calcium hydride and then distilled from the excess hydride; b.p. 141°.

n-Butyl bromide was Eastman Kodak White Label carefully distilled through a Todd column; b.p. 106.6°.

The magnesium used in this study was Fisher Grignard Reagent magnesium.

Method of gas analysis. The gases produced in the following reactions were analyzed by means of a Fisher Gulf Partitioner using the standard column provided with the instrument (tricresyl phosphate on firebrick). The eluting gas was helium. The peaks produced by an unknown sample were identified by comparison with those produced by a standard known mixture of light hydrocarbon gases (Fig. 1). The cyclobutane band was identified by inference from the products formed by the treatment of 1,4-dibromobutane with sodium in refluxing toluene.[3]

The mole percent of each component was calculated by the expression:

$$\text{mole } \% \text{ A} = \frac{\text{area under A}}{\text{total area}} \times 100$$

Apparatus. The apparatus consisted of a 100-ml., three-necked flask fitted with a dropping funnel and a condenser. All reactions were stirred by means of a magnetic stirrer. All gases were collected, after passing through the condenser, in a gas collection bottle filled either with mercury or a saturated salt solution.

Reaction of 1,4-dibromobutane with various metals. To a refluxing mixture of 2 g. of the appropriate metal and 20 ml. of solvent was slowly added 2.16 g. (0.01 mole) of 1,4-dibromobutane. The mixture was usually allowed to reflux overnight. The evolved gases were then measured and analyzed according to the above procedure. The metals, solvents, and reaction products are tabulated in Table I.

Reaction of 1,4-dibromobutane with methylmagnesium bromide and cobaltous bromide in various solvents. To a refluxing mixture of 2.16 g. (0.01 mole) of 1,4-dibromobutane and 2 g. of cobaltous bromide in 20 ml. of solvent, was added *ca.* 0.03 mole of methylmagnesium bromide in the same solvent. The solvents used were ethyl ether, butyl ether, and xylene. In the latter two solvents, the addition reagent was formed by mixing the solvent with the appropriate amount of methylmagnesium bromide in ethyl ether and then removing as much of the ethyl ether as possible by evacuating to water pump pressure. In xylene and butyl ether, the Grignard reagent was added in the form of a slurry. The gases produced were collected and analyzed as described previously.

Reactions of n-butyl bromide. (*a*) A mixture of 2.74 g. of *n*-butyl bromide (0.02 mole), 4.36 g. of cobaltous bromide (0.02 mole), and 1 g. of magnesium was refluxed in 15 ml. of ethyl ether for three hours. The reaction gas was collected and analyzed as before. The results are recorded in Table II.

(*b*) To a refluxing mixture of 2.74 g. of *n*-butyl bromide and 1 g. of cobaltous bromide in 15 ml. of ethyl ether was slowly added 25 ml. of *ca.* 1*M* methylmagnesium bromide. The yield of gas was quantitative based on the amount of methylmagnesium bromide. The analytical results are given in Table II.

Reaction of 4-phenoxybutyl bromide with magnesium and cobaltous bromide. 4-Phenoxybutyl bromide was prepared by the method of Kharasch, *et al.*;[10] m.p. 40–41.5°. A mixture of 1.2 g. (5.2 mmole) of 4-phenoxybutyl bromide, 1 g. of cobaltous bromide, and 2 g. of magnesium was refluxed for three days in 25 ml. of xylene. The rather small gas yield (25 ml.) was collected and analyzed as before. The results are recorded in Table II.

Acknowledgment. The author wishes to thank Dr. W. D. Huntsman of these laboratories for his many stimulating discussions of this problem.

ATHENS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

Synthesis of Tribenzocycloheptatriene and Related Compounds

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From the adduct (III) of butadiene and cinnamaldehyde, 4,5-tetramethyleno-2,3-benzosuberone (VI) has been prepared. Condensation of its 7-formyl derivative with the methiodide of β-diethylaminoethyl methyl ketone gave the tetracyclic hydroxyketone (X) from which by dehydration and dehydrogenation tribenzocycloheptatriene (II) has been obtained. The corresponding heptafulvene (XIV) does not differ in its physical properties from triphenylethylene; it has no "fulvenic" properties. Some other reactions of the adduct (III) and the ketone (VI) have also been explored.

The failure of the properties of the dibenzoheptafulvenes (I) to agree with those predicted by the theory, based on the linear combination of atomic orbitals (LCAO),[1–3] made it interesting to synthesize heptafulvenes derived from tribenzocycloheptatriene (II). The preparation of this compound started from the adduct (III) of butadiene and cinnamaldehyde, 2-phenyl-1,2,3,6-tetrahydrobenzaldehyde. The *trans*-structure of this aldehyde follows from the configuration of cinnamaldehyde[4] and from its oxidation to the known[5] 2-phenyl-1,2,3,-6-tetrahydrobenzoic acid, by means of silver oxide.[6]

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(1) E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman, and B. Pullman, *Bull. soc. chim. France*, **18**, 684 (1951).

(2) G. Berthier and B. Pullman, *Trans. Faraday Soc.*, **45**, 484 (1949).

(3) See, however, A. Julg and B. Pullman, *J. chim. phys.*, **52**, 481 (1951).

(4) M. Bourguel, *Bull. soc. chim. France* [4], **45**, 1086 (1929); G. Gomboni, V. Thens, and H. Schmitz, *Helv. Chim. Acta*, **38**, 255 (1955); H. Schinz, *Chem. Abstr.*, **49**, 6874 (1956).

