component was shown by infrared and other physical properties to be 1,3,5,7-nonatetraene, and the major component to be 1,3,6,8-nonatetraene. The pure compound possessed the following physical properties: b.p. 52° (20 mm.), n^{20}_{D} 1.5417, d^{20}_{4} 0.796. Comparative ultraviolet data for these compounds are shown in Table I and Figure 1.

Synthesis of 2-(bromomethyl)butadiene was accomplished in 88% yield according to the procedure of Krug and Yen.[11]

Synthesis of 3,6-Dimethylene-1,7-octadiene.—Magnesium (3.5 g., 0.15 g.-atom, freshly ground under ether) and 20 ml. of ethyl ether were added to a three-necked flask equipped with stirrer, reflux condenser, and constant-pressure addition funnel. The flask was flushed with nitrogen. About 30 ml. of a solution of 30.7 g. (0.21 mole) of 2-(bromomethyl)butadiene in 200 ml. of ethyl ether was added; the mixture was heated to reflux for 15 min. The remainder of the solution was added over a 1.5-hr. period at room temperature. The ether refluxed gently during addition. It was stirred an additional 0.5 hr. The flask was cooled in ice and 27 g. (0.5 mole) of ammonium chloride in 200 ml. of water was added slowly. This was stirred 30 min., and then the ether layer was separated, washed with water, and dried over magnesium sulfate.

The ether layer was distilled through a 25-cm. stainless steel packed vacuum-jacketed column. The residue was distilled through a 50-cm. spinning-band column, yielding 8.8 g. (62%), b.p. 64–65° (22 mm.), n^{20}_{D} 1.4934, d^{20}_{4} 0.7898. Infrared data showed the following absorptions: 3100 (m), 2950 (m), 1790 (m), 1630 (m), 1590 (s), 1460 (m), 1440 (m), 1420 (m), 1390 (m), 1380 (m), 1320 (w), and 1290 (w) cm.$^{-1}$. Ultraviolet data are found in Table I.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.5; H, 10.5. Found: C, 89.72, 89.27; H, 10.43, 10.58.

Synthesis of 3-Methyleneoctene.—Magnesium (4.5 g., 0.19 g.-atom), a small crystal of iodine, and 20 ml. of ethyl ether were placed in a three-necked flask equipped with stirrer, reflux condenser, and a constant-pressure addition funnel. The flask was flushed with nitrogen. A solution (10 ml.) of 27.4 g. (0.2 mole) of *n*-butyl bromide in 180 ml. of ethyl ether was added, and the reaction started easily. The remainder was added over a period of 30 min. at room temperature. Then 14.8 g. (0.1 mole) of 2-(bromomethyl)butadiene in 30 ml. of ethyl ether was added slowly while the flask was cooled in ice water. Ammonium chloride (0.2 mole) in 150 ml. of water was added slowly while the flask was still being cooled. The ether layer was washed with water and dried over magnesium sulfate. The ether was distilled through a 25-cm. stainless steel packed column, and the residue was distilled through a spinning-band column yielding 4.6 g. (37%), b.p. 60° (38 mm.). The infrared spectrum showed the following absorptions: 3100 (m), 2940 (s), 2880 (s), 1790 (w), 1630 (w), 1580 (s), 1470 (m), 1380 (m), 1220 (w), 1110 (w), 1030 (w), 990 (s), 893 (s), 760 (s), and 730 (w) cm.$^{-1}$. Ultraviolet data are found in Table I.

Anal. Calcd. for C_9H_{16}: C, 87.0; H, 13.0. Found: C, 87.16; H, 13.17.

