[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Transannular Reaction Products from 3,10-Dibenzylidene-1,2-cyclodecanedione[1]

BY NELSON J. LEONARD AND JOHN C. LITTLE[2]

RECEIVED MARCH 14, 1958

The treatment of 3,10-dibenzylidene-1,2-cyclodecanedione (I) in triethylene glycol at 300° with palladium-on-charcoal leads to two *transannular reaction products*, 1-benzyl-11-phenylbicyclo[6.2.1]hendecane-9,10-dione (IV) and 9-hydroxy-7,10-dibenzylbicyclo[5.3.0]-10-decen-9-one (V). The unusual structures were assigned on the basis of source, analyses, spectra and—in the case of V—further reactions. Also obtained in the palladium treatment of I were the partial hydrogenation products, 3,10-dibenzyl-1,2-cyclodecanedione (II) and 3-benzyl-10-benzylidene-1,2-cyclodecanedione (III).

The general utility of isoaromatization as a synthetic method for preparing aromatic compounds difficultly accessible by other means is exemplified in the following transformations: 2,6-dibenzylidenecyclohexanone to 2,6-dibenzylphenol,[3,4] 3,7-dibenzylidene-1,2-cycloheptanedione to 3,7-dibenzyltropolone.[5,6] 2,7-dibenzylidenecycloheptanone to 2,-7-dibenzyltropolone (with attendant dehydrogenation)[7] 1-methyl-3,5-dibenzylidene-4-piperidone to 1-methyl-3,5-dibenzyl-4-pyridone,[8] 3,5-dibenzylidenetetrahydro-4H-pyran-4-ones to 3,5-dibenzyl-4H-pyran-4-ones.[9] The most practical laboratory conditions for effecting such isoaromatizations have been found to be heating the dibenzylidene mono- or diketone with palladium-on-charcoal in a refluxing glycol solvent of appropriate boiling point (mono-,[8] di-[9] or triethylene glycol[6,7]).

As an extension of these studies, the possibility of a transannular reaction occurring along with aromatization (4 double bonds $\equiv$ 3 double bonds + 1 new ring) was investigated using 3,10-dibenzylidene-1,2-cyclodecanedione (I). The simplest prototype of the ten-membered ring, cyclodecane, has been observed to undergo transannular cyclization on heating with palladium-on-charcoal at 340°, with conversion to azulene (19.6%) and naphthalene (4.5%),[10] thus offering an encouraging precedent for aromatization.

Preliminary experiments indicated that the best conversion of 3,10-dibenzylidene-1,2-cyclodecanedione (I) could be realized by treatment of I with an equal weight of 10% palladium-on-charcoal in triethylene glycol at 290–300° for 45 minutes. The product proved to be a complex mixture, and we have concentrated on the identification of the components which were distillable under high vacuum, constituting up to 90–95% of the crude material. Infrared examination of the initial crude product showed phenolic or enolic hydroxyl bands at 3510 and 3400–3200 cm.$^{-1}$, as well as bands at 1745, 1750 and 1665 cm.$^{-1}$. Consideration of these absorptions indicated that both oxygens of I probably were retained during the reaction, and there was clear evidence of the presence of an unconjugated aromatic nucleus. Distillation of the crude mixture using a short-path apparatus under high vacuum was interrupted, in a large-scale (20 g.) run, after collection of half the weight of the original material. The distillate, with the appearance and consistency of an olive-green glass, was chromatographed on alumina, and four distinct products were isolated. In order of elution from the column they were: fraction A, a light blue hydrocarbon or mixture of hydrocarbons; fraction B, a light yellow solid, m.p. 95–96°; fraction C, an orange solid, m.p. 151–152°; and fraction D, a colorless solid, m.p. 170–171°. Evidence is presented in favor of structures for three of the four compounds.

