[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Macro Rings. V. Transannular Effects in the 1,4-Decamethylenebenzene Series[1]

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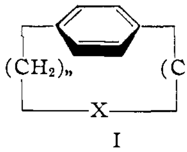
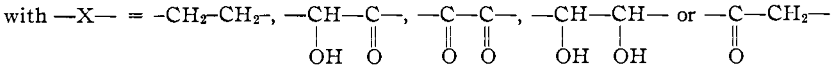


I

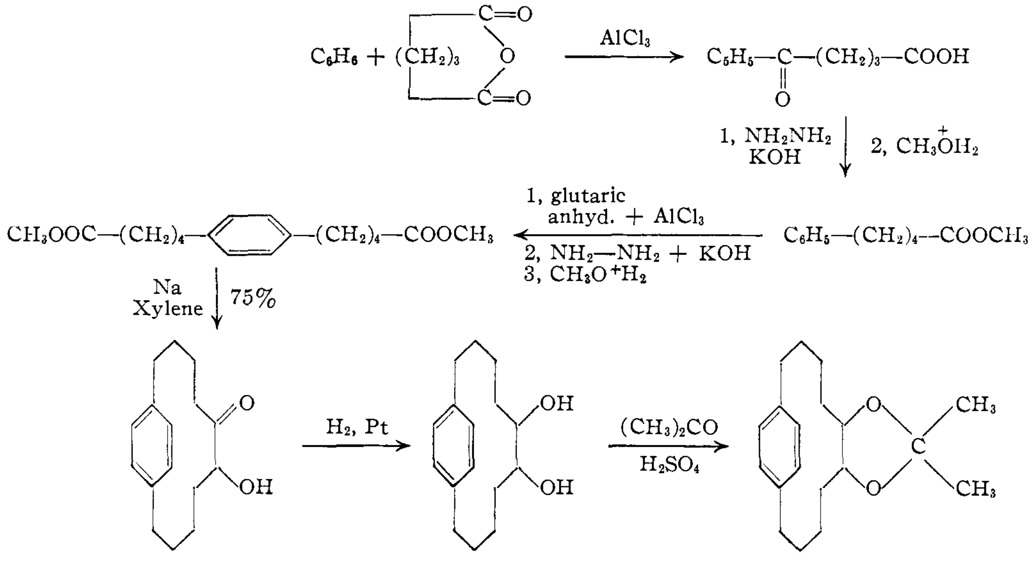
The preparation, reactions and physical properties are described for system I ($n = m = 4$) and allied compounds. The unique characteristics of this system are discussed in terms of the steric and electronic influences of the aromatic system on X.



with $—X— = -CH_2-CH_2-$, $—\underset{OH}{CH}—\underset{O}{\overset{\|}{C}}—$, $—\underset{O}{\overset{\|}{C}}—\underset{O}{\overset{\|}{C}}—$, $—\underset{OH}{CH}—\underset{OH}{CH}—$ or $—\underset{O}{\overset{\|}{C}}—CH_2—$

As part of a general investigation of transannular effects,[2] the construction of a system (I) has been undertaken that permits an evaluation of the effects of a phenyl group on a function which is held by methylene chains directly over the face of the π-electron cloud thrusting out from the aromatic ring. As a preliminary to the study of the substitution, elimination, rearrangement and addition reactions in this system, the synthesis and characterization of a number of compounds of general structure I ($n = m = 4$) are reported here along with a number of novel observations attributable to the peculiar relative geometry of the phenyl and X functions.

The parent cyclic compound III has previously been synthesized[3] by the acyloin ring closure of II, which in the present work was prepared by the route shown (formulas). The only poor step in the sequence is the second Friedel–Crafts reaction, (50% yield), and the over-all yield to II amounts to 35%. Another approach to the preparation of II was also tried (see formulas) through an adaptation of the procedures of Gardner, *et al.*,[5] to the problem at hand, but this synthesis was not developed because of poor yields. The two samples of the diacid VI were demonstrated to be identical through mixed melting point comparisons. Acyloin III (an oil) was characterized as its crystalline acetate and acetate semicarbazone. Catalytic reduction of this acyloin gave two diols (IVa and IVb) that were separated by a combination of chromatographic and fractional crystallization techniques, IVb being purified through the bis-*p*-nitrobenzoate derivative. Both diols were characterized by the preparation of their respective acetonides, Va and Vb, and their bis-*p*-nitrobenzoates.



III IVa, m.p. 101–102° b, m.p. 102–103° Va, m.p. 61.5–62.5° b, m.p. 84–85.5°

Oxidation of the acyloin III with bismuth oxide[6] gave a mixture of yellow diketone VII and colorless enol-ketone VIII as two distinct stable compounds along with small amounts of the diacid VI. The two isomers (VII and VIII) were separated by fractional crystallization, and each was found to be convertible to a mixture of the two in a solution of acetone and hydrochloric acid, the composition of the equilibrium mixture being estimated as about one to one. The diketo isomer VII possesses an infrared spectrum with λ_{max} 5.84 μ (carbonyl groups) and no bands below 3 μ, whereas the enol-ketone

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(1) This research was generously supported by the Upjohn Company.

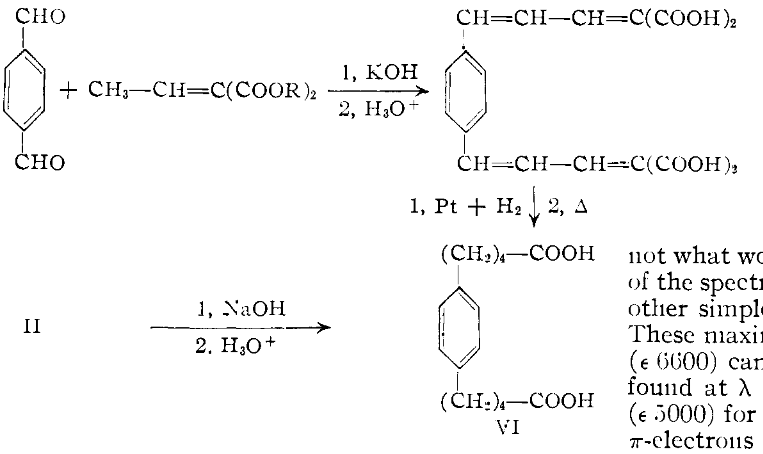
(2) See paper III in this series for a summary of recent references [D. J. Cram and N. L. Allinger, THIS JOURNAL, **76**, 726 (1954)].

(3) K. Wiesner, D. M. McDonald, R. B. Ingram and R. B. Kelly, *Can. J. Research*, **B28**, 561 (1950).

(4) To the authors' knowledge, only one other example of a Friedel–Crafts reaction involving an aromatic ester as starting material is known [L. F. Fieser and H. Heyman, THIS JOURNAL, **63**, 2333 (1941)].

(5) P. D. Gardner, W. J. Horton, G. Thompson and R. R. Twelves, *ibid.*, **74**, 5527 (1952).

(6) W. Rigby, *J. Chem. Soc.*, 793 (1951).



VIII has bands at 2.93 μ (O-H stretching), 6.14 μ (>C=C< stretching), and a shoulder at 6.04 μ (>C=O stretching).[7] With ferric chloride solution the enol-ketone gave an immediate dark green color whereas the diketone under the same conditions gave at first no color at all, but over a period of one-half hour the same green color developed. Both isomers reacted with *o*-phenylenediamine to give quinoxaline IX, with acetic anhydride to give the enol-acetate and with *p*-nitrobenzoyl chloride to give the enol-*p*-nitrobenzoate. The diketo isomer VII gave two derivatives when treated with dinitrophenylhydrazine in alcoholic hydrochloric acid, the bis- and monodinitrophenylhydrazones.

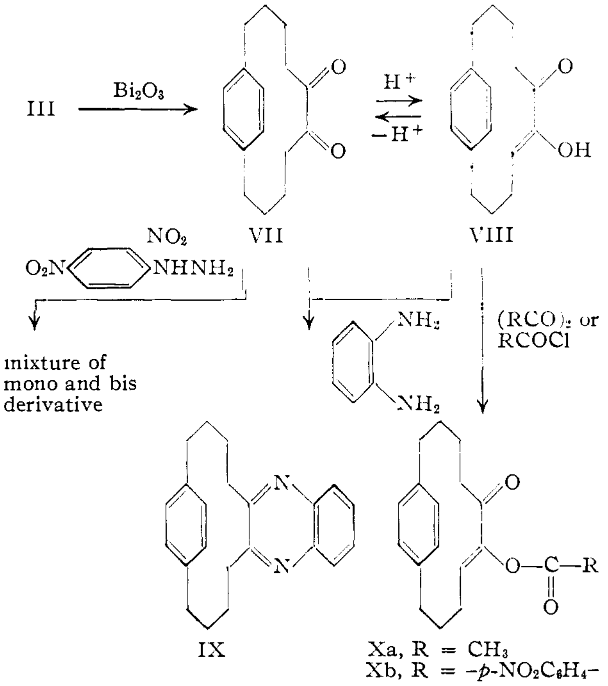
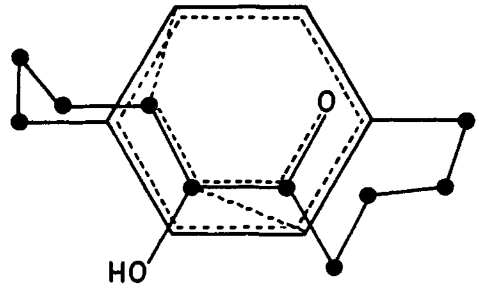


Figure 1 records the ultraviolet absorption spectrum of the diketone VII, of the enol-ketone VIII and of the acetate derivative Xa. The broad maximum at 419 mμ (log ε 1.17) in the spectrum of VII due to the 1,2-dicarbonyl function indicates that the two carbonyl groups are nearly in the same plane, either *cis* or *trans* to one another.[8] Molecular models of these two configurations indicate that both arrangements are sterically compatible. The band characteristic of α-diketones at 295–300 mμ (ε 30–50) is obscured by the end absorption of the aromatic system also present in VII.[9]

The spectrum of enol-ketone VIII is not what would be expected by the simple addition of the spectrum of the aromatic system[9] with that of other simple α-hydroxy-α,β-unsaturated ketones.[10] These maxima at λ 223 mμ (ε 8100) and λ 270 mμ (ε 6600) can be calculated and compared to maxima found at λ 226 (ε 9100), λ 269 (ε 5450) and λ 283 (ε 5000) for VIII. Again as in previous cases[11] the π-electrons of the two chain-insulated unsaturated systems appear to interact to produce transannular electronic effects. In every case, the absorption bands have moved to longer wave lengths and somewhat lower intensities. The molecular geometry of VIII suggests that the resonance hybrid might be roughly represented by structure XI.[12] The spectrum of the keto-enol acetate (Xa) also appears to be abnormal, probably for the same reasons.