A Direct Method for the Construction of Benzene Rings

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Reaction of 1,4-diacetoxybutadiene with dienophiles at elevated temperatures yields, in many cases, aromatic products resulting from elimination of acetic acid from the first-formed Diels–Alder adducts. This reaction provides a direct synthesis of benzene rings, especially useful in the synthesis of unsymmetrical biphenyls. Dienophiles used successfully include quinones, β-nitrostyrenes, chalcones, and acetylenes. The reaction of acetylenic dienophiles with 1-acetoxybutadiene also affords aromatic products. The adduct of 1,4-diacetoxybutadiene and benzonorbornadiene did not aromatize below temperatures of 450°, and then only with rearrangement, to yield dibenzocycloheptatriene.

Practical methods for the construction of benzene rings, especially on the base of an existing molecule, are rare and have not played any significant role in the synthesis of complex molecules.

We wish to report a simple and direct method of assembling a benzene ring from a dienophilic double bond, a method which makes possible the synthesis of a variety of aromatic compounds and which is particularly valuable for the preparation of unsymmetrical biphenyls. The synthesis is based on the addition of *trans,trans*-1,4-diacetoxybutadiene (I) to dienophiles. Diels–Alder adducts of structure II might be expected to aromatize readily by thermal elimination of acetic acid; indeed, several observations of such aromatizations have been noted.[2] We have found that heating various dienophiles with I, generally at temperatures of 110–120° for several days, often leads directly to aromatized products[3] (III). Table I lists representative examples.

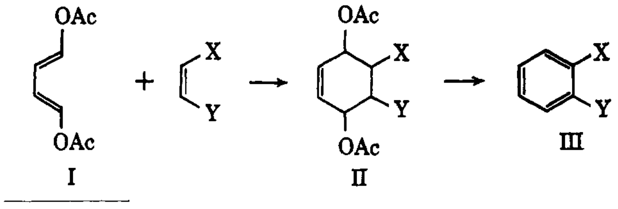

TABLE I

AROMATIC PRODUCTS FROM THE REACTION OF 1,4-DIACETOXYBUTADIENE WITH DIENOPHILES

Dienophile	Product	Yield, %
p-Benzoquinone	1,4-Naphthoquinone	73
	9,10-Anthraquinone	8
1,4-Naphthoquinone	9,10-Anthraquinone	45
β-Nitrostyrene	2-Nitrobiphenyl	20
3,4-Methylenedioxy-β-nitrostyrene	3,4-Methylenedioxy-2′-nitrobiphenyl	45
3,4-Dimethoxy-β-nitrostyrene	3,4-Dimethoxy-2′-nitrobiphenyl	26
Benzalacetophenone	2-Benzoylbiphenyl[a]	24
Benzonorbornadiene	1,2,5,6-Dibenzocycloheptatriene[a]	31
Dimethyl acetylenedicarboxylate	Dimethyl 3-acetoxyphthalate[b]	49
Phenylpropiolic acid	2-Phenyl-3-acetoxybenzoic acid	28

[a] The primary Diels–Alder adduct was isolated in this case and separately aromatized by heating at 575–600°. [b] Isolated as 3-hydroxyphthalic acid.

Quinones.—Quinones react readily with I, as had been noted previously for juglone.[2b] *p*-Benzoquinone, heated with 1 molar equiv. of I, gave a 73% yield of

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[1] Alfred P. Sloan Foundation Research Fellow.

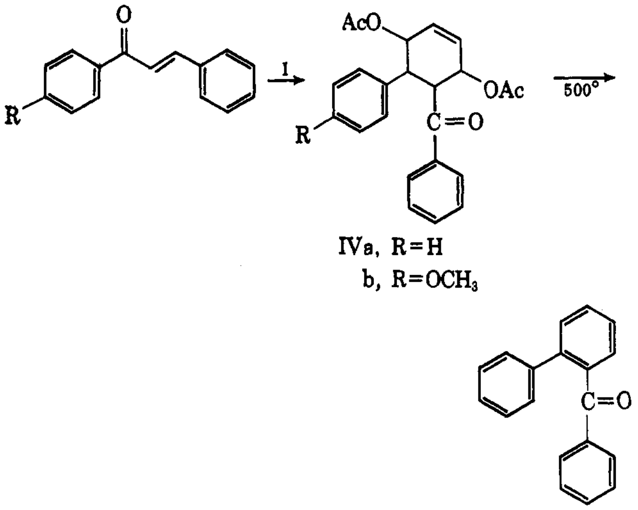
[2] (a) R. Criegee, W. Hörauf, and W. D. Schellenberg, *Chem. Ber.*, **86**, 126 (1953); (b) H. H. Inhoffen, J. Heimann-Trosien, H. Muxfeldt, and H. Krämer, *ibid.*, **90**, 187 (1957).

