EXPERIMENTAL

Melting points were determined in a Mel-Temp apparatus and are not otherwise corrected. Ultraviolet and visible region spectra were taken in a Cary recording spectrophotometer, Model 10. Infrared spectra were taken on potassium bromide pressings of the compounds, in a Perkin-Elmer Model 21 spectrophotometer. The 1,4-bis(*i*-propylamino)-anthraquinone used was a commercially available dye, Waxoline Blue AS, a product of I.C.I. It was 91% pure by spectral assay. Analyses were by A. Bernhardt, Mülheim (Ruhr), Germany.

Experiments are summarized in Table II. The products were isolated by one or more of the following procedures, then recrystallized to analytical purity. The crystallization solvent was ethanol except for compound VI (acetone), IX (pyridine), and II (toluene, petroleum solvent, b.p. 90–120°).

Isolation procedures. (A) Excess anhydride was decomposed with water, and the product crystallized on cooling. (B). The solvent was evaporated. (C) On cooling, the product crystallized. (D) After washing with water and drying, the organic solvent was evaporated. (E) The reaction was poured into excess dilute hydrochloric acid, and the precipitated product washed with water. (F) The product was chromatographed on Florisil from benzene solution. (G) The product was dissolved in dilute hydrochloric acid and precipitated with sodium hydroxide solution. (H) The catalyst was removed by filtration, and the filtrate diluted with water. (J) Solvent was steam distilled, and the residue washed with hexane.

Acknowledgment. We acknowledge with thanks helpful discussions with Drs. George R. Bird, Saul G. Cohen, and Sidney Kasman.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

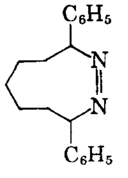
Preparation of a Nine-Membered Cyclic Diketone, 1,2-Dicarbethoxy-3,9-diphenyl-1,2-diaza-4,8-cyclononanedione[1]

C. G. OVERBERGER AND J. RICHARD HALL[2]

Received April 21, 1961

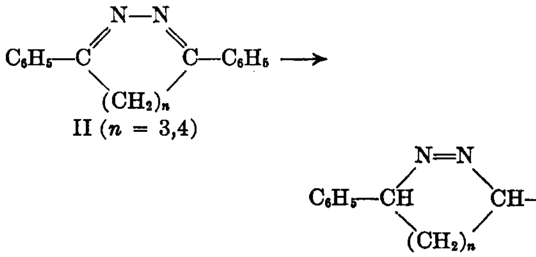
In an attempted synthesis of a nine-membered cyclic azo compound, 1,2-dibenzylidenecyclopentane was treated with ethyl azodicarboxylate to give a Diels-Alder adduct, which was hydroxylated with osmium tetroxide to give *cis*-1,6-dihydroxy-2,5-diphenyl-3,4-diazabicyclo[4.3.0]nonane. This product was cleaved to give 1,2-dicarbethoxy-3,9-diphenyl-1,2-diaza-4,8-cyclononanedione (VII). Attempts to reduce the keto groups of VII to methylene groups failed.

The synthesis of 3,9-diphenyl-1,2-diazacyclononene (I) and other medium-sized cyclic azo compounds is of particular interest as part of a continuing study of the preparation and properties of moderately active diradicals in solution.[3] Attempted synthesis of 3,9-diphenyl-1,2-diazacyclononene (I), although unsuccessful, led to several interesting compounds.



I

In previous work, the seven-[4] and eight-membered[5] cyclic azo compounds (III. $n = 3,4$) had been prepared from the corresponding cyclic azines (II. $n = 3,4$) by catalytic hydrogenation followed by oxidation of the intermediate hydrazine to give the azo compounds. Attempts to prepare the nine-, ten-, twelve-, and fourteen-membered cyclic azines



II ($n = 3,4$)

III ($n = 3,4$)

by a high dilution procedure[3] from the corresponding, α,ω-dibenzoylalkanes and hydrazine monohydrobromide, however, led to the dimeric eighteen-,[6] twenty-,[3a] twenty-four-,[3] and twenty-eight-[3] membered cyclic azines, which were converted to the corresponding azo compounds. The reaction of hydrazinium acetate and the appropriate diketone was successful in the case of eight-membered

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[1] This is the 37th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series see C. G. Overberger and N. P. Marullo, *J. Am. Chem. Soc.*, **83**, 1378 (1961).

[2] This paper comprises a portion of a thesis presented by J. Richard Hall in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] (a) C. G. Overberger, I. Tashlick, M. Bernstein, and R. G. Hiskey, *J. Am. Chem. Soc.*, **80**, 6556 (1958). (b) C. G. Overberger and M. Lapkin, *J. Am. Chem. Soc.*, **77**, 4651 (1955).