XI

In attempts to obtain the α,β-unsaturated ketone, the acyloin acetate (Xa) was pyrolyzed at 260° (5 hours), and although the starting material decomposed, no ketonic material could be isolated. In a further attempt, the acyloin III was passed over hot alumina according to a procedure that has proved successful in other systems.[13] About 70% of the starting material went to resin, the other 30% yielding a mixture of hydrocarbons from which was isolated pyrene (XII) (characterized by its ultra-

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[7] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, This Journal, **71**, 1068 (1949).

[8] N. J. Leonard and P. M. Mader, *ibid.*, **72**, 5388 (1950).

[9] The spectrum of 1,4-decamethylenebenzene is recorded in Fig. 2, and will be discussed in a later paper of this series.

[10] L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 1949, p. 194; L. Ruzicka and O. Jeger, *Helv. Chim. Acta*, **24**, 1182 (1941); L. Ruzicka, O. Jeger and P. Ringnes, *ibid.*, **27**, 972 (1944); L. Ruzicka, O. Jeger and J. Norymberski, *ibid.*, **27**, 1187 (1944); E. T. Stiller and O. Rosenheim, *J. Chem. Soc.*, 353 (1938); A. Stoll, D. Stauffacher and E. Seebeck, *Helv. Chim. Acta*, **36**, 2027 (1953).

[11] (a) E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 607 (1949); J. C. Lunt and F. Sondheimer, *ibid.*, 3361 (1950); (b) P. D. Bartlett and E. S. Lewis, This Journal, **72**, 1005 (1950); (c) D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951); (d) W. D. Kumler, L. A. Strait and E. L. Alpen, *ibid.*, **72**, 1463, 4558 (1950); D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952); W. B. Bennet and A. Burger, *ibid.*, **75**, 84 (1953).

[12] L. J. Andrews and R. M. Keefer [*ibid.*, **75**, 3776 (1953)] have recently found that the ultraviolet absorption spectra of dienophiles in benzene show new maxima at about 280 mμ (ε 1000 to 2000) due to a one to one complexing between the dienophiles and benzene [see also W. G. Barb, *Trans. Faraday Soc.*, **49**, 143 (1953)].

[13] M. Stoll, *Helv. Chim. Acta*, **30**, 1837 (1947).

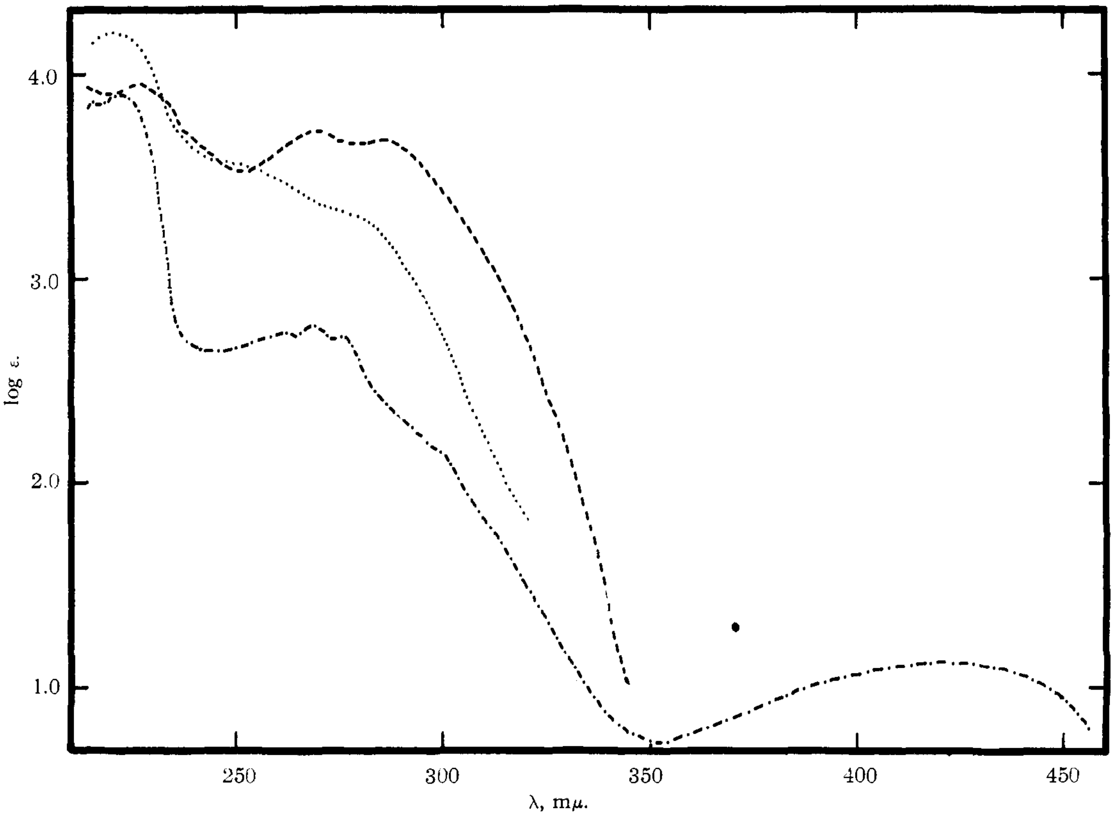
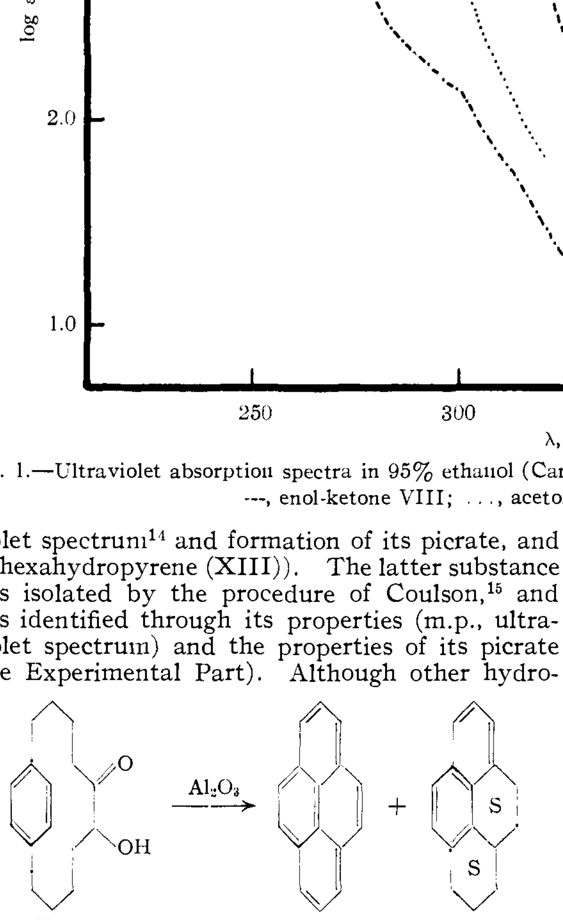


Fig. 1.—Ultraviolet absorption spectra in 95% ethanol (Cary recording spectrophotometer, model 11 PMS, quartz cells): ---, enol-ketone VIII; . . . , acetoxy-ketone XA; —·—, diketone VII.

violet spectrum[14] and formation of its picrate, and *as*-hexahydropyrene (XIII)). The latter substance was isolated by the procedure of Coulson,[15] and was identified through its properties (m.p., ultraviolet spectrum) and the properties of its picrate (see Experimental Part). Although other hydrocarbons were present, they were not isolated in a pure state. Treatment of the original distillable hydrocarbon mixture from the attempted dehydration with hot 10% palladium-on-charcoal gave an over-all yield of 6% pyrene.



III XII XIII

The above reaction represents a transannular aromatic substitution,[16] which could have taken place through an initial Diels–Alder reaction followed by aromatization, or by two successive electrophilic substitutions on benzene followed by aromatization. The stoichiometry of the system is such that XIII could have been formed only by the loss of one mole of hydrogen, and XII with the loss of four moles.