[3] Some of these results have been reported in a preliminary communication: R. K. Hill and R. M. Carlson, *Tetrahedron Letters*, 1157 (1964).

1,4-naphthoquinone and a small amount of anthraquinone. Naphthoquinone could be treated separately with more I to give a good yield of anthraquinone. 1,2-Naphthoquinone proved to be too sensitive to these reaction conditions and gave only tars.

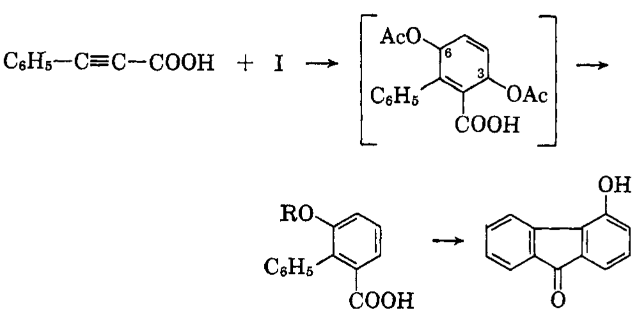
β-Substituted Styrenes.—The addition–aromatization reaction of I with styrenes carrying an electron-withdrawing β-substituent provides an attractive synthesis of *ortho*-substituted unsymmetrical biphenyls. *trans*-β-Nitrostyrenes were found to be among the best dienophiles for this purpose. Three representative nitrostyrenes gave yields of 20–45% of *o*-nitrobiphenyls (Table I). We have already reported a simple synthesis of the alkaloid ismine using one of these nitrobiphenyls as starting material.[3]

Other electron-withdrawing substituents were less satisfactory than nitro. No reaction was observed between I and cinnamic acid or 3,4-methylenedioxycinnamic acid. A number of β-aryl α,β-unsaturated carbonyl compounds were likewise recovered unchanged from heating with I; these included benzalacetone, piperonylideneacetone, β-(2-furyl)acrolein, and furfurylideneacetone. Chalcones were the only ketones tried which reacted with I, and gave stable, nonaromatized adducts (IV) in about 50% yield. Though elimination of acetic acid did not occur at 110°, pyrolysis of adduct IVa at 500° led to 2-benzoylbiphenyl.



IVa, R=H
b, R=OCH₃

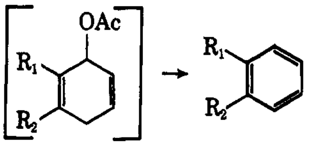
Acetylenes.—Several acetylenic dienophiles were found to react readily with I to form aromatics derived by the loss of only 1 mole of acetic acid. Dimethyl acetylenedicarboxylate reacted to form dimethyl 3-acetoxyphthalate, isolated as 3-hydroxyphthalic acid in good yield. Phenylpropiolic acid, in contrast to cinnamic acid, reacted readily to yield an acetoxybiphenylcarboxylic acid. In this case, only one of the two possible products, resulting from loss of either acetoxy group, was found. Whether the choice depends on the loss of the more acidic proton at C-6 or is determined by the loss of the 3-acetoxy group, which leaves behind the more stable carbonium ion, the predicted result is the same, loss of the 3-acetoxy function to yield 6-acetoxybiphenyl-2-carboxylic acid (V). This was verified by hydrolysis to the known 6-hydroxybiphenyl-2-carboxylic acid (VI) and further acid-catalyzed cyclization to the known 4-hydroxyfluorenone (VII).