(5) J. W. Cook, C. L. Hewett, and A. M. Robinson, *J. Chem. Soc.*, 168 (1939); G. Blumenfeld, *Ber.*, **74**, 524 (1941); C. D. Gutsche, *J. Am. Chem. Soc.*, **70**, 4150 (1948); K. Alder, H. Vagt, and W. Vogt, *Ann.*, **565**, 135 (1945); N. V. Organon, Brit. Patent **674,177** [*Chem. Abstr.*, **47**, 7540 (1953)].

(6) The isomeric 2-phenyl-1,2,5,6-tetrahydrobenzaldehyde has been prepared by E. Lehmann and W. Paasche, *Ber.*, **68**, 1146 (1935), and K. Alder, H. Vagt, and W. Vogt, ref. 5.

Condensation of III with malonic acid gave β-(2-phenylcyclohex-4-enyl)acrylic acid (IV); however, a pure product (m.p. 129°) could only be obtained after a number of recrystallizations, and the yield did not exceed 50%. It appears that a second product (a geometric isomer or, more likely, a compound with different location of the double bond) is formed, which, however, could not be isolated in pure form. The acid IV was characterized by its crystalline methyl ester and benzylisothiuronium salt.[7]

Hydrogenation of the acid (IV) gave the well known[8] *trans*-2-phenylcyclohexylpropionic acid (V) in 86% yield, which was also obtained in somewhat better over-all yield by the following alternative route: the diethyl acetal of (III) was hydrogenated and the hydrogenation product hydrolyzed to *trans*-2-phenylcyclohexanaldehyde. The latter condensed with malonic acid to yield the dihydro-analog of IV, which could be hydrogenated to V.

Cyclization of V with polyphosphoric acid gave in good yield 4,5-tetramethyleno-2,3-benzosuberone (VI) the key substance in the present synthesis.[9] It gave a 7-bromo derivative which, however, did not lend itself to further transformation. Reduction of the carbonyl group in VI with lithium aluminum hydride and dehydration of the secondary alcohol so formed gave 3,4-benzo-5,6-tetramethylenocyclohepta-1,3-diene (VII). This was dehydrogenated by means of palladium to a mixture of two hydrocarbons which could be separated by fractional distillation: 9-methylphenanthrene and the dihydro derivative (IX) of the expected 3,4,5,6-dibenzocyclohepta-1,3-5-triene (VIII), which did not give a picrate and had the same principal maximum (247 mμ; log ε 4.12) as 2-methyl-3,4,5,6-dibenzocyclohepta-3,5-diene (248 mμ; log ε 4.14) and the corresponding 2,4,7-trimethyl derivative (250 mμ; log ε 4.14), hydrocarbons which have only recently been described by Hall *et al.*[10,11]

A more convenient method for the preparation of the desired tetracyclic system was found in the Michael reaction between the 7-formyl derivative of VI and the methiodide of β-diethylaminoethyl methyl ketone in the presence of sodium ethoxide. The reaction product had the formula of the hydroxyketone X; it was characterized by a *mono*-2,4-dinitrophenylhydrazone, which exhibited a band at 365 mμ (4.23), as expected for a *saturated* ketone. The infrared spectrum of the compound revealed the presence of the hydroxyl group (3400 cm.$^{-1}$), but the carbonyl band appeared at the unexpectedly low frequency of 1675 cm.$^{-1}$ in the solid state, whilst in chloroform solution a doublet at 1724 and 1689 cm.$^{-1}$ was observed. It may be that the ketone contains some of the dehydration product (XI), and that some more of the latter was formed in the preparation of the potassium bromide disk. Potassium hydroxide in aqueous-alcoholic dioxane at room temperature dehydrated X to the tetracyclic ketone XI with a yield of 50%. The ultraviolet absorption spectrum of the 2,4-dinitrophenylhydrazone showed a band at 394 mμ (4.35), and that of the ketone itself at 292 mμ (4.10), as expected for an α,β-unsaturated cycloalkenone in which the double band is also conjugated with a phenyl group.[11a] Again, the infrared absorption of the carbonyl group had an unexpectedly low frequency, *viz.* 1650 cm.$^{-1}$ (in potassium bromide).

When XI was subjected to treatment with aluminum isopropoxide, not only was the keto group reduced to hydroxyl, but water was split off,[12] and the compound XII formed.

Dehydrogenation of XII gave II which both according to the analysis and the spectrum had the desired structure. Bromination of II with *N*-bromosuccinimide converted it into 1-bromo-2,3,4,5,6,7-tribenzocyclohepta-2,4,6-triene which was hydrolyzed to the corresponding secondary alcohol and oxidized further to the ketone XIII. This was characterized by its orange-red 2,4-dinitrophenylhydrazone and the infrared absorption band at 1667 cm.$^{-1}$.[13]

Reaction of XIII with benzylmagnesium chloride and subsequent dehydration gave the desired heptafulvene XIV, 1-benzylidene-2,3,4,5,6,7-tribenzocy-

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[7] The route chosen in this investigation is somewhat similar to that of J. W. Cook, G. T. Dickson, J. Jack, J. D. London, J. McKeown, J. Macmillan, and W. F. Williams [*J. Chem. Soc.*, 139 (1950)], who condensed the fully aromatic 2-phenylbenzaldehyde with malonic acid. When the authors attempted to cyclize the resulting *o*-biphenylylpropionic acid (corresponding to V), they obtained not a seven-, but a five-membered ring.

[8] C. D. Gutsche, see ref. 5.

[9] The substance has been prepared before by a different route. C. D. Gutsche, *J. Am. Chem. Soc.*, **73**, 786 (1951).

[10] D. M. Hall, J. E. Landburg, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 3475 (1956); *cf.* Cook and Turner, *J. Chem. Soc.*, 113 (1937); *cf.* also G. H. Beaven and E. A. Jonson, *J. Chem. Soc.*, 651 (1957), who have studied 2-methyl-3,4,5,6-dibenzocyclohepta-3,5-diene (248 mμ; log ε 4.18).