Fraction A (3% of the distillable product) was the only material not obtained in a pure state. Repeated chromatography removed most of the oxygen-containing material to leave a light blue oil which fluoresced strongly under ultraviolet light. Elemental analysis confirmed that it was a hydrocarbon or mixture of hydrocarbons. The infrared spectrum showed the presence of monosubstituted phenyl, a double bond possibly conjugated with phenyl and aliphatic hydrogen. The ultraviolet spectrum confirmed the presence of conjugated systems other than phenyl, with maxima (cyclohexane) at 229 mμ (ϵ 19,200),[11] 259 (13,400), 264 (13,600), 285(12,600), 307(7200, infl.) and 350(930), and in the visible spectrum there was absorption at 620(22), 678(17, infl.) and 759(4, infl.). The material did not form an adduct with picric acid. Nitration of the recovered material gave a brown oil showing bands in the infrared characteristic of the nitro group and a maximum at 259 mμ (15,600 ?). Insufficient fraction A was purified to attempt a quantitative hydrogenation, but further investigation would logically include such an experiment.

Fraction B, m.p. 96–96°, which constituted about 27% of the distillable product from the treatment of I with palladium, had an elemental composition indicating a molecular formula of $C_{24}H_{28}O_2$. The additional hydrogen—four atoms more than I—could have been provided from that adsorbed on the catalyst surface[12] or by disproportionation in

---

[1] Abstracted from the thesis submitted by John C. Little in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1957.

[2] National Science Foundation Fellow, 1954–1957.

[3] R. Weiss and J. Ebert, *Monatsh.*, **65**, 399 (1935).

[4] E. C. Horning, *J. Org. Chem.*, **10**, 263 (1945).

[5] N. J. Leonard aud G. C. Robinson, THIS JOURNAL, **75**, 2143 (1953).

[6] N. J. Leonard and J. W. Berry, *ibid.*, **75**, 4989 (1953).

[7] N. J. Leonard, L. A. Miller and J. W. Berry, *ibid.*, **79**, 1482 (1957).

[8] N. J. Leonard and D. M. Locke, *ibid.*, **77**, 1852 (1955).

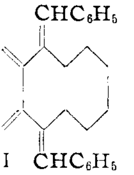
[9] N. J. Leonard and D. Choudhury, *ibid.*, **79**, 156 (1957).

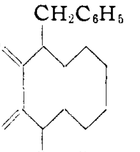
[10] V. Prelog and K. Schenker, *Helv. Chim. Acta*, **36**, 1181 (1953).

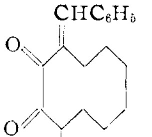
[11] Ultraviolet wave lengths are reported throughout in millimicrons (mμ); a number in parentheses following the wave length is the molecular extinction coefficient (ϵ) and a number in brackets is log ϵ. The ϵ-values given for fraction A are only approximate and are based upon the working hypothesis that it is C_{24}-material. A molecular weight determination was not conclusive.

[12] Prepared by direct hydrogenation of palladous chloride in the presence of charcoal, R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 685.

the reaction system. The melting point and analysis of the compound were suggestive of 3,10-dibenzyl-1,2-cyclodecanedione (II), which we have recently described,[13] and infrared and ultraviolet spectral comparisons, along with a mixed melting point determination, confirmed the structural assignment.

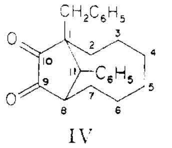

I


II


III

It is of corollary interest that the hydrogenation product III intermediate between I and II could be isolated when 3,10-dibenzylidene-1,2-cyclodecanedione was treated with palladium under less strenuous conditions. During a run at 250° for 30 minutes, about 35% of the original compound was recovered, and a yellow solid, m.p. 123–124°, was obtained which had an elemental composition indicative of the formula $C_{24}H_{26}O_2$. Assignment of the structure 3-benzyl-10-benzylidene-1,2-cyclodecanedione (III) to this product was directed by infrared and ultraviolet spectra.