V, R=Ac
VI, R=H

Acetylenes and 1-Acetoxybutadiene.—A corollary to the method described above is the synthesis of benzenes by aromatization of the adducts of acetylenic dienophiles and 1-acetoxybutadiene. The feasibility of this method was demonstrated with three acetylenes: dimethyl acetylenedicarboxylate, methyl phenylpropiolate, and benzyne generated from anthranilic acid. The products, formed in low to moderate yields, were, respectively, dimethyl phthalate, 2-carbomethoxybiphenyl, and naphthalene.

$$R_1-C\equiv C-R_2 + CH_2=CH-CH=CH-OAc \rightarrow$$



This direct synthesis of biphenyls, by spontaneous aromatization of Diels–Alder adducts, may be compared with other methods available for unsymmetrical *ortho*-substituted biphenyls. Unsymmetrical Ullman coupling[4] generally proceeds in low yield and necessitates the often tedious separation of mixed products. Methods involving arylation of substituted benzenes by diazonium salts[5] suffer from lack of control of orientation in linking the two rings. The 2-nitrobiphenyls which are readily available using this new method are useful starting materials for the preparation of phenanthridines[6] and carbazoles.[7]

Norbornenes.—The strained double bond in bicyclo[2.2.1]heptenes is known to take part in Diels–Alder reactions. We were unable, however, to effect the addition of I to norbornadiene, even at 190° for 2 days. Benzonorbornadiene, on the other hand, gave a good yield of adduct VIII, which retained both acetate groups. Pyrolysis of the adduct at 575–600°, in an attempt to prepare the interesting bridged anthracene IX,[8] gave instead 1,2,5,6-dibenzocycloheptatriene (X). It seems clear that pyrolysis of VIII to IX indeed took place, but that the temperature required for elimination of acetic acid is sufficient to bring about the well-known[9] rearrangement of bicycloheptadienes to tro-

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[4] P. E. Fanta, *Chem. Rev.*, **38**, 139 (1946); **64**, 613 (1964).

[5] W. E. Bachmann and R. A. Hoffman, *Org. Reactions*, **2**, 224 (1944).

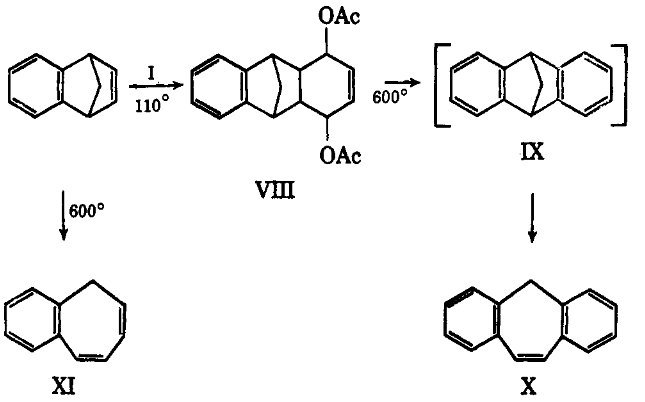
[6] G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 2447 (1931).

[7] H. C. Waterman and D. L. Vivian, *J. Org. Chem.*, **14**, 289 (1949).

[8] W. R. Vaughan and M. Yoshimine, *ibid.*, **22**, 7 (1957).

[9] (a) W. G. Woods, *ibid.*, **23**, 110 (1958); (b) W. M. Halper, G. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958); (c) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962); (d) W. C. Herndon and L. L. Lowry, *J. Am. Chem. Soc.*, **86**, 1922 (1964).

pilidenes. In support of this rearrangement, which has not been observed previously for benzo derivatives of bicycloheptadiene, we found that benzonorbornadiene itself is isomerized by heating to 1,2-benzocycloheptatriene (XI).