[11] The occurrence of hydrogenation in dehydrogenation reactions (hydrogen transfer) is not unusual, nor is the formation of phenanthrene compounds from dibenzocycloheptadiene derivatives unexpected; similar observations have been made in the colchicine series. See, *e.g.*, A. Windaus, *Ann.*, **439**, 59 (1924), and J. W. Cook *et al.*, *J. Chem. Soc.*, 746 (1947).

[11a] See, *e.g.*, 3-phenylcyclopent-2-en-1-one: 280 mμ (log ε 4.42). A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, T. C. Johnson, and C. H. Shunk, *J. Am. Chem. Soc.*, **69**, 1985 (1947).

[12] Such a secondary reaction is rare, but not altogether unknown: J. Doeuvre and H. Perret, *Bull. soc. chim. France*, [5], 2, 298 (1935); W. G. Grubb and J. Read, *J. Chem. Soc.*, 242 (1934); A. G. Short and J. H. Read, *J. Chem. Soc.*, 1306 (1939); W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **4**, 461 (1939).

[13] This compound has recently been obtained by the rearrangement of the diazonium salt of 9-(*o*-aminophenyl)-9-fluorenol (M. Stiles, A. J. Sisti, and A. J. Libbey, 131st Meeting, American Chemical Society, April 1957). We are grateful to the referee who informed us of this fact. See the paper by M. Stiles and A. J. Libbey, *J. Org. Chem.*, **22**, 1243 (1957).

clohepta-2,4,6-triene. The absorption spectrum of this compound shows practically no structure; maxima are observed at 230 mμ (4.65) and at 262 mμ (4.38) (Fig. 1). The analogous dibenzoheptafulvene (I, R. = C_6H_5) absorbs at 284 mμ (4.40).[1]

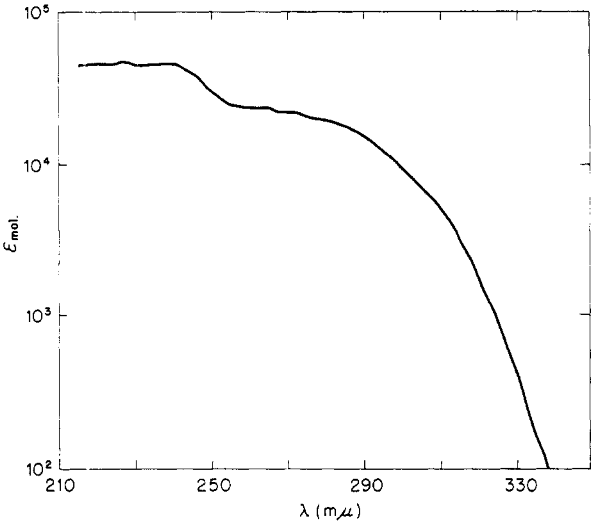


Fig. 1. Ultraviolet spectrum of 1-benzylidene-2,3,4,5,6-tribenzocyclohepta-2,4,6-triene (XIV) in ethanol

It follows, therefore, that XIV exactly as I is a fulvene only in name; its properties are not those one would have expected. One will have to assume that the incorporation of the double bonds of the cycloheptatriene system into aromatic rings deprives the system of its pseudo-aromatic character. The hypsochromic effect of the anellation of benzene rings to the system of the fulvenes derived from cyclopentadiene and the concomitant decrease in the polarity of the semicyclic double bond in these fulvenes are phenomena of the same character.[14]

In the course of this investigation, another route was explored in which the third ring was to be created through a Diels-Alder reaction. The aldehyde III was condensed with acetone, the ketone XV reduced to the secondary alcohol, and the latter dehydrated to 1-butadienyl-2-phenyl-cyclohex-4-ene (XVI). The yields in the three steps were fair (74%, 57%, 52%, respectively), but the condensation of XVI with maleic anhydride proved disappointing, and the method was abandoned.

EXPERIMENTAL

trans-2-Phenyl-1,2,3,4-tetrahydrobenzaldehyde (III). A mixture of 150 g. of freshly distilled cinnamaldehyde, 180 g. of butadiene, 4 g. of hydroquinone, and 350 ml. of benzene was heated at 200° for 20 hr. (autoclave) and distilled through a Vigreux column. A quantity of about 20 g. of cinnamaldehyde was recovered and 130–150 g. (yield, 62–71%) of the desired aldehyde, b.p. 171–173° (30 mm.), m.p. 36–37°, was obtained.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.9; H, 7.5. Found: C, 84.0; H, 7.8.

Ultraviolet spectrum: λ_{max}^{EtOH} 290 mμ (log ε 2.78); several minor (benzene) bands between 250 and 270 mμ (2.50–2.68).

Phenylhydrazone, bright yellow needles, from ethyl alcohol; m.p. 127°.

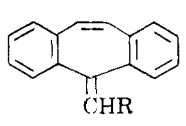
Anal. Calcd. for $C_{19}H_{20}N_2$: C, 82.6; H, 7.3. Found: C, 83.0; H, 7.3.

2-Nitrophenylhydrazone, yellow needles, from butyl alcohol, m.p. 180°. *Anal.* Calcd. for $C_{19}H_{19}N_3O_2$: C, 71.0; H, 6.0; N, 13.1. Found: C, 71.0; H, 6.0, N, 12.9.