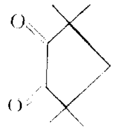
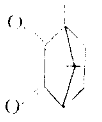
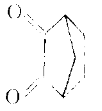
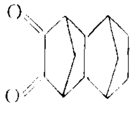
The third compound, C, constituting about 9% of the distillable mixture obtained from the attempted isomerization of 3,10-dibenzylidene-1,2-cyclodecanedione (I) under the conditions originally cited was an orange solid, m.p. 151–152°. Analysis indicated the composition $C_{24}H_{26}O_2$, so that the problem of structural assignment centered on the accommodation of the deeper chromophore in a molecule having two more hydrogens than the original. The infrared absorption spectrum exhibited a maximum at 1745 cm.$^{-1}$ with a shoulder at 1760 cm.$^{-1}$, and bands indicative of monosubstituted phenyl and aliphatic methylene groups. The ultraviolet absorption spectrum confirmed the presence of an unconjugated phenyl grouping, $\lambda_{\max}^{\text{cyclohexane}}$ 260(1,150) and shoulders at 269, 266, 253 and 248 mμ, and there were also present maxima at 473(53), 494(59) and 508 mμ, (66), indicative of a 1,2-diketone. The high frequency carbonyl infrared absorption (1745, 1760 cm.$^{-1}$) pointed to a five-membered ring 1,2-diketone, nonenolic. Since those five-membered ring vicinal diketones which are capable of enolization exist almost completely in the enolic form,[14–16] it was necessarily concluded that the diketone was either completely substituted on the α-carbons or that enolization was prevented or repressed sterically at a bridgehead α-carbon (Bredt's rule).[17] On the assumption that the formation of compound C has taken place by a simple reaction course (no complicated skeletal rearrangements), only one structure can be drawn which fits the assembled data (IV). The compound can be expected to exist almost exclusively in the diketo form since enolization would induce a high degree of steric strain. Examination of the infrared, ultraviolet and visible absorption of the model compounds listed in Table I shows that the formulation IV, 1-benzyl-11-phenylbicyclo[6.2.1]hendecane-9,10-dione, complies with the spectral prerequisites. The absorption maxima for 3,3,5,5-tetramethyl-1,2-cyclopentanedione provide the closest comparison. The other three diketones in Table I exhibit splitting (coupling?) of the infrared carbonyl absorption, as does C, and displacement of the pair of maxima to higher frequency due to the steric restraint of the additional five-membered ring,[19] whereas IV is made up of a five- and a nine-membered ring. Although we have not achieved rigorous structure proof of fraction C as IV by unequivocal synthesis, this formulation uniquely satisfies the accumulated data.



IV

TABLE I

SELECTED INFRARED AND VISIBLE MAXIMA OF 1,2-DIKETONES

Compound	$\nu_{\max}$, cm.$^{-1}$	$\lambda_{\max}$, mμ (ε)[a]	Ref.
Fraction C	1745 1760[b]	508(66) 494(59) 473(53)	
	1755[c]	508(38) 495(38)	18
	1776 1760[c]	484(32) 477(32)	19
	1771 1760[c]	493(20) 485(20) 478(20)	19
	1781 1762[c]	483(56) 474(56)	19

[a] Cyclohexane. [b] Chloroform. [c] Carbon tetrachloride.

Fraction D represented the largest portion (61%) of the distillable product from I. The colorless crystalline solid, m.p. 170–171°, which also had the composition $C_{24}H_{26}O_2$, accounted for the properties of the original crude mixture which were absent in A, B and C. Thus, compound D gave a strong ferric chloride test and had infrared hydroxyl bands (chloroform solution) at 3520 (sharp) and 3400–3150 cm.$^{-1}$ (broad), as well as strong bands at 1708 and 1660 cm.$^{-1}$ and the usual aromatic and aliphatic bands. The ultraviolet absorption spectrum exhibited maxima (cyclohexane) at 259.5 [4.00], 267 [3.98] and 272 mμ [3.90, infl.]. Recognition of the partial structure of D resulted from

---

[13] N. J. Leonard, J. C. Little and A. J. Kresge, THIS JOURNAL, **79**, 6436 (1957).