Three general methods of converting acyloins to simple ketones were applied to XII with somewhat unexpected results. In the first method,[17] XII was treated with zinc and hydrochloric acid in acetic acid. Chromatographic treatment of the products gave a 73% yield of hydrocarbon eluted with pentane, and 11% yield of an oil eluted with benzene which gave a positive carbonyl reaction. Fractional distillation of the hydrocarbon fraction indicated the presence of 1,4-decamethylenebenzene as the major component contaminated with other hydrocarbons with similar boiling points. The material was hydrogenated over platinum in acetic acid to give bicyclo-(10,2,2)-hexadecane (XIV), obtained as a pure crystalline compound (m.p. 13–14°) of probable *cis* configuration.[18] Dehydrogenation of this material gave what we consider to be pure 1,4-decamethylenebenzene (XV).[19] No trace of pyrene was present, which easily could have been detected in the ultraviolet spectrum. Dehydrogenation of the hydrocarbon impurities from the crystallization of XIV gave a small amount of pyrene, as did one of the fractions obtained on distillation of the original hydrocarbon mixture. It is probable that the hydropyrene ring system was formed during the treatment of acyloin III with

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[14] E. Clar, *Ber.*, **69**, 1671 (1936).

[15] E. A. Coulson, *J. Chem. Soc.*, 1298 (1937).

[16] See also W. Baker, F. Glockline and J. F. W. McOmie, *ibid.*, 1118 (1951).

[17] V. Prelog, K. Schenker and H. H. Gunthard, *Helv. Chim. Acta*, **35**, 1598 (1952). This reaction was also carried out by Wiesner, *et al.* (ref. 3), who obtained a 68% yield of hydrocarbon and 30% of carbonyl containing compound.

[18] O. Miller, *Bull. soc. chim. belg.*, **44**, 513 (1935).

[19] Experience with similar compounds indicates that these types of dehydrogenations can be carried out in almost quantitative yields (ref. 2).

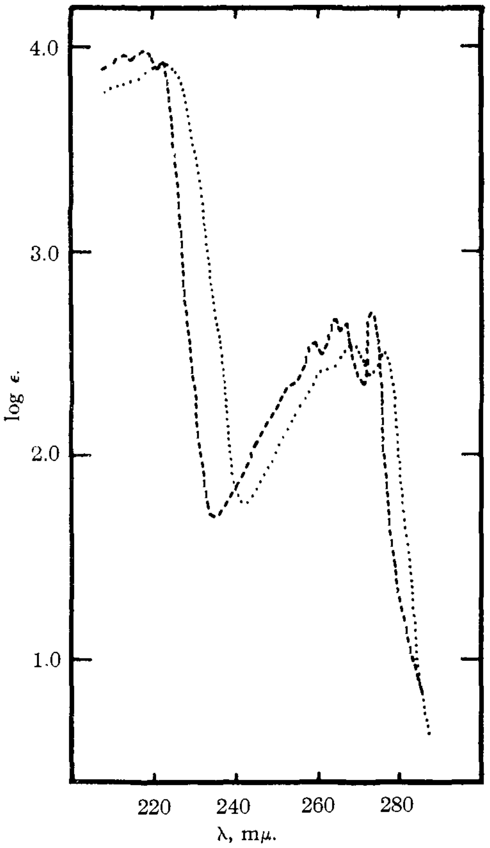
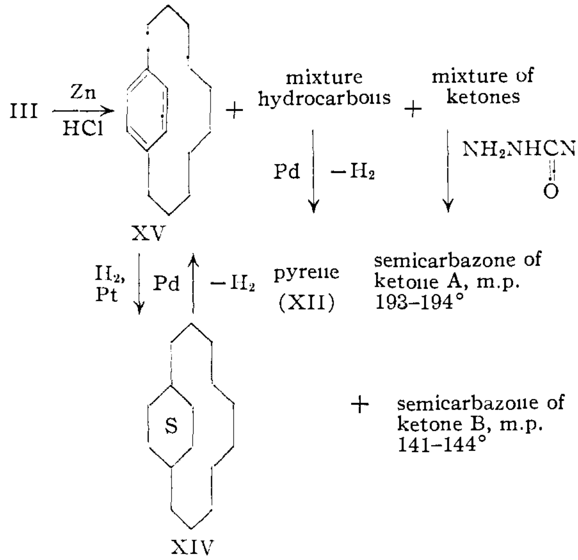
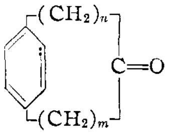


Fig. 2.—Ultraviolet absorption spectra in 95% ethanol (Cary recording spectrophotometer, model 11 PMS, quartz cells): ---, 1,4-bis-(*n*-pentyl)-benzene (XVII); ..., 1,4-decamethylenebenzene (XV).

acid by a double transannular electrophilic substitution reaction, and that this polycyclic hydrocarbon was converted to pyrene with palladium.



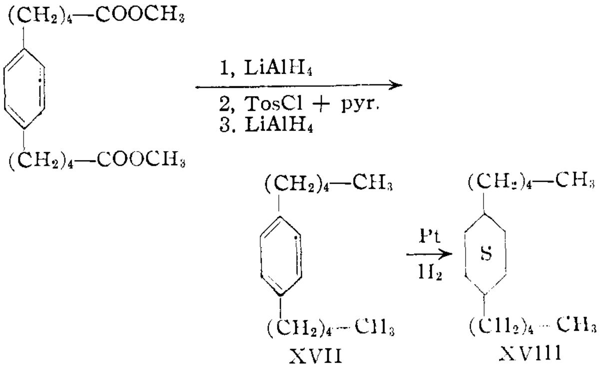
The ketone fraction from the original zinc reduction reaction was converted to a mixture of semicarbazones from which were isolated two materials, semicarbazones A and B, the latter of which corresponds in properties with that prepared by the above reaction sequence by Wiesner, *et al.*[3] (derivative A was not reported by these authors). Hydrolysis of semicarbazone A gave ketone a, whose infrared and ultraviolet spectra are consistent with structure XVI. Hydrolysis of semicarbazone B gave ketone b, m.p. 34–37°, whose melting point was raised by admixture with ketone a to 49–51°. The definite presence of ketone a in b was demonstrated by the isolation of the 2,4-dinitrophenylhydrazone of A when ketone b was treated with the hydrazine reagent.



$n + m = 9$
XVIa, (m.p. 57.5–58.5°)
c, (m.p. 13–14.5°)

A second method of transforming acyloin III to simple ketone was tried using zinc and dry hydrogen chloride in dioxane,[20] and resulted in a 45% yield of hydrocarbon and 24% yield of ketonic material isolated as its semicarbazone, and purified as its 2,4-dinitrophenylhydrazone. The same ketone was produced by the reduction of the acetate of III with zinc and acid by a third method,[21] but in only very poor yields. This ketone (c) was obtained as its semicarbazone (m.p. 177–178°) and proved to be different from either ketone a or b as shown by its m.p. (13–14.5°), and the melting points of both its semicarbazone and 2,4-dinitrophenylhydrazone. Its analysis, mode of preparation and infrared spectrum are all compatible with structure XVI. The substance is distinctly different from either ketone a or b as shown by its physical properties and those of its derivatives (see Experimental Part).

For purposes of spectral comparisons, 1,4-bis-(*n*-pentyl)-benzene (XVII) and the corresponding cyclohexyl compound (XVIII) were prepared (see formulas), and Fig. 2 records the ultraviolet spectrum of XVII along with that of 1,4-decamethylenebenzene (XV). The differences between these two compounds although small are nevertheless distinct,[9] and can be used to differentiate cycles of this type from non-cycles, as indicated in the data of Table I. Thus all of the cycles of Table I have spectra almost identical with one another (ketone XVIa is an exception), and slightly different from



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[20] Firmenich and Co., British Patent 663,183 (1951) or *C. A.*, **47**, 608 (1953).

[21] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4223 (1952).

that of the open chain model. These spectra suggest that ketone XVIc is the expected 1,4-(5′-ketodecamethylene)-benzene, and that ketone XVIa possesses an anomalous structure. However, definitive structural assignments to these two ketones must await further work.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRAL DATA[a]

Compound	Max. in mμ (log ε)			
1,4-Di-*n*-pentylbenzene (XVII)[b]	273.5 (2.69)	267.5 (2.64)	265 (2.66)	223.5 (3.90)
1,4-Decamethylenebenzene (XV)	276.5 (2.505)	268.5 (2.54)	263[c] (2.415)	223 (3.91)
1,4-(5′-Keto-6′-acetoxy)-decamethylenebenzene	2.76 (2.56)	269 (2.58)	263[c] (2.47)	223 (3.91)
Ketone a (XVIa)	274 (2.50)	266.5 (2.53)	266[c] (2.41)	222.5 (3.85)
Ketone b	274.5 (2.49)	267.5 (2.55)	261[c] (2.43)	223 (3.88)
Ketone c (XVIc)	276 (2.50)	268.5 (2.54)	263[c] (2.43)	223 (3.89)
Diol (IVa)	276 (2.50)	268.5 (2.53)	262[c] (2.42)	223 (3.94)
Diol (IVb)	276.2 (2.49)	269 (2.53)	262.5[c] (2.41)	223 (3.92)
Acetonide (Va)	276 (2.535)	269 (2.56)	262[c] (2.44)	223 (3.93)
Acetonide (Vb)	267.5 (2.50)	268 (2.58)	262.5[c] (2.47)	223 (3.94)

[a] Taken in 95% ethanol on a Cary Spectrophotometer (model 11PMS). [b] Other maxima occur at 259.5 (2.54), 219.5 (3.97) and 214 (3.94), with a shoulder at 254 (2.35). [c] Shoulder.