2,4-Dinitrophenylhydrazone, yellow needles, from alcohol; m.p. 161°.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.7; H, 5.1; N, 15.5. Found: C, 62.9; H, 5.0; N, 15.3.

trans-2-Phenyl-1,2,3,4-tetrahydrobenzoic acid. To a solution of 2.2 g. of sodium hydroxide in 50 ml. of water, silver oxide, prepared from 8.5 g. of silver nitrate, and 9 g. of the aldehyde (III) were added successively with stirring and cooling with ice. The product was kept at room temperature for 30 min., filtered, and acidified. The acid was recrystallized from ligroin and melted at 104° (lit.:[5] 107–108°); yield, 50%.



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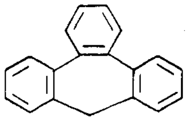

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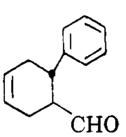

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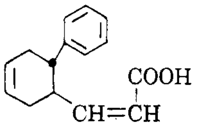

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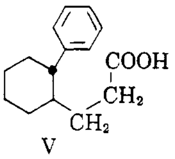

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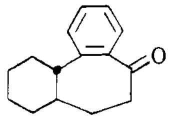

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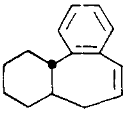

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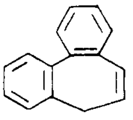

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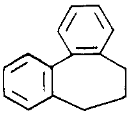

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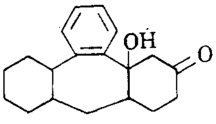

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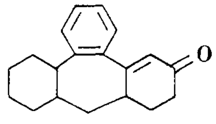

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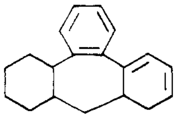

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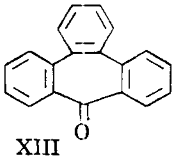
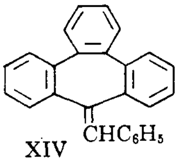
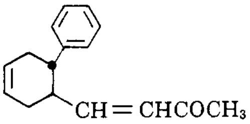


XIII



XIV



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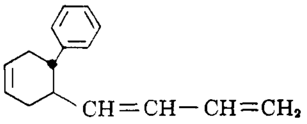

XVI

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.2; H, 6.9. Found: C, 77.2; H, 7.1.

β-(2-Phenylcyclohex-4-enyl)acrylic acid (IV). A mixture of 130 g. of the aldehyde (III), 143 g. of malonic acid, 280

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[14] E. D. Bergmann, "The Fulvenes," in *Progress in Organic Chemistry*, Vol. 3, Butterworth's Scientific Publications, London, 1955, p. 81.

ml. of pyridine, and 5 ml. of piperidine was heated for 3 hr. at 100° and for 30 min. at 150°, and poured into ice cold hydrochloric acid. The product was extracted with ether and transferred again into 5% sodium carbonate solution. Acidification gave 150 g. (94%) of a yellowish product (m.p. 95–110°) which was recrystallized twice from cyclohexane and then melted at 126° (yield, 80–90 g.; 53%). Another recrystallization from benzene raised the m.p. to 129°. ν_{max}^{KBr} (in cm.$^{-1}$) 2950 (associated hydroxyl); 1685 (CO of an α,β-unsaturated acid); 1625 (C=C); 705 (CH wagging frequency in a *cis*-olefin).

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.0. Found: C, 79.6; H, 6.8.

Methyl ester, prepared with diazomethane, b.p. 164–165° (3.5 mm.); m.p. 63° (from methanol).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.4. Found: C, 79.5; H, 7.1.

The methyl ester (in ethanol) does not show a very characteristic ultraviolet absorption spectrum; at 262 mμ, an inflection (log ε 2.64) is observed. This may be due to steric influences.

Benzylisothiuronium salt, m.p. 161° (from ethanol).

Anal. Calcd. for $C_{23}H_{26}N_2O_2S$: C, 70.0; H, 6.6. Found: C, 70.0; H, 6.6.

β-(2-Phenylcyclohexyl)propionic acid (V). A solution of 63 g. of the acid IV in 250 ml. of glacial acetic acid was hydrogenated at ordinary temperature and pressure in the presence of 0.7 g. of 10% palladium-charcoal. The solvent was distilled off and the residue recrystallized from petroleum ether (60–90°), m.p. 85° (lit.:[8] 83.5–84.5°); yield, 54 g. (86%).

The same acid was obtained in almost quantitative yield, when β-(2-phenylcyclohexyl)acrylic acid (*vide infra*) was hydrogenated in ethanol solution and in the presence of 10% palladium-charcoal as catalyst. The hydrogenation proceeded rapidly at ordinary temperature and pressure.

Diethyl acetal of the aldehyde III. A mixture of 12.4 g. of the aldehyde (III), 8.3 g. of ethyl orthoformate, 30 ml. of anhydrous ethanol, and some drops of saturated alcoholic hydrochloric acid was kept at room temperature for 12 hr., neutralized by stirring with an excess of solid carbonate for 15 min., diluted with an equal volume of ether, filtered, and distilled, b.p. 120–122° (0.9 mm.). The yield was 15.2 g. (87%).

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.5; H, 9.2. Found: C, 78.4; H, 9.0.

With the dinitrophenylhydrazine reagent, the acetal gives the above-described 2,4-dinitrophenylhydrazone of III.

Diethyl acetal of 2-phenylhexahydrobenzaldehyde. The solution of 13.7 g. of the foregoing acetal in 50 ml. of ethanol was hydrogenated at ordinary temperature and pressure in the presence of 0.5 g. of 10% palladium-charcoal. The theoretical amount of hydrogen was absorbed in 40 min. The product distilled at 115–117° (0.7 mm.); and weighed, 12.7 g. (100%).

Anal. Calcd. for $C_{17}H_{26}O_2$: C, 77.9; H, 10.0. Found: C, 78.0; H, 10.0.