[14] G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 663 (1947).

[15] G. Hesse and G. Krehbiel, *Ann.*, **593**, 35, 42 (1955).

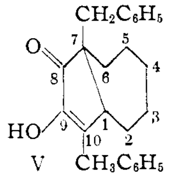
[16] G. S. Hammond, Chap. 9 in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 425 ff.

[17] F. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

[18] C. Sandris and G. Ourisson, *Bull. soc. chim. France*, 958 (1956).

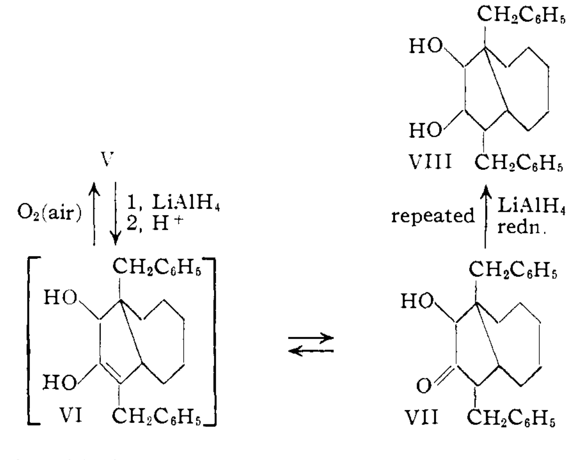
[19] K. Alder, H. K. Schäfer, H. Esser, H. Krieger and R. Reubke, *Ann.*, **593**, 23 (1955).

the observation that certain cyclopentenone derivatives had similar absorption spectra. In particular, 3-ethyl-2-methylcyclopentenone showed strong infrared maxima at 1695 (C=O) and 1647 cm.$^{-1}$ (C=C) as the pure liquid,[20] and 1,2-cyclopentanedione (enol) had an ultraviolet maximum at 247 mμ (10,000) in hexane.[20,21] Alkyl or aralkyl substitution at the 3-carbon in a 2-hydroxy-Δ^2-cyclopentenone system would be predicted to shift this maximum to longer wave length by approximately 12 mμ,[22] bringing it close to that observed for D. Consideration of these arguments and of the logical structural possibilities led us to favor V,



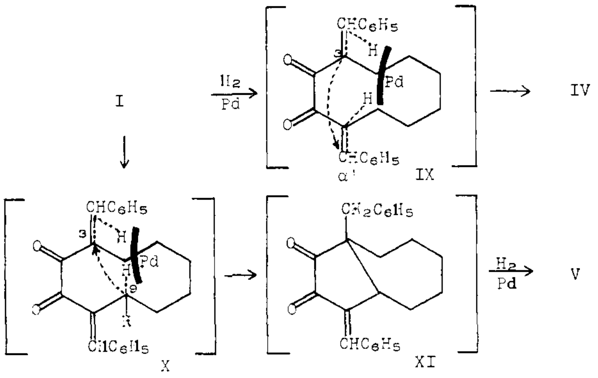
V

9-hydroxy-7,10-dibenzylbicyclo[5.3.0]-10-decen-8-one, as the most reasonable expression for fraction D. Some convincing evidence was provided unexpectedly when reduction of fraction D was attempted with excess lithium aluminum hydride. Infrared examination of the colorless noncrystalline material which resulted showed, in addition to bands ascribable to D, maxima typical of a five-membered ring hydroxyketone, $\nu_{\max}^{\text{chloroform}}$ 1745, 3510 cm.$^{-1}$. Bearing in mind that the lithium aluminum hydride reduction of an enol such as 1,2-cyclohexanedione produces the corresponding α-hydroxyketone, adipoin,[23] the course of similar reduction of V may be represented as (→ VI → VII)