It is interesting to compare the infrared spectra of 1,4-decamethylenebenzene (XV) and *cis*-bicyclo-(10,2,2)-hexadecane (XIV) with those of the open chain analogs, 1,4-bis-(*n*-pentyl)-benzene (XVII) and 1,4-bis-(*n*-pentyl)-cyclohexene (XVIII), respectively. Both bicyclic compounds show a weak band at 3.74 μ which is absent in the spectra of the two open chain compounds. The spectrum of 1,4-decamethylenebenzene possesses a weak band at 6.15 μ which is not visible in those of the other three hydrocarbons. That this band is not due to an impurity is demonstrated by its presence with the same intensity in the spectra of a number of different samples of the cycle which were prepared by different routes (*e.g.*, by reduction of the acyloin and dehydrogenation of the saturated hydrocarbon). The spectra in the 7–8 μ region (associated with methylene groups) is complicated with more bands in the cycles than in the non-cycles. This phenomenon appears to be generally present in the spectra of medium sized rings as compared to their open chain analogs.[17] In the present case, the same thing is true for the whole fingerprint region.

Experimental Part

Ethyl δ-Phenylvalerate.—From 1240 ml. of pure benzene, 750 g. of anhydrous sublimed aluminum chloride and 287 g. of glutaric anhydride (m.p. 53–55°) was prepared crude γ-benzoylbutyric acid (m.p. 125–127°)[22] which was reduced directly to δ-phenylvaleric acid as follows.[23] The crude, wet keto-acid was added to a mixture of 2 l. of diethylene glycol, 320 g. of 85% hydrazine hydrate and 500 g. of potassium hydroxide. The resulting solution was held at reflux at 150–160° for three hours, and then the excess hydrazine and water was allowed to distil until the temperature reached 220°. The bath temperature was maintained at this point for six hours, the mixture was cooled and mixed with 2.5 l. of water. The resulting mixture was heated at 100° until homogeneous, given a charcoal decolorizing treatment, and acidified with 5.7 l. of 4 *N* hydrochloric acid. The product that separated was twice recrystallized from pentane to give 405.5 g. (90% yield, over-all) of δ-phenylvaleric acid, m.p. 58–59.5° (lit. m.p. 58–59°[24]). A solution of 208 g. of this acid and 30 g. of concentrated sulfuric acid in 300 ml. of absolute ethyl alcohol was held at reflux for three hours, and then 120 ml. of ethanol was distilled. To the cooled mixture was added 500 ml. of water containing the calculated amount of sodium carbonate to neutralize the sulfuric acid. The mixture was extracted with ether, the ether was washed with water, dried and evaporated. The residue was distilled at 13 mm., wt. 226 g. of colorless oil (94% yield), b.p. 151–152°.

γ-(4-δ-Valeric Acid)-benzoylbutyric Acid.—To a stirred solution of 10 g. of ethyl δ-phenylvalerate (use of the acid lowers the yield drastically) and 5.7 g. of glutaric anhydride dissolved in 70 ml. of twice-distilled tetrachloroethane held at −5° in a salt–ice-bath was added portionwise (two hours) 20 g. of anhydrous sublimed aluminum chloride. The temperature was not allowed to rise above −5°. The resulting yellow solution was stirred for another four hours below 0° and then at room temperature for 36 hours. Ice (24 g.) and 7.5 ml. of concentrated hydrochloric acid were then added, the layers were separated, and the aqueous layer was washed with ether. The combined organic layers were washed with water, dried and the solvent was distilled under vacuum. The residual yellow oil was held at reflux for one hour with 100 ml. of 10% potassium hydroxide in methanol. A white precipitate (dipotassium salt of the desired keto-diacid) separated when the solution was cooled to 0° which was collected, dissolved in 130 ml. of water and decolorized with charcoal. To the resulting colorless solution was added 24 ml. of concentrated hydrochloric acid; the mixture was cooled to 0° and the acid collected and dried. Recrystallization of this material from ethanol gave 7.5 g. of the diacid, m.p. 173–177°, yield 52%. Recrystallization of a small sample of this acid (three times) gave material m.p. 177–178.5°.

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90; neut. equiv., 146. Found: C, 65.53; H, 7.02; neut. equiv., 146.

In a larger run 90 g. of ethyl δ-phenylvalerate was converted to 154 g. of the dipotassium salt of γ-(4-δ-valeric acid)-benzoylbutyric acid, and this material was used directly in the next step (see below).

***p*-Phenylene-bis-(δ-valeric Acid) (VI).**—The dipotassium salt of γ-(4-δ-valeric acid)-benzoylbutyric acid (154 g.) was added to a mixture of 350 ml. of diethylene glycol, 54 g. of 85% hydrazine hydrate and 56 g. of potassium hydroxide. The mixture was held at reflux for 2.5 hours at 150°, and then water and excess hydrazine hydrate was allowed to escape until the temperature reached 195°, where it was held for six hours. The solution was then cooled, diluted with 1200 ml. of water and given a charcoal treatment. The dark red solution was neutralized with concentrated hydrochloric acid, the resulting mixture was cooled to 0° and the acid was collected, washed well with water and dried in vacuum over solid potassium hydroxide. This crude material (91 g., m.p. 155–178°, 75% yield based on ethyl δ-phenylvalerate) was recrystallized twice from 95% ethanol to give 60 g. of the diacid (50% over-all yield from mono acid), m.p. 176–180°. A small sample was recrystallized twice from ethanol, m.p. 179–182°.[25]

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97; neut. equiv., 139. Found: C, 69.48; H, 8.14; neut. equiv., 140, 138.6.

Dimethyl *p*-Phenylene-bis-(δ-valerate) (II).—A mixture of 56.5 g. of *p*-phenylene-bis-(δ-valeric acid), 50 ml. of absolute methanol, 120 ml. of ethylene dichloride and 0.5 g. of concentrated sulfuric acid was held at reflux for eight hours. The mixture was cooled, washed with water, 5% aqueous

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(22) Procedure was essentially that described in "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 81.

(23) Procedure patterned after that of Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(24) J. von Braun and H. Deutsch, *Ber.*, **45**, 2178 (1912).

(25) This material was still somewhat colored and further recrystallization did not improve the melting point. Purer diacid (m.p. 183.5–184.5°) was obtained by saponification of the diester (see below).

sodium bicarbonate solution and twice again with water. The organic layer was dried, and the solvent was evaporated. The oily residue was distilled twice, b.p. 182–184° (0.4 mm.), wt. 52.3 g. (83% yield). The distillate solidified at 0°, m.p. 23°; three recrystallizations from pentane did not change the melting point.

Anal. Calcd. for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.57; H, 8.28.

Saponification of a small amount of this material gave a pure sample of diacid, m.p. 183.5–184.5°.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 68.04; H, 7.97. Found: C, 68.99; H, 8.04.

1,4-(5′-Hydroxy-6′-ketodecamethylene)-benzene (III).—A solution of 61 g. of diester II in 600 ml. of pure, dry xylene was added over a period of 44 hours to 20 g. of sodium stirred at 8000 r.p.m. in 2 l. of boiling xylene.[26] The reaction product was purified by distillation in an atmosphere of pure, dry nitrogen, b.p. 158–161° (0.4 mm.), wt. 37 g. (75% yield).

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.10; H, 9.08.

1,4-(5′-Acetoxy-6′-ketodecamethylene)-benzene.—A solution of 25 g. of acyloin (III), 75 ml. of pure acetic anhydride and 125 ml. of pyridine was heated at 100° for five minutes on a steam-bath and allowed to stand at 25° for eight hours. The oily residue was shaken with a mixture of ether and water, the ether layer was washed with dilute acid, dilute base and finally twice with water. The organic layer was dried, the ether was evaporated and the residual oil solidified. This solid was recrystallized twice from pentane to give 25 g. (85% yield) of acetate, m.p. 47–49°.

Anal. Calcd. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.05; H, 8.42.

Semicarbazone of 1,4-(5′-Acetoxy-6′-ketodecamethylene)-benzene.—Semicarbazide hydrochloride (4.0 g.) and crystalline sodium acetate (7.0 g.) were ground in a mortar until a liquid was obtained. Absolute methanol (20 ml.) was added, and the well-mixed suspension was filtered. The residue was washed with 10 ml. of absolute methanol. To the solution of semicarbazide acetate was added 5 g. of the acyloin acetate, and the mixture was warmed until a clear solution resulted. After standing at room temperature for eight hours, the solution was evaporated, and the remaining solid residue was washed with sodium carbonate solution and water. The material was recrystallized from 200 ml. of methanol to give 5.4 g. (90% yield) of colorless crystals, m.p. 190–192° dec.

Anal. Calcd. for $C_{19}H_{27}O_3N_3$: C, 66.06; H, 7.88. Found: C, 65.89; H, 7.73.

1,4-(5′,6′-Diketodecamethylene)-benzene (VII) and its Tautomer VIII.—To a solution of 10 g. of the acyloin III in 40 ml. of glacial acetic acid was added 7.55 g. of bismuth oxide.[6] The mixture turned black immediately when heated to 100°. After being held at this temperature under vigorous stirring for 45 minutes, the mixture was cooled, filtered and to the filtrate was added 50 ml. of water. This mixture was then extracted three times with benzene and the combined benzene layers were washed with 5% aqueous sodium bicarbonate solution and twice with water. The solution was dried and the solvent was evaporated in vacuum under nitrogen to give 9.5 g. of yellow oil which solidified when allowed to stand. This material when recrystallized from ether gave 1.7 g. of yellow crystals, m.p. 108–112°, which when crystallized three more times from ether gave m.p. 110.5–112.5°. From the initial mother liquor was obtained a second crop of 2.5 g. of a mixture of yellow and colorless crystals, m.p. 90–98°. Of these two components, the yellow isomer was the more insoluble, but the colorless one crystallized faster, and making use of these properties a total of 1.5 g. of the yellow diketone VII, m.p. 110.5–112.5 (big rectangular plates) and 0.6 g. of colorless enol ketone VIII, m.p. 98.5–100.5°, were obtained. The diketone gave a dark green color with ferric chloride only after standing for about 30 minutes in aqueous alcohol solution. Its infrared spectrum in methylene dichloride showed no band from 1.8–3.0 μ, but a strong carbonyl band at 5.84 μ.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.81; H, 8.25.