2-Phenylhexahydrobenzaldehyde. The solution of 11 g. of the saturated acetal in 10 ml. of alcohol was heated on the water bath for 1 hr. with 50 ml. of 2% aqueous hydrochloric acid, and extracted with benzene. The product (7 g., 90%) distilled at 115–118° (1 mm.).

Anal. Calcd. for $C_{13}H_{16}O$: C, 83.0; H, 8.5. Found: C, 83.8; H, 8.7.

2,4-Dinitrophenylhydrazone, from butyl alcohol, m.p. 174°.

Anal. Calcd. for $C_{19}H_{20}N_4O_4$: C, 61.9; H, 5.4; N, 15.2. Found: C, 61.6; H, 5.3; N, 14.9.

β-(2-Phenylcyclohexyl)acrylic acid. In the manner described above, 37 g. of 2-phenylhexahydrobenzaldehyde, 40 g. of malonic acid, 80 ml. of pyridine, and 2 ml. of piperidine gave 31 g. (72%) of the desired acid, from ligroin, m.p. 113–114°.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.3; H, 7.8. Found: C, 78.9; H, 8.0.

Benzylisothiuronium salt, m.p. 169° (from ethanol).

Anal. Calcd. for $C_{23}H_{28}N_2O_2S$: N, 7.1. Found: N, 6.9.

trans-4,5-Tetramethyleno-2,3-benzosuberone (VI). A mixture of 55 g. of the pure acid V and 900 g. of polyphosphoric acid[15] was heated at 100° for 3 hr., diluted with water, and extracted with benzene. The product boiled at 163–165° (1.5 mm.) and solidified spontaneously. Recrystallization from petroleum ether gave 32 g. (60%) of m.p. 55°.[9] $\bar{\nu}_{max}^{KBr}$ 1667 cm.$^{-1}$ This is a rather low carbonyl frequency, as benzosuberone has this band at 1690 cm.$^{-1}$; incidentally, in the Raman spectrum, the corresponding figure is 1676 cm.$^{-1}$.[16] In chloroform (40.9 mg.; 1 ml.) the carbonyl frequency was observed at 1690 cm.$^{-1}$ This extreme influence of the potassium bromide pellet is very unusual.

7-Bromo-4,5-tetramethyleno-2,3-benzosuberone. To a solution of 4.3 g. of the ketone VI in 20 ml. of carbon tetrachloride, there was added, over a period of 25 min., a solution of 3.2 g. of bromine in 30 ml. of carbon tetrachloride. After further 30 min., the solvent was evaporated *in vacuo* and the residue recrystallized from ligroin (b.p. 90–100°). The yield was 3.5 g. (60%) of colorless needles, m.p. 117–118°. $\bar{\nu}_{max}^{KBr}$ 1678 cm.$^{-1}$.[17]

Anal. Calcd. for $C_{15}H_{17}BrO$: C, 61.5; H, 5.8. Found: C, 61.6; H, 6.0.

4,5-Tetramethyleno-2,3-benzocyclohept-2-en-1-ol. To 0.5 g. of lithium aluminum hydride in 30 ml. of ether, there was added, during 30 min. and with stirring, a solution of 9 g. of the ketone VI in 50 ml. of ether. After 12 hr. at room temperature, the reaction product was decomposed and acidified. The product, a yellow-greenish oil boiled at 162–164° (0.1 mm.); yield, 7.5 g. (83%). It could not be obtained in analytically pure state; probably, even *in vacuo* some dehydration takes place. λ_{max}^{EtOH} 250 mμ (log ε 2.63); $\bar{\nu}_{max}^{liq.}$ 3500 cm.$^{-1}$

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.3; H, 9.3. Found: C, 84.9; H, 9.8.

5,6-Tetramethyleno-3,4-benzocyclohepta-1,3-diene (VII). The foregoing alcohol (5 g.) was subjected to azeotropic distillation with 0.5 g. of *p*-toluenesulfonic acid in 80 ml. of xylene. After 90 min., the reaction mixture was washed with water and distilled; b.p. 105–110° (0.15 mm.); yield, 4.5 g. (quantitative). λ_{max}^{EtOH} 248 mμ (log ε 4.02).

Anal. Calcd. for $C_{15}H_{18}$: C, 90.9; H, 9.1. Found: C, 91.0; H, 9.4.

3,4,5,6-Dibenzocyclohepta-3,5-diene (*VIII*) *and 9-methylphenanthrene.* A mixture of 3.4 g. of VII and 1 g. of 10% palladium-charcoal was heated in a carbon dioxide atmosphere for 1 hr. at 310°, for 25 min. at 320°, and finally for 45 min. at 340°. The organic product was extracted with benzene and fractionated. Thus, two products were obtained: an oil (2 g.) of b.p. 156° (6 mm.) and a fraction (0.5 g.) of b.p. 170° (6 mm.) which solidified. This hydrocarbon was recrystallized from methanol, melted at 92°, gave the analytical figures required for, and exhibited an ultraviolet spectrum identical with that of, 9-methylphenanthrene. Also the mixture with an authentic specimen melted at 92°.

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(15) F. Uhlig, *Angew. Chem.*, **66**, 435 (1954).

(16) R. N. Jones and C. Sandorfy, *Chemical Application of Spectroscopy*, Interscience Publishers Inc., New York, N. Y., 1956, p. 449.

(17) It has been observed that a bromine atom α to a carbonyl either increases the frequency of the carbonyl absorption or leaves it practically unchanged, depending upon the conformation of the brominated product. In cycloheptanone, *e.g.*, α-bromination shifts the carbonyl band by 8 cm.$^{-1}$ *Cf.* E. J. Corey, *J. Am. Chem. Soc.*, **75**, 2301 (1953); E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **77**, 5418 (1955); R. N. Jones *et al.*, *J. Am. Chem. Soc.*, **74**, 2828 (1952). G. Chiurdoglu, *Bull. soc. chim. France*, 1018 (1956); *Cf.* W. D. Kumler and A. C. Huitric, *J. Am. Chem. Soc.*, **78**, 3369 (1956); M. Josien, C. Castinel, and G. Chiurdoglu, *Compt. rend.*, **244**, 2383 (1957).