Air oxidation of the acyloin VII during the isolation procedure would account for the presence of the initial substance D. Further treatment of the reduction mixture with lithium aluminum hydride in tenfold excess led to a product having infrared bands assignable to D, the intermediate acyloin VII and the expected glycol VIII. Persistent (four times) treatment of the material with excess lithium aluminum hydride produced VIII in analytically and spectroscopically pure form, although it could not be induced to crystallize or to form a solid derivative. The structure V assigned to fraction D is a sufficient and practically exclusive representation to account for the accumulated physical and chemical data and a *necessary* representation if one restricts consideration to conversions of I not involving a drastic disordering of the atoms in the molecule. Final structure proof by unequivocal synthesis would seem desirable and would be worth considering.

There is some indication that the products obtained in the attempted isomerization of 3,10-dibenzylidene-1,2-cyclodecanedione (I) in triethylene glycol using palladium-on-charcoal may have been produced partially by disproportionation, including the observation that heating I in triethylene glycol alone or in the presence of charcoal yielded crude material having infrared bands ascribable to I and D (not actually isolated), along with additional bands at 1702 and 1615 cm.$^{-1}$. However, the identified products (II, III, IV, V) are more conveniently accounted for by assuming that C=C reduction occurs (II, III and possibly IV) in contact with the hydrogen adsorbed on the catalyst[24] and that hydrogen transfer occurs within the molecule[4-9] along with hydrogenation (IV, V). The sequences (I → IX → IV and I → X → XI → V) depict possible routes for the formation of IV and V. Scale molecular models show the conformational proximity of the 3- and 9-carbons and of the 3- and α′-carbons, so that transannular bond formation is a logical consequence.[25-30]



---

[20] Spectra on file in the Department of Chemistry and Chemical Engineering, University of Illinois.

[21] The ultraviolet maximum for an enolized β-diketone in the five-membered ring series, 2-ethyl-4-*n*-propyl-1,3-cyclopentanedione, may also be cited for comparison: $\lambda_{\max}^{\text{EtOH}}$ 255 mμ [4.12] (R. B. Woodward and E. R. Blout, THIS JOURNAL, **65**, 562 (1943)).

[22] See L. F. Fieser and Mary Fieser, "Natural Products Related to Phenanthrene," third edition, Reinhold Publishing Corp., New York, N. Y., 1949, p. 190.

[23] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[24] The reduction of C=O does not occur as readily, as indicated by the ketonic nature of the identified products and by the fact that sebacil undergoes little change when subjected to the same conditions. Catalytic hydrogenation (C=C) would account for the fact that up to 90% of the total product is richer in hydrogen than the starting material.

[25] A. C. Cope and G. Holzman, THIS JOURNAL, **72**, 3062 (1950).

[26] A. C. Cope, S. W. Fenton and C. F. Spencer, *ibid.*, **74**, 5884 (1952).

[27] V. Prelog, K. Schenker and A. Küng, *Helv. Chim. Acta*, **36**, 471 (1953).

[28] V. Prelog and K. Schenker, *ibid.*, **35**, 2044 (1952).

[29] A. C. Cope, R. J. Cotter and G. G. Roller, THIS JOURNAL, **77**, 3594 (1955).

[30] V. Prelog and A. Küng, *Helv. Chim. Acta*, **39**, 1394 (1956).

Experimental[31]

Treatment of 3,10-Dibenzylidene-1,2-cyclodecanedione with 10% Pd/C.—To 50 ml. of triethylene glycol was added 20 g. (58.2 mmoles) of 3,10-dibenzylidene-1,2-cyclodecanedione (I)[13] and 20 g. of 10% palladium-on-charcoal.[12] The mixture was stirred well, the system was swept with nitrogen and then immersed in a salt-bath[32] maintained at 290–310° for 45 minutes. A vigorous boiling was observed, and moisture condensed in the cooler parts of the system (higher condensation of the triethylene glycol). The mixture was cooled to about 150° and then filtered through Filter-Cel. The filter cake was washed with water and chloroform, and the resulting two-phase system was separated. The organic layer was washed thoroughly with water, given a preliminary drying with magnesium sulfate and concentrated to an opaque brown oil. This mixture was distilled in high vacuum through a short-path distillation column until about 10 g. of an olive-green glass had been collected. The distillation was interrupted at this point, and the product was chromatographed in two portions on Activity II neutralized alumina. Small-scale runs indicated that up to 90–95% of the crude product was distillable, providing a total distillate approximating the composition of that here described.