Experimental

Melting points were taken in capillaries and are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 21 spectrophotometer. N.m.r. spectra were measured on a Varian A-60 spectrometer, with tetramethylsilane as an internal standard.

1,4-Diacetoxybutadiene (I).—The procedure of Reppe, *et al.*,[10,2a] was modified as follows. To a stirred suspension of mercuric acetate (160 g.) in 400 ml. of glacial acetic acid was rapidly added cyclooctatetraene (52 g.). The addition compound[11] which appeared after 10–15 min. was decomposed by heating at 70–75° for 2 hr., and the warm mixture was poured into 4 l. of water. After standing a few hours, the solid was filtered, pressed as dry as possible, and air dried overnight.

The diacetate (83 g.) and dimethyl acetylenedicarboxylate (54 g.) were dissolved in 250 ml. of benzene and refluxed for 6 hr. The mixture was filtered and distilled at reduced pressure. At 140–155° (20 mm.) a mixture of I and dimethyl phthalate distilled, from which I crystallized in the cooled receiver. The solid was triturated with petroleum ether (b.p. 60–70°) and filtered, pressed between filter paper to remove dimethyl phthalate, and recrystallized from acetone–petroleum ether. The colorless needles of I weighed 26–31 g. (40–48%) and melted at 102–104° (lit.[2a] m.p. 103–104°).

Reaction of 1,4-Diacetoxybutadiene with Quinones. A.—A solution of I (1.70 g.) and *p*-benzoquinone (1.08 g.) in 25 ml. of benzene was refluxed for 4 days. On standing overnight at room temperature, the solution deposited 0.07 g. (7%) of anthraquinone, whose infrared spectrum was identical with that of an authentic sample. The yellow filtrate was evaporated to dryness under reduced pressure and the crude solid was washed with hexane to afford 1,4-naphthoquinone (1.15 g., 73%), m.p. 119–124°. The melting point was unchanged on mixing with an authentic sample, m.p. 125°, and the infrared spectra of the two were identical.

B.—A solution of I (0.89 g.), 1,4-naphthoquinone (0.74 g.), and hydroquinone (0.01 g.) in 15 ml. of benzene was refluxed for 3 days. The solution was clarified with charcoal and concentrated to a small volume; cooling gave 0.47 g. (45%) of a light brown solid, identified as anthraquinone by its infrared spectrum.

Reaction of 1,4-Diacetoxybutadiene with β-Nitrostyrenes. A.—A mixture of I (0.90 g.), β-nitrostyrene (0.75 g.), and a pinch of hydroquinone was heated in a sealed tube at 110–120° for 3 days. The dark reaction mixture was chromatographed on alumina, eluting with benzene. From the early fractions was obtained 0.20 g. (20%) of 2-nitrobiphenyl, whose infrared and ultraviolet spectra were identical with those of an authentic sample.

B.—A mixture of I (0.90 g.), 3,4-dimethoxy-β-nitrostyrene (1.04 g.), and a pinch of hydroquinone was heated in a sealed tube at 110–120° for 3 days. The dark reaction mixture was chromatographed on alumina and eluted with benzene. A yellow band, eluted early, gave 0.33 g. (26%) of golden crystals of 3,4-dimethoxy-2′-nitrobiphenyl, m.p. 87–92°. Recrystallization from acetone raised the melting point to 96–97.5°. The n.m.r. spectrum, in carbon tetrachloride, showed a singlet (with a shoulder) of 6 protons at τ 6.13 (2OCH$_3$), a broad group of 4 protons at 2.5, (protons on nitrobenzene ring), and a narrow group of 3 protons at 3.17 (protons on dimethoxybenzene ring). Melting points of 98 and 99° have been reported[12] for 3,4-dimethoxy-2′-nitrobiphenyl prepared by mixed Ullman coupling.