The enol ketone VII gave an immediate dark green color with ferric chloride. Its infrared spectrum in methylene dichloride gave the following bands: strong band at 293 μ due to –OH; strong band at 6.14 μ (due to >C=C<) with a broad shoulder at 6.04 μ (due to >C=O); strong band at 8.13 μ (due to >C=C—O—).

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.34, 78.17; H, 7.34, 8.75.

Chromatographic examination of the filtrates from the above crystallizations revealed the presence of *p*-phenylene-bis-(δ-valeric acid).

Equilibration of the Diketone VII and the Enol Ketone VIII.—A solution of 0.105 g. of VII in 10 ml. of acetone and 3 drops of concentrated hydrochloric acid was held at reflux for four hours. The mixture was cooled, diluted with water and extracted with ether. The ether layer was washed with sodium bicarbonate solution, twice with water, was dried, and the solvent was evaporated. The crystalline residue was a mixture of colorless and yellow crystals, which were separated by fractional crystallization from ether to give diketone VII, m.p. 110–112° (m.m.p. with authentic material, 110.5–112.5°) and enol ketone VIII, m.p. 95–98° (m.m.p. with authentic material, 100–101°). A completely analogous result was obtained when enol ketone VIII was substituted as starting material.

Derivatives of Diketone VII and Enol Ketone VIII. Quinoxaline (IX).—The cyclic diketone (0.101 g.) and *o*-phenylenediamine (0.104 g.) were dissolved in 5 ml. of glacial acetic acid, and the solution was held at reflux for one hour. To the cooled solution was added 10 ml. of water, and the resulting mixture was cooled to 0°. The solid that separated was collected, dried and recrystallized from ethanol to give 0.080 g. of slightly yellow quinoxaline (IX), m.p. 100–101°.

Anal. Calcd. for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.58; H, 7.63; N, 8.88.

The ultraviolet absorption spectrum (95% alcohol) of IX was as follows: λ_{max} 237 mμ (log ε 4.51), 270 mμ (log ε 3.45), 277.5 mμ (log ε 3.46), 318 mμ (log ε 3.92); $\lambda_{shoulder}$ 262 mμ (log ε 3.44), 310 mμ (log ε 3.85).

The above procedure when applied to enol ketone VIII gave identical results.

Dinitrophenylhydrazones.—The cyclic diketone (0.100 g.), 2,4-dinitrophenylhydrazine (0.400 g.), 1 ml. of concentrated hydrochloric acid and 10 ml. of absolute ethanol were mixed and heated at 100° for ten minutes. After standing at 25° for 12 hours, the solution deposited a pink precipitate which was collected. This material was added to 5 ml. of boiling ethanol in which it partially dissolved. The insoluble material was recrystallized three times from a one-to-one alcohol–chloroform mixture to give red crystals, m.p. 260–300° dec. This material analyzes for the bis-2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_{28}H_{28}N_8O_8$: C, 55.62; H, 4.67. Found: C, 55.76; H, 4.87.

The alcohol-soluble portion crystallized when the alcohol solution was cooled, and the orange needles were twice recrystallized from ethanol, m.p. 229–230° dec. This material analyzed for the monodinitrophenylhydrazone of VII, slightly contaminated with bis-derivative.

Anal. Calcd. for $C_{22}H_{24}O_5N_4$: C, 62.25; H, 5.70. Found: C, 61.65; H, 5.65.

The infrared spectrum of this material (nujol mull) gave one strong band at 5.91 μ (probably the free >C=O group) and no detectable band in the 3 μ region. Attempts to obtain crystalline hydrazones of the diketone VII failed.

***p*-Nitrobenzoate (Xb).**—A mixture of cyclic diketone (0.055 g.) *p*-nitrobenzoyl chloride (0.057 g.) and 0.5 ml. of dry pyridine was heated at 100° for 30 minutes, and after the solution cooled, 5 ml. of 5% aqueous sodium carbonate solution was added. The oil that separated crystallized at 0°, and the solid was collected and recrystallized four times from absolute ethanol to give colorless needles, m.p. 122–122.5°.

Anal. Calcd. for $C_{22}H_{23}O_6N$: C, 70.21; H, 5.89. Found: C, 70.10; H, 6.05.

A similar treatment of enol ketone VIII gave identical results.

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[26] This procedure is described in detail in paper I of this series; D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5702 (1951). See also ref. 3.

Keto-enol Acetate (Xa).—A mixture of cyclic diketone (0.20 g.), 5 ml. of acetic anhydride and 5 ml. of dry pyridine was heated at 120° for five hours. The solution was then evaporated to dryness and the residue was dissolved in acetone, and the mixture was filtered from a small amount of black residue. The red solution was then passed through 3 g. of neutral alumina and the yellow solution resulting was evaporated. The solid that separated was recrystallized three times from ether–pentane to give 0.18 g. of colorless plates, m.p. 107–107.5°.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 75.49; H, 7.74. Found: C, 75.14; H, 7.72.

The infrared spectrum (in methylene dichloride) gave strong bands at 5.68 μ ($\text{O–}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{–CH}_3$), 5.94 μ (>C=O), 8.16 μ (C–O–C) and a weak shoulder at 6.06 μ (probably >C=C<).

A similar treatment of the enol ketone VIII gave identical results.

1,4-(5′,6′-Dihydroxydecamethylene)-benzene (Isomer IVa and IVb).—The acyloin (III) (5.0 g.) was dissolved in 50 ml. of ethanol and shaken with 0.250 g. of platinum oxide under a hydrogen atmosphere. Within 30 minutes the hydrogen was no longer absorbed (0.11 mole), and the solution was filtered and evaporated. The resulting colorless oil (5.0 g.) crystallized on standing, m.p. 85–95°, and three recrystallizations of this material from chloroform–ether (one-to-six) gave 2.6 g. (52% yield) of colorless crystals, m.p. 99.5–101°. Three more crystallizations from ether gave needles, m.p. 101–102°.[27] This material was sublimed at 95° (0.05 mm.) to give an anhydrous sample for analysis.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.25; H, 9.53.

The infrared spectrum of this material (8% solution in methylene dichloride) was as follows: 2.77 μ (s) attributable to OH, doublet at 9.47 μ (s) and 9.75 μ (m) attributable to $>\overset{|}{\text{C}}\text{–O–}$, doublet at 6.58 μ (w) and 6.83 μ (m) due to phenyl.

The mother liquors from the first three recrystallizations of IVa were evaporated to give 2.8 g. of material that was chromatographed on 90 g. of neutral alumina (activity II/III),[28] the column eluate being cut into 28 100-ml. fractions. Fractions 1–5 with benzene, fractions 6–8 with 9-to-1 benzene–ether, fractions 9–10 with 4-to-1 benzene–ether, fractions 11–13 with ether, fractions 14–15 with 9-to-1 ether–chloroform, fractions 16–18 with 4-to-1 ether–chloroform and fractions 19–21 with chloroform contained only traces of material. The subsequent fractions contained the following amounts of material: 22 (chloroform–methanol, 9:1), 0.090 g.; 23 (same), 0.158 g.; 24 (same), 0.090 g.; 25 (chloroform–methanol, 4:1), 0.080 g.; 26 (same), 0.030 g.; 27 (methanol), 0.040 g.; 28 (same), 0.050 g. This material in fractions 22 and 23 was recrystallized from ether to give 1.16 g. of diol IVa, m.p. 100.5–102° (undepressed by admixture with authentic material). This material brings the yield of this isomer to 75%.

The mother liquors from the above crystallizations plus fractions 24 and 25 were evaporated and the residue was rechromatographed on 50 g. of alumina (neutral, activity IV),[28] 50-ml. fractions of the column eluate being taken. Fractions 5–7 (benzene–ether) contained 0.74 g. of material which formed a bis-*p*-nitrobenzoate derivative that could not be purified. Fractions 8–9 (ether) contained 0.48 g. of material which gave a bis-*p*-nitrobenzoate derivative (see procedure below), m.p. 154–165°. This material when recrystallized from acetone gave a mixture of big yellow and fine colorless crystals which were separated by hand sorting. The former when recrystallized from acetone gave a product, m.p. 203–203.5°, which did not depress the melting point of the bis-*p*-nitrobenzoate of diol IVa. The latter when recrystallized from acetone gave 0.40 g. of product, m.p. 172–173°, m.m.p. with bis-*p*-nitrobenzoate of IVa, 162°. This material is the bis-*p*-nitrobenzoate of IVb, over-all yield, 3.5%.

Anal. Calcd. for $C_{30}H_{30}N_2O_8$: C, 65.92; H, 5.53. Found: C, 65.75; H, 5.51.

This diester (0.270 g.) was held at reflux in a solution of 15% potassium hydroxide in methanol–water, two-to-one (75 ml.). The solution was cooled, filtered and the filtrate was extracted three times with ether. The combined ether extracts were washed with dilute aqueous hydrochloric acid, with aqueous sodium bicarbonate solution and twice with water. The solution was dried, the solvent was evaporated and the residual oil (0.12 g.) was twice recrystallized from ether–pentane to give slightly brown prisms, m.p. 102–103°, m.m.p. with IVa, 80–82°. This material was sublimed at 95° (0.05 mm.) to give colorless crystals of diol IVb.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.34; H, 9.85.