Elution with hexane brought through a mixture of fractions A and B as a rapid-moving green band, followed by fraction B and then a mixture of fractions B and C. The latter two fractions were removed completely by a gradual change in solvent from hexane to benzene to ether. Fraction D (ferric chloride test) was first eluted from the column when an ether–methanol (9:1) solvent was used. Removal was completed with methanol.

Fraction A and B mixture was rechromatographed three times on Activity I alumina, which resulted in the isolation of a light blue, rather mobile oil designated as somewhat impure **fraction A**. Analysis showed that the mixture consisted of at least 98% carbon and hydrogen (Found: C, 90.13; H, 7.71), indicating that it was probably an impure hydrocarbon or mixture of hydrocarbons. The infrared spectrum (5% solution in chloroform) showed absorption characteristic of both aliphatic and aromatic hydrocarbons with bands at 3060, 3010, 2935, 2865, 1610, 1504, 1473 and 696 cm.$^{-1}$.

Chromatography cuts containing **fraction B** were refractionated on Activity I alumina to yield a yellow semi-solid material which was purified by recrystallization from hexane to yield light yellow needles of **3,10-dibenzyl-1,2-cyclodecanedione** (II), m.p. 94–95°, identical in every respect with the previously described material[13] obtained by hydrogenation of the starting dibenzylidene diketone with platinum.

In another treatment of 5.0 g. of 3,10-dibenzylidene-1,2-cyclodecanedione with 1.0 g. of 10% palladium-on-charcoal at *ca.* 260° for 30 minutes, some 35% of the starting material was recovered, and an attempt to methylate the residue was made using methyl *p*-toluenesulfonate and potassium hydroxide in methanol.[33] The only crystalline materials which could be isolated were products which apparently survived the methylation attempt without change, namely, the dibenzylidene diketone starting material and a new compound with properties very similar to those of the starting material. This compound crystallized from absolute ethanol as hexagonal yellow platelets, m.p. 123–124°, and the source, analysis and spectra led to its structural assignment as **3-benzyl-10-benzylidene-1,2-cyclodecanedione** (III).

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.22, 83.46; H, 7.22, 7.39.

The infrared spectrum (5% solution in chloroform) showed the same bands as the dibenzylidene diketone with the exception of a shoulder at 1690 cm.$^{-1}$; the spectrum in Nujol mull was quite different from that of the starting material, showing bands at 1695 (C=O); 1669 (conj. C=O); 1608, 1576, 1499, 749 and 699 cm.$^{-1}$ (C=C and aromatic). The ultraviolet absorption spectrum showed maxima at (cyclohexane) 306 mμ [log ε 4.28] and 231 [4.04].

Fraction C was obtained in crystalline form after double chromatography of the intermediate cuts and was purified by sublimation and recrystallization from hexane to yield small clusters of orange prisms, m.p. 151–152°, assigned the structure **1-benzyl-11-phenylbicyclo[6.2.1]hendecane-9,10-dione** (IV).

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.49, 83.41; H, 7.78, 7.60.

The infrared spectrum (5% solution in chloroform) showed bands at 1745 with a shoulder at 1760 (C=O); 1610, 1505 and 699 cm.$^{-1}$ (aromatic); (Nujol mull), 1738 with a shoulder at 1755 (C=O); 1605, 1500, 760 and 699 cm.$^{-1}$ (aromatic). The ultraviolet absorption spectrum has been described in the Discussion.

