, 60.75; H, 5.53. Found: C, 60.83; H, 5.51.

Formation of the Olefin. Method A. Treatment of 1-Bromo-2a,3,4,5-tetrahydroacenaphthene (VI) with Ethanolic Potassium Hydroxide.—Thirty grams of VI was refluxed for 3 hr with 250 ml of a 10% ethanolic potassium hydroxide solution. The solution was evaporated to semidryness *in vacuo* and then diluted with 500 ml of cold water. The resulting heterogeneous mixture was extracted twice with benzene and the benzene extracts were washed with dilute hydrochloric acid solution and water. The benzene extracts were dried over anhydrous magnesium sulfate and the benzene was removed *in vacuo*. The residue was distilled from an oil bath at 130–145°, bp 94–110° (0.64–0.80 mm). Vapor phase chromatography of a dilute acetone solution of the distillate on an SE-30 column at 133° and a flow rate of 30 ml/min showed the distillate to be composed of four components with retentions of 4.09, 5.07, 10.9, and 12.9 in. (chart speed, 1 in./min). The first two components were identified as the 1,7- and 3,4-trimethylenindene by comparison of the nmr spectra and vpc retention times of independently prepared samples. The latter two components were separated as one fraction and were composed of the isomeric 1-ethoxy-2a,3,4,5-tetrahydroacenaphthenes (VIII and IX). An nmr spectrum of the mixture of ethers was quite complex. It showed aromatic absorptions centered at δ 6.50, a quartet at 4.78 ($J = 3.7$ cps), a doublet at 4.50 ($J = 5$ cps), a quintet at 3.45 ($J = 7$ cps), and a complex pattern of peaks between 2.7 and 0.9. Integration of the proton absorption peaks was consistent with $C_{14}H_{18}O$.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.87; H, 8.63.

Method B. Treatment of 1-Bromo-2a,3,4,5-tetrahydroacenaphthene (VI) with Pyridine.—A solution of 11.9 g of VI in 100 ml of pyridine was refluxed for 20 hr. Three-fourths of the pyridine was removed *in vacuo* and the remaining pyridine solution was poured into 250 ml of cold water and extracted twice with 125-ml portions of benzene. The benzene extracts were washed three times with 200 ml of water, twice with 10% acetic acid solution, and twice with 200 ml of water. The benzene solution was dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo*. The dark oil remaining was distilled at 62–63° and 0.2-mm pressure (oil bath at 90–95°), to give 1.53 g (20%) of 1,7-trimethylenindene, a white semisolid, as the only product. The nmr spectrum showed aromatic absorptions centered at δ 6.99 (3 H), a quintet at 5.82 (1 H, $J = 2$ cps), a quartet at 3.15 (2 H, $J = 2$ cps), a multiplet at 2.60 (4 H), and a multiplet centered at 1.80 (2 H).

Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.82.

Method C. Xanthate Pyrolysis.—All apparatus was dried in an oven overnight at 110°. In a 500-ml, three-necked Morton flask with a Herschberg stirrer, a dropping funnel, and a reflux condenser (protected with calcium chloride drying tubes) was placed a solution of 13.0 g of 1-hydroxy-2a,3,4,5-tetrahydroacenaphthene in 200 ml of anhydrous ether. To this solution 1.75 g of powdered sodium was added and the mixture was stirred vigorously at room temperature for 42 hr. Carbon disulfide (5.0 ml) was then added portionwise and the yellow solution (containing a small amount of unreacted sodium) was stirred at room temperature for 3 hr. Methyl iodide (9.8 ml) was then added and the reaction mixture was allowed to stir overnight. More methyl iodide (4 ml) was then added and stirring was continued for 1 hr. The insoluble material was filtered off and washed well with ether and the ether was removed by distillation from a steam bath. The residue from the ether solution was placed in 50-ml flask equipped with a Dean–Stark trap and reflux condenser and heated on a steam bath at a pressure of 0.30 mm for 2 hr until no gas was evolved as judged by an external bubbler. The residue distilled at 59–61° at 0.18 mm to give 7.45 g (64%) of a pale yellow oil.

An nmr spectrum exhibited an AB quartet centered at δ 6.57 ($J = 5$ cps) that had been split into an octet ($J = 2$ cps). Integration of the proton absorption peaks was consistent with $C_{12}H_{12}$.

An unsatisfactory elemental analysis was obtained and believed to be due to the presence of trace amounts of sulfur and to the instability of the product.

The olefins obtained by methods B and C were dehydrogenated with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). Thus, a solution of 0.5 g of 2a,3,4,5-tetrahydroacenaphthylene prepared by method A dissolved in 25 ml of anhydrous benzene was refluzed for 0.5 hr with 0.8 g of DDQ after which an additional 1.2 g of DDQ was added and refluxing was continued for 2 hr. The dark green solution was cooled to room temperature, diluted (50 ml of Skellysolve B), and filtered. The filtrate was chromatographed on alumina. Elution with Skellysolve B and removal of the solvent *in vacuo* gave 0.25 g of acenaphthylene, mp 90–91° after two crystallizations from ethanol–water. There was no depression of a mixture melting point with an authentic sample.

1,7-Trimethylenindene, obtained by treating 1-bromo-2a,3,-4,5-tetrahydroacenaphthene with pyridine (method B), was also dehydrogenated with DDQ to give acenaphthylene.

Tetracyclone Adduct of 2a,3,4,5-Tetrahydroacenaphthalene.—Tetraphenylcyclopentadienone (0.5 g) and 0.5 g of 2a,3,4,5-tetrahydroacenaphthylene contained in a test tube were heated with a microburner to an internal temperature of 300°. The reddish mass was cooled, treated with a small amount of ethanol,

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[12] M. Protiva, J. O. Jilek, Z. J. Vejdelek, and P. Finglova, *Chem. Listy*, **47**, 584 (1953).

[13] W. S. Johnson and H. J. Glenn, *J. Amer. Chem. Soc.*, **71**, 1087 (1949).

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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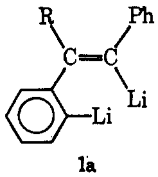
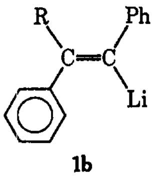
Received March 6, 1968

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.

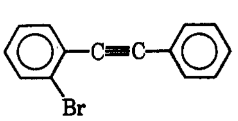
In previous papers[1] reactions of organolithium compounds and acetylenes have been described. The reaction of diphenylacetylene (DPA) with an excess of primary organolithium compounds yields deuterolysis or carbonation products arising very largely from the dilithiated intermediate **1a**. Only very 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

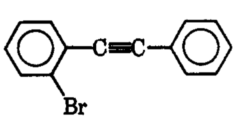


1b

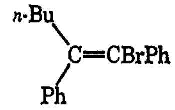


1c

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



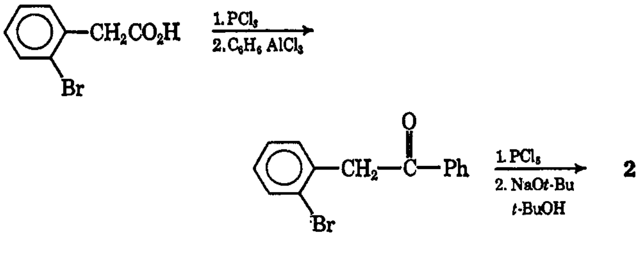
2



3

Results

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



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[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).