The infrared spectrum (5% solution in methylene dichloride) was as follows: 2.77 μ (s) due to OH's; 9.38 μ (s) due to C–O; doublet at 6.59 μ (w) and 6.83 μ (m) due to phenyl. This spectrum differs substantially from the diol IVa in the region from 9 to 11 μ.

Derivatives of Diols IVa and IVb. Bis-*p*-nitrobenzoate of IVa.—Diol IVa (0.250 g.), *p*-nitrobenzoyl chloride (0.50 g.) and 2 ml. of pyridine were heated at 100° for 40 minutes and cooled. A 7% aqueous sodium carbonate solution was then added (10 ml.), and the yellow oil that separated crystallized when cooled to 0°. This material was collected, washed, dried and recrystallized (three times) from acetone to give a slightly yellow product, m.p. 203.5–204.5°.

Anal. Calcd. for $C_{30}H_{30}N_2O_8$: C, 65.92; H, 5.53. Found: C, 65.67; H, 5.25.

Acetonides Va and Vb.—A solution of 0.50 g. of diol IVa, 10 drops of concentrated sulfuric acid in 5 ml. of pure acetone was allowed to stand at room temperature for 20 hours. Water was then added, the mixture was extracted three times with pentane, and the combined extracts were washed with dilute base and water. The solution was dried, evaporated and the residual oil (0.55 g.) crystallized, m.p. 59–61°. Recrystallization of this material from methanol (three times) gave colorless needles of acetonide, m.p. 61.5–62.5°.

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.79. Found: C, 79.10; H, 9.56.

The infrared spectrum (10% solution in methylene dichloride) gave bands at 7.22 μ (s) due to *gem*-dimethyl groups, a broad band at 8.02–8.15 μ (s), a doublet at 9.34 μ (s) and 9.72 μ (m) probably due to $>\overset{|}{\text{C}}\text{–O–}$, and a doublet at 6.60 μ (w) and 6.87 μ (m) due to phenyl.

The acetonide (Vb) of diol IVb was prepared by the same procedure to give colorless prisms (methanol), m.p. 84–85.5°, mixed melting point with Va, 52–54°. This material was sublimed at 75° (0.05 mm.).

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.79. Found: C, 79.19; H, 9.77.

Attempts to induce diols IVa and IVb to undergo pinacol-like rearrangements to give carbonyl-containing products failed when concentrated sulfuric acid was employed as the reagent.

Reduction of Acyloin III with Zinc and Hydrochloric Acid in Acetic Acid.[17]—The acyloin (22.5 g.) was held at reflux in a mixture of 36 ml. of glacial acetic acid, 36 ml. of concentrated hydrochloric acid and 36 g. of finely cut zinc foil. Within three hours, four portions of 36 ml. of concentrated hydrochloric acid were added. The unreacted zinc was then collected and the cooled filtrate was extracted with three 500-ml. portions of ether. The combined extracts were washed with aqueous sodium carbonate solution and water, dried, and the solvent was evaporated to give 20 g. of a yellow oil which was submitted to chromatographic absorption on 600 g. of neutral alumina (activity II).[28] Fractions of 300 ml. were cut from the column eluate. Fractions 1–10 were taken with distilled pentane as eluate, and these when evaporated gave 15.35 g. of hydrocarbon which was distilled in a Hickman still (the first 0.5 g. being discarded). Three fractions were collected. Fraction A, b.p. 168° (16 mm.), 7.16 g. of colorless oil, was redistilled from sodium and then flash distilled, $n^{25}\text{D}$ 1.5331, $d^{25}{}_4$ 0.961.

Anal. Calcd. for $C_{16}H_{24}$ (1,4-decamethylenebenzene (XV)): C, 88.82; H, 11.18. Found: C, 88.73; H, 11.17.

The ultraviolet spectrum (in 95% ethanol) gave λ_{max} 223.5 mμ (log ε 3.91), 269 mμ (log ε 2.57), 276.2 mμ (log ε 2.56) and $\lambda_{\text{shoulder}}$ 263 mμ (log ε 2.44). The spectrum in cyclohexane was identical to that in alcohol. The infrared

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[27] K. Wiesner, *et al.*, also carried out this reaction (ref. 3) and reported m.p. 102–103° for material that probably possessed the same configuration.

[28] V. Prelog, J. Schenker and H. H. Gunthard, *Helv. Chim. Acta*, **35**, 1598 (1952).

spectrum (liquid film, 0.03 mm. thick) gave bands at 6.57 μ (s) due to phenyl and 12.30 μ (V.S.) associated with *p*-disubstituted phenyl.

Fraction B, b.p. 120-125° (bath temperature) (0.25 mm.), 5.8 g., was a colorless oil that was twice redistilled under high vacuum, the first time from sodium, $n^{25}\text{D}$ 1.5360, d^{25}_4 0.959. This material gave a negative test for picrate formation.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.56; H, 11.35.

The ultraviolet absorption spectrum (in 95% ethanol) gave $\lambda_{\max}$ 211 mμ (log ε 3.90), 223 mμ (log ε 3.91), 269 mμ (log ε 2.55) and 276.2 mμ (log ε 2.55).

Fraction C, b.p. 135° (bath temperature) (0.6 mm.), 0.55 g., was a yellow oil which was twice distilled under high vacuum, the first time from sodium, $n^{25}\text{D}$ 1.5392.

The ultraviolet absorption spectrum in 95% ethanol gave $\lambda_{\max}$ 211 mμ (log ε 3.96), 222.5 mμ (log ε 3.91), 269.5 mμ (log ε 2.52) and 276.5 mμ (log ε 2.58).

This oil (0.52 g.) was heated with 10% palladium-on-charcoal to 300° for two hours, 25 ml. of hydrogen (atmospheric conditions) being evolved within the first 20 minutes. The cooled oil was dissolved in pure pentane, and the solution was filtered to give a blue fluorescent solution. The solvent was evaporated, and the residual oil was dissolved in 2 ml. of 95% ethanol and treated with 2 ml. of a saturated ethanolic solution of picric acid. A brown-red picrate separated as needles (0.050 g. or 4.5% yield of pyrene picrate). The substance was recrystallized from 1 ml. of ethanol to give red needles, m.p. 219-225° dec., undepressed with an authentic sample of pyrene picrate. The ultraviolet spectrum of the free hydrocarbon proved to be identical with that of authentic pyrene.

Fractions 11-15 (pentane-benzene) and 16-17 (benzene) from the original chromatogram gave negative carbonyl tests, and contained 1.23 g. of solute. Fractions 18-23 (benzene) gave positive carbonyl tests and contained 2.39 g. of material, whereas fractions 24-40 (benzene-ether, ether, ether-chloroform, chloroform, chloroform-methanol, and methanol in succession) gave negative carbonyl tests. Each of fractions 18-23 was evaporated separately and each residual oil was treated with semicarbazide acetate (see procedure applied to acyloin acetate above). Fractions 19 and 20 gave semicarbazone derivatives, m.p. 192-195°, which were combined and recrystallized from methanol to give 0.570 g. (2% yield) of semicarbazone of ketone a, m.p. 192-193°. Two more recrystallizations from methanol gave m.p. 192-193°.

Anal. Calcd. for $C_{17}H_{25}ON_3$: C, 71.04; H, 8.77. Found: C, 71.10; H, 8.84.

The above derivative (0.45 g.) was dissolved in 2 g. of pyruvic acid (gentle heat), and allowed to stand eight hours at room temperature.[29] The solution was then diluted with 20 ml. of water, 3 g. of sodium bicarbonate was added, and the resulting emulsion was extracted three times with pentane. The pentane extracts were washed with water, dried and evaporated to give 0.300 g. of an oil that crystallized on standing at room temperature, m.p. 51.5-52.5°. Three recrystallizations of this material from methanol gave m.p. 57.5-58.5° (ketone a).

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.30; H, 9.70.

The infrared spectrum (10% solution in carbon tetrachloride) gave the following bands: 5.85 μ (s) due to >C=O, 6.62 μ (ms) due to benzene.

The 2,4-dinitrophenylhydrazone of this ketone was prepared in the usual way, and recrystallized four times from ethanol to give m.p. 193.5-194.5°.

Anal. Calcd. for $C_{22}H_{26}O_4N_4$: C, 64.37; H, 6.39. Found: C, 64.32; H, 6.38.

Fractions 21-23 gave semicarbazone derivatives, m.p. 141-145°, which were recrystallized from benzene-pentane to give 0.600 g. of derivative (2% yield), m.p. 141-143°,[30] m.m.p. with semicarbazone of ketone a, 115-165°. This material was recrystallized four times from benzene-pentane without change in melting point.

Anal. Calcd. for $C_{17}H_{25}ON_3$: C, 71.04; H, 8.77. Found: C, 71.21; H, 8.59.

Ketone a was obtained from the semicarbazone by the procedure recorded above, 0.500 g. giving 0.250 g. of a colorless oil which gave a small amount of crystalline material when cooled in methanol, m.p. 34-37°, m.m.p. with ketone a, 49-51°. This material (0.080 g.) was distilled twice under high vacuum at a bath temperature of 140-150°.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.30; H, 9.53.

The infrared spectrum of this material was indistinguishable from that of ketone a.

The 2,4-dinitrophenylhydrazone of ketone a was prepared in the usual way, but had to be recrystallized seven times (methanol) before a constant melting point was realized, 189-190° (1 mg. of yellow needles). This material proved to be slightly contaminated derivative of a, m.m.p. 192-194°.