Anal. Calcd. for $C_{15}H_{12}$: C, 93.7; H, 6.2. Found: C, 93.4; H, 6.3.

Picrate, from methanol, m.p. and mixed m.p. with pure 9-methylphenanthrene picrate, m.p. 153°.

Anal. Calcd. for $C_{25}H_{15}N_3O_7$: C, 59.9; H, 3.6. Found: C, 60.2; H, 3.4. $\lambda_{\max}^{\mathrm{EtOH}}$ 349 mμ (log ϵ 2.47); 341 mμ (2.28); 333 mμ (2.42); 326 mμ (2.28); 318 mμ (2.29); 296 mμ (4.02); 285 mμ (4.01); 253 mμ (4.66). The oily product gave an analysis corresponding to $C_{15}H_{14}$; it has the structure IX and shows a spectrum in accordance with this structure, 247 mμ (4.20) in ethanol.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.8; H, 7.2. Found: C, 92.6; H, 6.7.

4,5-Tetramethyleno-7-formyl-2,3-benzosuberone. To a suspension of dry sodium methoxide, freshly prepared from 1.4 g. of sodium metal[18] in 100 ml. of benzene, 4.8 g. of ethyl formate and then, at 0°, a solution of 6.4 g. of the ketone VI in 50 ml. of benzene were added. One stirred for 1 hr. at room temperature and for 1 hr. at reflux temperature, extracted the benzene solution with 5% sodium hydroxide solution, and isolated the product by acidification of the alkaline extract. From methanol, m.p. 117°; yield, 5.8 g. (80%).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.4. Found: C, 79.6; H, 7.8.

Tetracyclic hydroxyketone (1a-hydroxy-8-keto-1,1a,2,3,4,-4a,6a,7,8,9,9a-dodecahydrotribenzo[a,c,e]cycloheptatriene) (X). To a solution of 0.7 g. of sodium in 50 ml. of ethanol, there were added, successively, 6.0 g. of the foregoing product and a solution of 4-diethylamino-2-butanone methiodide (prepared from 4 g. of the aminoketone and 4 g. of methyl iodide) in 40 ml. of ethanol. After 24 hr. at room temperature, water and benzene was added to the reaction mixture. The benzene solution was extracted with 5% sodium hydroxide solution from which 3 g. (50%) of the initial formyl compound was precipitated by acidification. (Prolongation of the reaction time to 48 hr. did not improve the conversion.) The benzene solution gave, upon distillation, an oil (3.1 g.; 46%) of b.p. 190° (0.1 mm.), which according to the analysis and the spectrum was the hydroxyketone X. It crystallized on standing and showed, after recrystallization from alcohol, the m.p. 82°. $\bar{\nu}_{\max}^{\mathrm{KBr}}$ cm.$^{-1}$ 3400 (hydroxyl), 1670 (carbonyl); $\lambda_{\max}^{\mathrm{EtOH}}$ 250 mμ (log ϵ 3.56); 282 mμ (log ϵ 3.10). In chloroform solution (45.0 mg. in 1 ml.), the carbonyl frequency is a doublet (1724; 1689 cm.$^{-1}$). It is assumed that the hydroxy-ketone contains a small amount of the unsaturated ketone (XI); in the preparation of the potassium bromide pellet, perhaps, some further dehydration takes place. Even so, the influence of the physical state on the carbonyl frequency is surprising.

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.3; H, 8.4. Found: C, 80.0; H, 8.1. In accordance with formula X, the 2,4-dinitrophenylhydrazone was yellow; from butyl acetate, m.p. 168°. $\lambda_{\max}^{\mathrm{CHCl_3}}$ 365 mμ (log ϵ 4.36).

Anal. Calcd. for $C_{22}H_{28}N_4O_5$: C, 64.7; H, 6.1; N, 12.1. Found: C, 64.9; H, 6.5; N, 12.1.

Tetracyclic ketone (2-oxo-2,3,4,4a,6,6a,7,8,9,9a-decahydrotribenzo[a,c,e]cycloheptatriene) (XI). To a solution of 5 g. of (X) in 60 ml. of dioxan and 110 ml. of anhydrous ethyl alcohol, 110 ml. of a 10% aqueous solution of potassium hydroxide was added in an atmosphere of nitrogen and the mixture kept at room temperature for 48 hr. Dilute sulfuric acid was added and the product extracted with benzene. The product (2.5 g.; 50%) boiled at 207–210° (0.3 mm.) and solidified spontaneously. Recrystallization from alcohol yielded colorless crystals of m.p. 141°. $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1650 cm.$^{-1}$ (carbonyl); $\lambda_{\max}^{\mathrm{EtOH}}$ 287 mμ (log ϵ 4.15); 292 mμ (log ϵ 4.18).

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.7; H, 8.3. Found: C, 85.8; H, 8.6. The red 2,4-dinitrophenylhydrazone was recrystallized from butyl acetate and melted at 250°. $\lambda_{\max}^{\mathrm{CHCl_3}}$ 268 mμ (log ϵ 4.20); 296 mμ (4.11); 394 mμ (4.52).

Anal. Calcd. for $C_{25}H_{26}N_4O_4$: C, 67.3; H, 5.8. Found: C, 68.1; H, 6.4.