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 65.17; H, 4.92; N, 5.55.

The reaction of I with 3,4-methylenedioxy-β-nitrostyrene has been described elsewhere.[13]

Reaction of 1,4-Diacetoxybutadiene with Benzalacetophenone.—A mixture of I (0.89 g.), benzalacetophenone (1.04 g.), and a pinch of hydroquinone was heated in a sealed tube at 110–120° for 3 days. Trituration of the crude reaction mixture with benzene gave a colorless solid (0.95 g., 49%), m.p. 190–199°. Four recrystallizations from acetone–heptane gave the pure adduct IVa, 4-benzoyl-3,6-diacetoxy-5-phenylcyclohex-1-ene, m.p. 199–201°. The infrared spectrum (Nujol) showed carbonyl bands at 1733 (acetate) and 1695 cm.$^{-1}$ (benzoyl).

Anal. Calcd. for $C_{23}H_{22}O_5$: C, 73.00; H, 5.86. Found: C, 72.81; H, 5.92.

Substitution of *p*-anisylideneacetophenone for benzalacetophenone in the above procedure led to the adduct IVb, 4-benzoyl-3,6-diacetoxy-5-*p*-anisylcyclohex-1-ene, m.p. 189.5–191° after recrystallization from benzene–heptane, in 18% yield.

Anal. Calcd. for $C_{24}H_{24}O_6$: C, 70.57; H, 5.92. Found: C, 70.80; H, 6.15.

Pyrolysis of Adduct IVa.—IVa was recovered unchanged from heating a short time at its melting point (200°). Consequently, 200 mg. of IVa was passed over a column of glass helices heated to 500° in a stream of dry nitrogen. The oily product soon solidified; recrystallization from hexane gave 2-benzoylbiphenyl (71 mg., 48%), m.p. 84–85°, whose identity was shown by mixture melting point determination and comparison of infrared spectra with an authentic sample, m.p. 90°.

Reaction of 1,4-Diacetoxybutadiene with Acetylenes. A.—A mixture of I (0.89 g.), dimethyl acetylenedicarboxylate (0.71 g.), and hydroquinone (0.01 g.) was heated in a sealed tube at 120° for 3.5 days. The reaction mixture was taken up in a 10% potassium hydroxide solution in 50% aqueous ethanol and refluxed for 3 hr. The solution was concentrated to a small volume, acidified with 30% sulfuric acid, and extracted with three 50-ml. portions of ether. The ether extracts were dried, decolorized with charcoal, and concentrated to yield 0.45 g. (49%) of pale yellow crystals of 3-hydroxyphthalic acid, m.p. 155–160° with evolution of gas; the acid gave a violet ferric chloride test. 3-Hydroxyphthalic acid is reported[14] to melt around 150° with formation of the anhydride, and to give a violet ferric chloride test.

B.—A mixture of I (0.89 g.), phenylpropiolic acid (0.73 g.), and hydroquinone (0.01 g.) was heated in a sealed tube at 110–120° for 5 days. The reaction mixture was triturated with 1:1 benzene–hexane and the solid was collected to give 0.07 g. of the dimer of phenylpropiolic acid, 1-phenylnaphthalene-2,3-dicarboxylic anhydride, m.p. 235–245° dec., identified by comparison of infrared spectra with an authentic sample prepared by the method of Michael.[15] The filtrate was diluted with ether and extracted with two 25-ml. portions of aqueous sodium bicarbonate. The alkaline solution was acidified with 30% sulfuric acid, cooled, and scratched, to provide 0.35 g. (28%) of 6-acetoxybiphenyl-2-carboxylic acid (V), m.p. 81–85°. Four recrystallizations from acetone–hexane gave the analytical sample, m.p. 120–121°. The infrared spectrum showed bands due to acetate (1735 cm.$^{-1}$) and carboxyl (3330–2940, 1695 cm.$^{-1}$).