Bicyclo-(10,2,2)-hexadecane (XIV).—Fraction A of the hydrocarbon obtained by the action of zinc and hydrochloric on acyloin III (3.8 g.) was dissolved in 70 ml. of glacial acetic acid and shaken in an atmosphere of hydrogen with 0.30 g. of platinum oxide as catalyst. Within three hours the theoretical amount of hydrogen was absorbed and no more hydrogen was consumed in the next 15 hours. The catalyst was collected and 200 ml. of water was added to the filtrate. The resulting suspension was extracted three times with pentane, the extracts were washed with water, aqueous sodium carbonate and again with water. The solution was dried and the solvent was evaporated through a short column to give a colorless oil that was distilled from sodium at 0.5 mm., 130° bath temperature, and again without sodium to give 3.4 g. of colorless oil. This material was crystallized from 95% ethanol at −70°, m.p. 12.5-13.5°, and three more times to give large colorless crystals of constant m.p. 13-14°. This material was distilled twice under high vacuum, the first time from sodium, to give 1.68 g. of XIV, $n^{25}\text{D}$ 1.5001, d^{25}_4 0.921.

Anal. Calcd. for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.66; H, 13.41.

This material had no ultraviolet absorption from 210 to 350 mμ. The infrared spectrum contained no bands attributable to functional groups.

The product from the mother liquors was distilled under high vacuum over sodium to give 1.3 g. of colorless oil (see below).

1,4-Decamethylenebenzene (XV).—Pure bicyclo-(10,2,2)-hexadecane (XIV) (1.68 g.) was heated to 280° with 0.3 g. of 10% palladium-on-charcoal. Within three hours, 2.94 moles of hydrogen was evolved (98% of theory). The mixture was cooled, dissolved in pure pentane and filtered. The solution was evaporated and the colorless residue was twice distilled at 0.2 mm. at 120° (bath temperature), the first few drops coming over being discarded each time. A colorless oil, 1.35 g. (83% yield) was obtained, $n^{25}\text{D}$ 1.5290, d^{25}_4 0.942.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.69; H, 11.24.

The infrared spectrum (liquid film, 0.03 mm. thick) gave bands at 6.57 μ (s) due to phenyl and 12.30 μ (V.S.) typical of *p*-disubstituted benzenes.

The colorless oil (1.3 g.) obtained from the mother liquors of the recrystallization of bicyclo-(10,2,2)-hexadecane (XIV) was heated at 290-300° with 0.2 g. of 10% palladium-on-charcoal for four hours (hydrogen was evolved). The resulting oil was dissolved in pentane, filtered and the filtrate was evaporated to a colorless oil. This material was distilled at 0.5 mm., 125-130° (bath temperature) to give a colorless oil with a blue fluorescence (0.70 g., $n^{25}\text{D}$ 1.5362) and a small pot residue of colorless oil that crystallized on standing at room temperature, m.p. 120-135°. The crystalline material was recrystallized from 0.2 ml. of ethanol to give a few slightly yellow crystals, m.p. 145-149°, which were sublimed under high vacuum at 90-95° to give colorless crystals, m.p. 147.5-150°, m.m.p. with an authentic sample of pyrene, 150-150.5°.

The ultraviolet absorption spectra of the two samples of pyrene were indistinguishable. A picrate of the pyrene from the dehydrogenation was prepared, red needles, m.p. 222-224° dec., undepressed by admixture with an authentic sample.

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[29] Procedure is patterned after that of A. C. Cope and B. D. Tiffany, THIS JOURNAL, **73**, 4158 (1951).

[30] This is the compound apparently obtained by K. Wiesner, *et al.*, ref. 3.

An ultraviolet absorption spectrum of the above distillate showed that it contained about 1.5% pyrene (the maximum at 333.5 mμ was used for this estimate).

Reduction of Acyloin III with Zinc and Hydrogen Chloride in Dioxane.[20]—To 2.0 g. of III in 80 ml. of dioxane was added 10 g. of finely cut zinc foil, and the mixture was heated to reflux. Dry hydrogen chloride gas was bubbled into the mixture for three hours. The mixture was then cooled, filtered and flooded with water. The resulting mixture was extracted three times with ether, and the combined extracts were washed with aqueous sodium carbonate, water, dried and the solvent was evaporated. The residual dark oil (1.93 g.) was dissolved in 100 ml. of distilled pentane and chromatographed on 60 g. of alumina (neutral, activity II),[28] fractions of 100 ml. of eluate being taken of pentane, 50 ml. of the other developers. Fractions 1–5 (pentane) contained a total of 0.790 g. (fraction 2 contained the most material). The eluants for the other fractions are as follows: 6 and 7, pentane–benzene, 9-to-1; 8–11 pentane–benzene, 4-to-1; 12–18, benzene; 19, benzene–methanol, 1-to-1; 20, methanol. Fractions 10–16 containing 0.840 g. of material all gave carbonyl tests, and gave semicarbazones that melted (after recrystallization from methanol) somewhere between 158° and 170°, and which when combined amounted to 0.550 g. (24% yield). This material was recrystallized six times from methanol to give m.p. 170–171° (shrinks at 168°).

Anal. Calcd. for $C_{17}H_{25}ON_3$: C, 71.04; H, 8.77. Found: C, 71.73; H, 8.83.

The semicarbazone (0.500 g.) was converted to the free ketone by the usual method (see above) to give 0.450 g. of an oil that partially solidified on standing. This material was recrystallized twice from ether-pentane and sublimed under high vacuum at 90°, m.p. 163.5–164.5°, wt. 5 mg. (this material appeared to be much more volatile than ketone a and c, and is some foreign contaminant).

Anal. Found: C, 59.46; H, 6.44.

From the filtrates was obtained an oil from which a 2,4-dinitrophenylhydrazone was prepared which was recrystallized from ethanol (yellow needles), m.p. 134.5–135° or 144–147°, m.m.p. with the same derivative of ketone a, 132–134°. Further recrystallizations of this material did not change its melting point.

Anal. Calcd. for $C_{22}H_{26}O_4N_4$: C, 64.37; H, 6.39. Found: C, 64.14; H, 6.44.

The above substance is labeled the 2,4-dinitrophenylhydrazone of ketone c (see below).

Reduction of 1,4-(5′-Acetoxy-6′-ketodecamethylene)-benzene (Acyloin Acetate) with Zinc in Acetic Anhydride.[21]—The acyloin acetate (22 g.) was dissolved in 220 ml. of redistilled acetic anhydride and heated to boiling under anhydrous conditions. Commercial zinc dust (220 g.) was added to the vigorously stirred solution, and the mixture was stirred under reflux for ten minutes and then cooled to 0°. The zinc was collected and washed with acetic anhydride and ether. The filtrate was evaporated under reduced pressure to a yellow oil, which was dissolved in ether. The solution was washed with 10% aqueous sulfuric acid, 1 *N* sodium carbonate solution and twice with water. The ether solution was dried, evaporated, and the residual oil (22.5 g.) crystallized on standing at 0°, m.p. 43–45°. Two recrystallizations of this material from pentane gave 13.6 g. (62% recovery) of acyloin acetate, m.p. 52.5–54.5°, m.m.p. with authentic material 53–55°.[31] A semicarbazone prepared from this material melted at 190–191.5° dec. (after five recrystallizations from methanol), m.m.p. with the semicarbazone of the acyloin acetate 191.5–192.5° dec.

The mother liquors from the purification of the acyloin acetate were concentrated to give 7.1 g. of an oil that was chromatographed on 200 g. of alumina (neutral, activity II)[28] with pentane as the first solvent. With pentane as the developer, 200-ml. fractions of the column filtrate were taken, 100-ml. fractions being taken with the other solvents. Fractions 1–4 (pentane) and 5–6 (pentane–benzene, 9-to-1) contained 0.260 g. of material that was discarded. Fractions 7–10 (pentane–benzene, 4-to-1), containing a total of 1.16 g. each, gave a semicarbazone (one recrystallization from methanol), m.p. 169–172°. These samples were combined (1.0 g.) and given two more recrystallizations from methanol, m.p. 170–172°, m.m.p. with semicarbazone of ketone c obtained previously (m.p. 170–171°, softens at 168°), 168.5–171°. Four more recrystallizations gave a constant melting point of 177–178° (after standing for six weeks at room temperature the melting point went to 168–178°).

Anal. Calcd. for $C_{17}H_{25}ON_3$: C, 71.04; H, 8.77. Found: C, 70.98; H, 8.39.

From 0.950 g. of this semicarbazone was liberated 0.90 g. of oily ketone from which was crystallized (pentane) a small amount of relatively volatile material, m.p. 163.5–164.5°, undepressed by admixture with the volatile contaminant similarly isolated in the last experiment. The oil from the mother liquors was crystallized from 3 ml. of methanol at −70° to give 0.210 g. of material, m.p. 12–14°. This ketone was again recrystallized, washed with cold pure pentane, dried and twice distilled at 0.3 mm., bath temperature 145°, to give ketone XVIc, m.p. 13–14.5°, n^{25}_D 1.5383.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.03; H, 9.32.

The infrared spectrum of this ketone (liquid film, 0.03 mm. thick) gave the following bands: 5.86 μ (s) due to >C=O, 6.63 μ (m) due to phenyl, 12.3 μ (s and broad) typical of *p*-disubstituted benzenes. This spectrum differed considerably from that of ketone a in the 8 μ and fingerprint region, but was nearly identical in the 2 to 7 μ region.

The 2,4-dinitrophenylhydrazone was prepared in the usual manner, and was recrystallized three times from ethanol, m.p. 135.5–136.5, resolidified and remelted at 146°, m.m.p. with same derivative of ketone c reported above, 135–136°.

From fractions 11–16 of the chromatogram was isolated 1.2 g. of acyloin acetate as its semicarbazone derivative, m.p. (3 recrystallizations from methanol) 191–192° dec., undepressed by admixture with an authentic sample. The total amount of recovered starting material was 67%. Other variations of this procedure gave even less promising results.