Hydrocarbon (XII). *(4,4a,6,6a,7,8,9,9a-octahydrotribenzo-[a,c,e]cycloheptatriene).* During 5 hr., 1.4 g. of XI and 2 g. of aluminium isopropoxide in 70 ml. of anhydrous isopropylalcohol were distilled slowly in a Vigreux column. After cooling, ice and concentrated hydrochloric acid was added and the product isolated by extraction with benzene. The product distilled at 140–145° (0.01 mm.); yield, 1 g. (78%). $\lambda_{\max}^{\mathrm{EtOH}}$ 234 mμ (log ϵ 4.00); 290 mμ (log ϵ 3.63).

Anal. Calcd. for $C_{19}H_{22}$: C, 91.2; H, 8.8. Found: C, 91.4; H, 8.6.

Tribenzocycloheptatriene (II). A mixture of the foregoing product (0.8 g.) and 10% palladium-charcoal (0.4 g.) was heated for 30 min. at 270–280°, for 20 min. at 290–310° and for 30 min. at 330°. 80% of the theoretical amount of hydrogen was collected. The product was extracted with benzene and the benzene residue triturated with ethanol, whereupon a white solid of m.p. 105–115° (0.3 g.; 40%) separated. Purification by chromatography on activated alumina with petroleum ether and recrystallization again from methanol raised the melting point to 121°. $\lambda_{\max}^{\mathrm{EtOH}}$ 239 mμ (log ϵ 4.59); 256 mμ (4.26; inflection). $\bar{\nu}_{\max}^{\mathrm{KBr}}$ (cm.$^{-1}$) 3100, 2900, 1475, 1441, 762, 758, 740.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.2; H, 5.8. Found: C, 94.6; H, 6.2.

1-Bromo-2,3,4,5,6,7-tribenzocyclohepta-2,4,6-triene. A mixture of 0.6 g. of tribenzocycloheptatriene (II), 0.3 g. of *N*-bromosuccinimide and 10 ml. of carbon tetrachloride was refluxed for 3 hr. in the presence of a trace of benzoyl peroxide. The filtered solution was evaporated and the residue triturated with petroleum ether and recrystallized from cyclohexane, m.p. 173–174°; yield, 0.5 g. (62%).

2,3,4,5,6,7-Tribenzocyclohepta-2,4,6-trien-1-one (XIII). A mixture of 0.3 g. of the foregoing compound in 10 ml. of acetone and of 4 ml. of a 5% aqueous solution of sodium carbonate was refluxed for 8 hr., the acetone evaporated and the residue extracted with benzene. The residue of the benzene solution was triturated with cyclohexane and the crude secondary alcohol (0.2 g.) oxidized as follows [the alcohol crystallized from aqueous methanol (80%) in white rods of m.p. 118°].

The solution of the product in 30 ml. of glacial acetic acid was refluxed for 1 hr. with a solution of 0.2 g. of sodium dichromate in 4 ml. of water. Water was added and the solid filtered and recrystallized from ethanol. M.p. 180° (lit.[13]: 178–179°); yield, 0.16 g. $\bar{\nu}_{\max}^{\mathrm{KBr}}$ 1667 cm.$^{-1}$; $\bar{\nu}_{\max}^{\mathrm{CHCl_3}}$ 1672 cm.$^{-1}$ (carbonyl): $\lambda_{\max}^{\mathrm{EtOH}}$ 239 mμ (log ϵ 4.43); 323 mμ (log ϵ 3.27).

Anal. Calcd. for $C_{19}H_{12}O$: C, 89.1; H, 4.7. Found: C, 88.8; H, 4.7. The orange-colored 2,4-dinitrophenylhydrazone had m.p. 260°, after recrystallization from butyl alcohol.

Anal. Calcd. for $C_{25}H_{16}N_4O_4$: C, 68.8; H, 3.7. Found: C, 68.4; H, 3.8.

1-Benzylidene-2,3,4,5,6,7-tribenzocyclohepta-2,4,6-triene (XIV). To a solution of benzylmagnesium chloride, prepared from 1.25 g. of benzyl chloride and 240 mg. of magnesium, 500 mg. of the foregoing ketone XIII in 10 ml. of benzene was added; the mixture was refluxed for 1.5 hr. and worked up as usual. The crude product was dissolved in petroleum ether and chromatographed on activated alumina (40 g.). Elution of the adsorbate with benzene gave 1-benzyl-1-hyroxy-2,3,4,5,6,7-tribenzocyclohepta-2,4,6-triene; the benzene was evaporated, the residue heated in toluene for 2 hr. in the presence of 0.1 g. of *p*-toluenesulfonic acid and the solution evaporated. The product was chromatographed from petroleum ether on activated alumina (40 g.) and eluted with petroleum ether in 30-ml. fractions. The fifth and sixth fraction contained a colorless solid of m.p. 150–152°; the melting point was raised to 152–153° by recrystallization from ethanol. The yield was 0.4 g.

Anal. Calcd. for $C_{25}H_{18}$: C, 94.3; H, 5.7. Found: C, 94.6; H, 5.6.

1-(β-Acetylvinyl)-2-phenylcyclohex-4-ene (XV). At −10°, a few drops of a solution of 1.4 g. of sodium in 45 ml. of

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[18] A. S. Wilds and C. Djerassi, *J. Am. Chem. Soc.*, **68**, 1715 (1946).

methanol were added to a solution of 19 g. of the aldehyde III in 150 ml. of anhydrous acetone. The temperature rose to 0°. When the temperature had fallen again to $-10°$, the balance of the sodium methoxide solution was added and the stirring continued for 30 min. at $-10°$ and for 1 hr. at 25°. The mixture was neutralized with dilute sulfuric acid, diluted with water, and extracted with benzene to yield 17 g. (74%), b.p. 175–177° (1 mm.); $\lambda_{\max}^{\mathrm{EtOH}}$ 292 mμ (log ε 3.40); $\bar{\nu}_{\max}^{\mathrm{liq.}}$ 1675 cm.$^{-1}$ (carbonyl).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.9; H, 8.0. Found: C, 84.3; H, 8.2.