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.46; H, 4.68.

6-Hydroxybiphenyl-2-carboxylic Acid (VI).—A solution of 130 mg. of V in 5 ml. of 5% aqueous potassium hydroxide was refluxed for 40 min. Acidification with 30% sulfuric acid gave 90

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[10] W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 87 (1948).

[11] A. C. Cope, N. A. Nelson, and D. S. Smith, *J. Am. Chem. Soc.*, **76**, 1100 (1954).

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[13] R. K. Hill and R. M. Carlson, *J. Org. Chem.*, **30**, 1571 (1965).

[14] I. Remsen and H. N. Stokes, *Am. Chem. J.*, **6**, 282 (1884).

[15] A. Michael, *Ber.*, **39**, 1908 (1906).

mg. (82%) of acidic product, m.p. 150.5–152° after one recrystallization from acetone–heptane. 6-Hydroxybiphenyl-2-carboxylic acid is reported[16] to melt at 154°, while the 3-hydroxy isomer[17] melts at 159°.

4-Hydroxyfluorenone (VII).—A solution of 40 mg. of VI in 2.0 g. of concentrated sulfuric acid was allowed to stand for a few minutes, then diluted with water to precipitate an orange-yellow solid, m.p. 238–243°. The infrared spectrum (Nujol) showed hydroxy absorption at 3195 and a carbonyl band at 1695 cm.$^{-1}$. 4-Hydroxyfluorenone is reported[16] to melt at 249°, while the isomeric 1-hydroxyfluorenone[18] melts at 115°.

Reaction of I with Benzonorbornadiene.—A mixture of I (1.78 g.), benzonorbornadiene (1.50 g.), and a pinch of hydroquinone was heated in a sealed tube at 150° for 89 hr. The product a reddish brown oil, readily crystallized, and was washed with a few milliliters of cold ethanol to yield 2.14 g. (65%) of the light brown adduct VIII, m.p. 110–135°. Four recrystallizations from acetone–heptane gave the pure material as colorless needles, m.p. 155–158°. The infrared spectrum showed a strong acetate band at 1740 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.06; H, 6.46.

Dibenzocycloheptatriene (X).—The above adduct (VIII) was recovered unchanged from passing over glass helices heated at 400–450°. Pyrolysis was effected by passing VIII (0.38 g.) in a stream of nitrogen over glass helices at 575–600°. The light brown crude product was purified by sublimation at reduced pressure, then recrystallized from heptane to give white plates (0.11 g., 47%) of 1,2,5,6-dibenzocycloheptatriene[19] (X), m.p. 132–133°. In accord with this assignment of structure, the n.m.r. spectrum (in CS_2) showed three singlets, at τ 3.45 (8H), 3.7 (2H), and 7 (2H). The melting point was not depressed by mixing with an authentic sample,[20] m.p. 132°.

Pyrolytic Rearrangement of Benzonorbornadiene.—Benzonorbornadiene (0.25 g.) was passed over glass helices at 575–600° in a stream of nitrogen. The liquid (0.2 g.) that collected in the cooled receiver had different infrared and ultraviolet spectra than the starting material. It was assigned the structure of 1,2-benzocycloheptatriene (XI) on the basis of its ultraviolet spectrum, λ_{max} 282 mμ, λ_{min} 241 mμ (lit.[21] λ_{max} 276 mμ, λ_{min} 240 mμ).

Reaction of 1-Acetoxybutadiene with Acetylenes. A.—A mixture of 1-acetoxybutadiene[22] (1.12 g.), dimethyl acetylenedicarboxylate (1.42 g.), and hydroquinone (0.01 g.) was heated in a sealed tube at 115–120° for 6 days. The oily product was taken up in 80% aqueous ethanol, 5.0 g. of sodium hydroxide was added, and the mixture was refluxed for 4 hr. The dark solution was acidified with 30% sulfuric acid and extracted with eight 20-ml. portions of ether; the combined extracts were dried over sodium sulfate and filtered through charcoal. Concentration of the ether solution gave pale yellow plates of phthalic acid (0.72 g., 43%), m.p. 206–209°. The infrared spectrum was identical with that of authentic phthalic acid, m.p. 206–208°.