Attempted Dehydration of Acyloin III on Alumina.—The acyloin (3.8 g.) was distilled through a 3-by-12-cm. column packed with a mixture of pure asbestos and alumina (neutral, activity II).[28] The column was heated to 365° by means of nichrome wire wrapping and the reaction was carried out under nitrogen and at a pressure of 0.6 mm. Over a period of 12 hours the bath temperature was raised slowly from 100 to 200°. During this time a slightly red liquid (*ca.* 1.0 g.) distilled through the column, the rest remaining in the column as red tarry material.

The distillate was dissolved in ether which was washed with dilute acid, dilute base and again with water. The solution was then evaporated to give 1.0 g. of a red, pentane-soluble oil that was distilled at 0.2 mm., b.p. 120°, to give a product that gave a negative carbonyl test and a negative test with ferric chloride. This distillate (0.7 g.) was dissolved in 20 ml. of a saturated alcoholic solution of picric acid, from which separated 0.130 g. of red crystals, m.p. 143–147° dec. This material was recrystallized four times from ethanol to give 2 mg. of product, m.p. 214–220° dec., m.m.p. with authentic pyrene picrate, 219–223° dec. This material was dissolved in ethanol and filtered through a small column of alumina (neutral, activity II–III).[28] The column eluate was evaporated and the residue (less than 1 mg.) was sublimed at 0.05 mm., pot temperature 90°. The ultraviolet absorption spectrum of this material was indistinguishable from that of pyrene.

From the mother liquors of the second and third recrystallizations of the pyrene picrate were obtained orange crystals, m.p. 141–143°. They were dissolved in ethanol and passed through a column of 5 g. of alumina (neutral, activity II–III).[28] Evaporation of the column filtrate gave a colorless crystalline material, m.p. 75–85°, which was recrystallized twice from ethanol at −70° to give 5 mg. of slightly brown crystals, m.p. 102–103°. This material was sublimed at 0.05 mm. (pot temperature of 85°) to give colorless crystals of what is probably *asym*-hexahydropyrene.[32]

Anal. Calcd. for $C_{16}H_{16}$: C, 92.25; H, 7.75. Found: C, 92.22; H, 7.83.

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(31) This compound appears capable of existing in two polymorphic modifications, one m.p. 46.5–49° and the other at 53–55°.

(32) This compound has been reported to have m.p. 104.5–106° [W. E. Bachmann and R. O. Edgerton, THIS JOURNAL, **62**, 2970 (1940)].

This material formed a picrate, m.p. 148°,[33] and possessed an ultraviolet absorption spectrum (95% ethanol) dissimilar to that of *sym*-hexahydropyrene,[34] and which possessed the following characteristics: λ_{max} (mμ) 226.5 (log ε 4.84), 232 (log ε 5.00), 272.5 (log ε 3.83); 283 (log ε 3.82), 286.5 (log ε 3.81), 294.5 (log ε 3.72), 311 (log ε 3.20), 319 (log ε 3.24), 325 (log ε 3.32), 334 (log ε 3.19); $\lambda_{shoulder}$ (mμ) 262.5 (log ε 3.69). The spectrum of this compound could not be found in the literature.

The non-picrate forming part of the alumina column distillate (0.52 g.) could not be crystallized from ethanol nor could a picrate be formed with a saturated benzene solution of picric acid.[35] The material was distilled from sodium at 0.1 mm. (115–120°, bath temperature) and gave 0.50 g. of a slightly yellow oil with a pleasant odor. An ultraviolet absorption spectrum showed the possible presence of pyrene and napththalene derivatives, but no indication of the presence of a phenanthrene derivative.[36] This oil (0.490 g.) was heated with 10% palladium-on-charcoal to 300° for two hours, 40 ml. of hydrogen being evolved in the first 20 minutes. The mixture was cooled, dissolved in pentane, the solution was filtered and the solvent was evaporated. The residual oil (blue fluorescence) was dissolved in 3 ml. of ethanol and added to 5 ml. of a saturated ethanolic solution of picric acid. Red needles (0.180 g.), m.p. 218–220° dec., were obtained which were twice recrystallized from ethanol, m.p. 225–227° dec., undepressed by admixture with authentic material.

***p*-Phenylene-bis-δ-valerol.**—Lithium aluminum hydride (4.5 g.) was stirred with 200 ml. of dry ether, and a 10% solution of 10 g. of dimethyl *p*-phenylene-bis-(δ-valerate) in ether was added dropwise. After the addition was complete, the solution was stirred for 20 minutes, and 15 ml. of ethyl acetate followed by 150 ml. of 10% sulfuric acid were added. The two layers were separated, the organic layer was washed with dilute hydrochloric acid and twice with water. The solution was dried and the solvent evaporated to give 8.3 g. of colorless oil that crystallized, m.p. 46–48°. Recrystallization of this diol from 20 ml. of ether gave 7.25 g. (89% yield) of colorless crystals, m.p. 47–49°. A small sample was recrystallized three more times from ether and finally distilled at 0.05 mm. and 80° bath temperature to give material of m.p. 48.5–49.5° (hygroscopic).

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.49; H, 10.53.

The diacetate of this material was prepared by the usual pyridine–acetic anhydride method, m.p. 31–31.5° (pentane).

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.80; H, 8.87.

The bis-*p*-nitrobenzoate was also prepared, m.p. 107.5–108.5° (ethanol).

Anal. Calcd. for $C_{30}H_{32}N_2O_8$: C, 65.58; H, 5.88. Found: C, 65.36; H, 5.61.

Bis-*p*-toluenesulfonate of *p*-Phenylene-bis-δ-valerol.—To a stirred mixture of 6 g. of diol in 15 ml. of pyridine was added 10 g. of *p*-toluenesulfonyl chloride in portions over a period of ten minutes (the mixture was cooled). After stirring the mixture for three hours at room temperature, 100 ml. of ice-water and 30 ml. of concentrated hydrochloric acid were added and the mixture was cooled to 0°. The white precipitate was collected, washed with water and methanol and dried under vacuum. Recrystallization of this material from chloroform–ether (1-to-1) gave 9.7 g. (77% yield) of slightly yellow material, m.p. 87–89°, resolidifying and remelting at 111–114°. Six more recrystallizations of the crystals from the same solvent gave colorless product, m.p. 88.5–90°.

Anal. Calcd. for $C_{30}H_{38}O_6S_2$: C, 64.48; H, 6.85. Found: C, 64.33; H, 6.98.

1,4-Bis-(*n*-pentyl)-benzene (XVII).[37]—To a gently boiling stirred mixture of 2.0 g. of lithium aluminum hydride in 60 ml. of ether was added 7.0 g. of the above bis-*p*-toluenesulfonate in small portions over a period of 25 minutes. The mixture was stirred at reflux temperature for eight hours, and to the cooled mixture was added first 10 ml. of ethyl acetate, followed by 80 ml. of water and 20 ml. of concentrated hydrochloric acid. The mixture was filtered, and the ether layer was washed with aqueous sodium bicarbonate solution and twice with water. The solution was dried and evaporated through a short column to give 2.5 g. (71% yield) of a colorless oil. This material was dissolved in pure pentane and passed through 80 g. of alumina (neutral, activity II).[28] The first 200 ml. of column eluate was evaporated (small column) to give 2.4 g. of colorless oil which was distilled from sodium at 25 mm. and 170–175° bath temperature, the first few drops being discarded. A second similar distillation without sodium gave XXII, n^{25}_{D} 1.4843, d^{25}_{4} 0.850.

Anal. Calcd. for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 88.20; H, 11.88.

The infrared spectrum (liquid film, 0.03 mm. thick) gave the following bands: 6.53 μ (s) due to phenyl; 12.29 μ (V.S.) typical of *p*-disubstituted benzenes.

1,4-Bis-(*n*-phenyl)-cyclohexane (XVIII).—A mixture of 1.6 g. of 1,4-bis-(*n*-pentyl)-benzene, 50 ml. of pure glacial acetic acid and 0.20 g. of platinum oxide was shaken in an atmosphere of hydrogen. Within 30 minutes the theoretical amount of hydrogen was absorbed and the reaction stopped. The catalyst was collected and two volumes of water were added. The mixture was extracted with pure pentane, the pentane solution was washed with water, with dilute sodium carbonate and again with water. The solution was dried, evaporated through a short column and the colorless residue (1.7 g.) was distilled from sodium at 0.5 mm. (bath temperature, 110°) to give 1.4 g. of product. This material was crystallized three times from ethanol at −78° to give material, m.p. −17–15°, and which was twice distilled at 0.5 mm., the first time from sodium, n^{25}_{D} 1.4532, d^{25}_{4} 0.818.

Anal. Calcd. for $C_{16}H_{32}$: C, 85.63; H, 14.37. Found: C, 85.77; H, 14.19.

The compound showed no ultraviolet absorption from 210 to 350 mμ. The infrared spectrum possessed no bands due to phenyl or functional groups.

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(33) The m.p. of the picrate of *asym*-hexahydropyrene has been reported as 148.5–150° (ref. 32).

(34) M. Pestemer and F. Manchen, *Monatsh.*, **68**, 92 (1936).

(35) *sym*-Hexahydropyrene forms a stable picrate only in benzene (ref. 15).

(36) E. Heilbronner, H. U. Daeniker and P. A. Plattner, *Helv. Chim. Acta*, **32**, 1732 (1949).

(37) Other cases of similar reductions are H. Schmid and P. Karrer, *ibid.*, **32**, 1371 (1949), and D. J. Cram, THIS JOURNAL, **74**, 2149, 2153 (1952).