The 2,4-dinitrophenylhydrazone precipitated as an oil which crystallized on trituration with butyl alcohol. From the same solvent or from ethanol, orange-red crystals, m.p. 112–114°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 385 mμ (log ε 4.45).

1-Butadienyl-2-phenylcyclohex-4-ene (XVI). The ketone IX (14 g.) was reduced in the usual manner with 14 g. of aluminum isopropoxide and 100 ml. of isopropyl alcohol. The product, which boiled at 150–153° (2 mm.) (yield, 8 g., 57%) showed in the infrared no residual carbonyl absorption and the hydroxyl band at 3400 cm.$^{-1}$ It was heated with 1.5 g. of freshly fused potassium hydrogen sulfate at 140° *in vacuo*. The desired diene distilled at 130–132° (3 mm.); yield, 4.2 g. (52%). $\lambda_{\max}^{\mathrm{EtOH}}$ 230 mμ (log ε 4.06); 292 mμ (log ε 2.72). $\bar{\nu}_{\max}^{\mathrm{liq}}$ (cm.$^{-1}$) 1600; 1650 (substituted butadiene);[19] 660 (terminal═CH$_2$).[20]

Anal. Calcd. for $C_{16}H_{18}$: C, 91.4; H, 8.6. Found: C, 91.4; H, 8.4.

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[19] W. Bruegel, *Einfuehrung in die Ultrarotspektroskopie* Steinkopff, Darmstadt, 1954, p. 272.

[20] R. S. Rasmussen, R. R. Brattain, and P. S. Zucco, *J. Chem. Phys.*, **15**, 135 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Attempts to Prepare Pyracylene. 1,2-Dihydropyracylene[1,2]

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The preparation of pyracene derivatives having eliminable functional groups on the five-membered rings and the attempted conversion of these to pyracylene is described. 1,2-Dihydropyracylene has been prepared by reaction of pyracene with chloranil or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Since the initiation of the work on the synthesis of pyracene[3] one of the objectives has been to obtain the conjugate-unsaturated nonalternant hydrocarbon pyracylene (I).[4] Our interest in this compound arose from two considerations. First, it would have a total of 14 π-electrons associated with a cyclocondensed ring structure in which 12 of the electrons could be viewed as being in the planar perimeter and 2 in the ethylene core of the molecule.[5] The molecule would thus be an important addition to the type exemplified by pleiadiene (II) and acepleiadylene (III)[6] and provide a further test for the various theories of electronic structure of complex molecules.[7] Further, Brown[8] has calculated the resonance energy of pyracylene to be about 88 kcal./mole as compared to values of 61 and 36 for naphthalene and benzene obtained by the same method. The value for pyracylene is probably incorrect because of the neglect of strain considerations in the calculations (herewith).

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[1] From the Ph.D. thesis of Robert G. Anderson.

[2] Support for a part of this work by contract DA-04-200-ORD-235 with the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

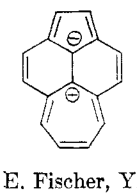
[3] A. G. Anderson, Jr. and R. H. Wade, *J. Am. Chem. Soc.*, **74**, 2274 (1952).

[4] The only report indicating the existence of pyracylene is that of S. H. Hastings, B. H. Johnson, and H. E. Lumpkin, *Anal. Chem.* **28**, 1243 (1956), who found that mass spectral data on a minor component of the aromatic fraction of virgin gas oil fit the molecular formula. Dibenzo[*a,g*]pyracylene and several of its derivatives are known; *cf.* E. Clar, *Ber.* **64**, 2199 (1931); B. P. Federov, *Bull. Acad. Sci., U. S. S. R. Classe Sci. Chem.*, 397 (1947); C. Dufraisse and R. Girard, *Bull. soc. chim., France* (5) **1**, 1359 (1934); C. Dufraisse, (5) **3**, 1857 (1936); C. Dufraisse and R. Horelois, (5) **3**, 1894 (1936); H. W. D. Stubbs and S. H. Tucker, *J. Chem. Soc.*, 2936 (1951).

[5] J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954); W. T. Simpson, *J. Chem. Phys.*, **17**, 1218 (1949).

[6] V. Boekelheide, W. E. Langeland, and C.-T. Liu, *J. Am. Chem. Soc.*, **73**, 2432 (1951); V. Boekelheide and G. K. Vick, *J. Am. Chem. Soc.*, **78**, 653 (1956).

[7] For a theoretical interpretation of the pleiadienes see J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 1261, 4217 (1956). Profs. H. J. Dauben and W. T. Simpson have suggested (private communication) that an explanation based on the valence bond method which is consistent with the observed chemical and spectral properties and with the molecular orbital description may be advanced. This derives from a qualitative consideration of the reasonable valence bond structures with the inclusion of the dipolar sesquifulvalenoid structure shown. Since calculations [B. Pullman, A. Pullman, E. D. Bergman, H. Berthod, E. Fischer, Y. Hirschberg, D. Lavie, and May Mayot, *Bull soc. chim. France*, **73** (1952)] indicate that the resonance stabilization of sesquifulvalene would be almost the same as that of naphthalene, the sesquifulvalenoid and naphthalenoid structures would be expected to contribute almost equally to the hybrid (strain will be the same in both types of structure).



[8] R. D. Brown, *J. Chem. Soc.*, 2391 (1951). The molecular orbital method with overlap was used.