B.—A mixture of 1-acetoxybutadiene (1.12 g.), methyl phenylpropiolate (1.60 g.), and hydroquinone (0.01 g.) was heated in a sealed tube at 110° for 6 days. The oily product was saponified as described in part A, acidified, and extracted with chloroform. The crude biphenyl-2-carboxylic acid obtained by evaporation of theext racts did not crystallize and was therefore converted to fluorenone for ease of isolation. The oil was taken up in 10 ml. of concentrated sulfuric acid, kept for a few minutes, then carefully added to water. The solution was extracted with five 50-ml. portions of ether and the extracts were washed with saturated sodium bicarbonate solution and brine, then dried. Concentration of the extracts and chromatography of the residue on alumina gave a yellow substance, eluted with 50% benzene–hexane, and identified as fluorenone (0.10 g., 5.5%), m.p. 82–83° (lit. m.p. 84°) from its infrared spectrum.

C.—To a stirred and refluxing solution of 1-acetoxybutadiene (2.24 g.) and *n*-butyl nitrite (2.22 g.) in 20 ml. of methylene dichloride was added dropwise, over a period of 70 min., a solution of anthranilic acid (3.00 g.) in 10 ml. of tetrahydrofuran. After refluxing for an additional 15 min., the solution was concentrated at reduced pressure, and the red oily residue was chromatographed on alumina. Elution with hexane gave naphthalene (0.29 g., 11%), m.p. 76–78°, in the early fractions. Its infrared spectrum was identical with that of authentic naphthalene, m.p. 80°.

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[18] G. Heyl, *ibid.*, **31**, 3033 (1898).

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[20] We are grateful to Professor M. P. Cava of The Ohio State University for sending us a sample for comparison; *cf.* M. P. Cava, R. Pohlke, B. W. Erickson, J. C. Rose, and G. Fraenkel, *Tetrahedron*, **18**, 1005 (1962).

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The Synthesis of Silyl Hydroperoxides and Bissilyl Peroxides[1]

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Triphenylsilyl, methyldiphenylsilyl, tribenzylsilyl, and tri-*n*-hexylsilyl hydroperoxides have been synthesized from the corresponding silylamines. Practical laboratory syntheses starting with chlorosilanes, ammonia, and hydrogen peroxide, proceed through silylamine intermediates. The hydroperoxides are so stable that they may be stored indefinitely at room temperature. Bis(triphenylsilyl) and bis(tribenzylsilyl) peroxides were prepared and found to be even more stable than the corresponding hydroperoxides.

The hydroperoxides and bis peroxides of silicon constitute a field of research which has received little attention. The only hydroperoxide isolated, trimethylsilyl hydroperoxide,[2] was characterized merely by peroxide content and was reported to decompose below room temperature.

The papers which have appeared on bissilyl peroxides have usually described compounds of limited purity. Berry[3] claimed to have prepared a solution of bis(triphenylsilyl) peroxide but did not isolate the compound. Buncel and Davies[4] attempted to crystallize pure bis(triphenylsilyl) peroxide but obtained an unstable solid with only a 70% content of the theoretical

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[1] (a) Supported in part by the U. S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G242 and in part by a Texaco Company Fellowship. (b) Taken in part from the dissertation of George Jalics, submitted June 1964, to the Graduate School of Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963.

[2] W. Hahn and L. Metzinger *Makromol. Chem.*, **21**, 113 (1956).

[3] K. L. Berry, U. S. Patent 2,692,887 (1952).

[4] E. Buncel and A. G. Davies, *J. Chem. Soc.*, 1550 (1958).