Fraction D.—Rechromatography of the initial fractions containing this material was useful in removing the (colored) diketone impurities. Molecular distillation of the resulting material resulted in a faintly yellow glass which was dissolved in hexane and chilled with seeding to induce crystallization. Purification was accomplished by sublimation and recrystallization from hexane to yield colorless thick, hexagonal platelets of **9-hydroxy-7,10-dibenzylbicyclo[5.3.0]-10-decen-8-one** (V), m.p. 170–171°.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.30, 83.42; H, 7.78, 7.67.

The infrared absorption spectrum (5% solution in chloroform) showed bands at 3520 (sharp) and 3400–3150 (broad) (OH); 1708 (conj. C=O in five-membered ring); 1660 (conj. C=C in five-membered ring); 1610, 1505 and 700 cm.$^{-1}$ (monosubstituted phenyl); (0.5% in chloroform) 3505 (sharp), 1710, 1664, 1604 and 1496 cm.$^{-1}$; (Nujol mull) 3300, 1697, 1657, 1605, 1587, 1502, 758 and 700 cm.$^{-1}$. The ultraviolet absorption spectrum has been described in the Discussion.

Reduction of fraction D with lithium aluminum hydride was carried out by adding 50 mg. (0.146 mmole) of the material to 30 mg. (0.79 mmole) of hydride in 5 ml. of dry ether. The mixture was stirred for 15 minutes. Ethyl acetate was added to destroy excess hydride, followed by cold dilute sulfuric acid. The resulting ether phase was washed with water, dried over anhydrous magnesium sulfate and concentrated to yield a nearly colorless glass, which was a mixture of approximate proportion: 10% of starting material and 90% of a material tentatively identified as **8-hydroxy-7,10-dibenzylbicyclo[5.3.0]decan-9-one (VII)**. The infrared absorption spectrum (5% solution in chloroform) showed, in addition to bands ascribable to starting material, maxima at 3510 (OH); 1745 (C=O, five ring); 1606, 1500 and 703 cm.$^{-1}$ (aromatic).

The exhausiive reduction of fraction D was carried out by treating 100 mg. of the material with excess lithium aluminum hydride, washing and drying as above and repeating the process three more times with excess reducing agent. The residue from the last reduction was subjected to molecular distillation to yield a small amount of a colorless glass which was assigned the structure **7,10-dibenzylbicyclo[5.3.0]decane-8,9-diol** (VIII).

Anal. Calcd. for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.04; H, 8.88.

The infrared absorption spectrum (10% solution in chloroform) showed no trace of ketonic impurities, but had secondary hydroxyl bands at 3590 (sharp), 3440 (broad) and 1096 cm.$^{-1}$; 1606, 1500 and 703 cm.$^{-1}$ (aromatic). The ultraviolet spectrum showed absorption (cyclohexane) at 261.5(647), 267(607) and 274.5 mμ (414).

Fraction D failed to react or react cleanly with characterizing reagents such as *o*-phenylenediamine, hydroxylamine, semicarbazide, phenylhydrazine and its nitro derivatives, alkaline and acidic peroxides, and various acid chlorides or anhydrides.[13] Indications are that methyl *p*-toluenesulfonate and also isopropenyl acetate may have reacted with the material, but no pure products could be isolated.

URBANA, ILLINOIS

---

[31] All melting points are corrected. Infrared absorption spectra were recorded on a Perkin–Elmer model 21 double beam recording instrument by Mr. James Brader and his associates. Ultraviolet spectra were determined on a Cary recording instrument by Mrs. Gerardine M. La Croix and Mr. Mou-shu Chao; all solutions were prepared immediately before running, in the solvent designated. Microanalyses were performed by Mr. Josef Nemeth and his associates.

[32] J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1950, p. 222.

[33] S. J. Kanewskaja, *Arch. Pharm.*, **271**, 462 (1933).