[4] C. G. Overberger and J. G. Lombardino, *J. Am. Chem. Soc.*, **80**, 3009 (1958).

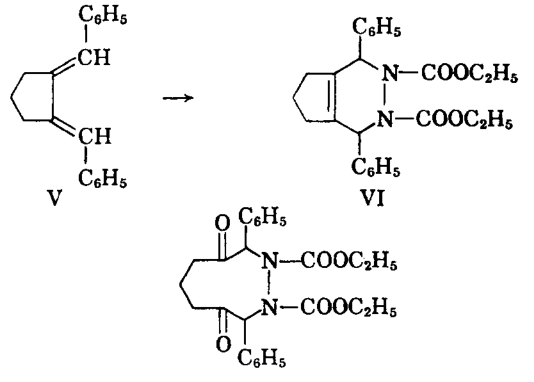
[5] C. G. Overberger and I. Tashlick, *J. Am. Chem. Soc.*, **81**, 217 (1959).

[6] J. R. Hall, Ph.D. thesis, Polytechnic Institute of Brooklyn, 1961.

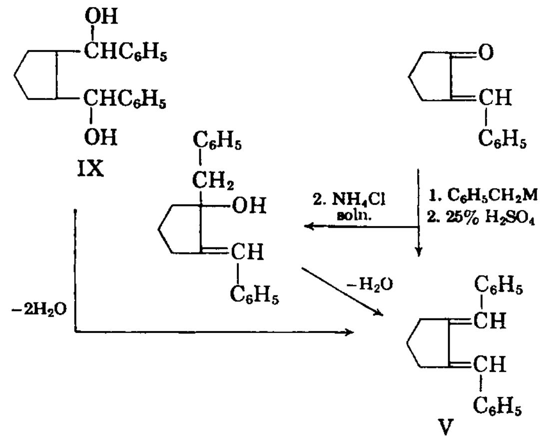
cyclic azines,[5,7] but gave only low polymers instead of ten-[6] and twelve-membered[8] cyclic azines.

Attempted cyclization of methyl β-benzoylpropionate azine by the acyloin condensation in xylene[9] and in either–liquid ammonia[10] and attempted cyclization of methyl γ-benzoylbutyrate azine by the Dieckmann reaction[11] were unsuccessful. Undoubtedly, the similarity of the azomethine groups to a carbonyl group is partly responsible for failure; furthermore, the Dieckmann reaction gives very poor results in the medium-sized ring series.[12] It was also found that acetophenone azine was cleaved to give α-phenethylamine with sodium in an ether–liquid ammonia solution.[6]

3,6-Diphenyltetrahydropyridazine (III. $n = 2$) has been synthesized by the Diels-Alder reaction of 1,4-diphenylbutadiene and ethyl azodicarboxylate, hydrogenation of the adduct, removal of the carbethoxy groups by saponification and decarboxylation, and air oxidation of the hydrazine to give the azo compound.[13] A modification of this method offered an attractive route to bicyclic intermediates which might be cleaved to nine- and ten-membered cyclic diketones, and then, by several steps, converted to the corresponding cyclic azo compounds.



1,2-Dibenzylidenecyclopentane (V) was synthesized from 2-benzylidenecyclopentanone[14] by treatment with benzylmagnesium chloride (0–10% excess) followed by direct dehydration of the complex with 25% sulfuric acid. Initial yields were low (8–14%) and were not improved by isolation of 1-benzyl-2-benzylidenecyclopentanol (IV) and dehydration of the purified alcohol. The most practical procedure proved to be the use of a 50% excess of benzylmagnesium chloride followed by direct dehydration with 25% sulfuric acid to give the diene (V) in 22.5% yield. Presumably, the low yield was caused by preferential dehydration of the tertiary alcohol to give the endocyclic olefin, 2-benzyl-3-benzylidenecyclopentene, although none was isolated.



Dehydration of 1-benzyl-2-benzylidenecyclopentanol (IV) with *p*-toluenesulfonic acid in refluxing benzene, with thionyl chloride and pyridine, *via* the Chugaev reaction, and with potassium hydroxide at 200°[15] gave either low yields or intractable products.

trans-1,2-Dibenzoylcyclopentane[16] was reduced with lithium aluminum hydride to *trans*-cyclopentane-1,2-di(phenylcarbinol) (IX), in 91% yield. Attempts to dehydrate IX with phosphorus pentoxide, with *p*-toluenesulfonic acid in refluxing toluene, and *via* the Chugaev reaction gave intractable products; none of V could be isolated. Since acid-catalyzed dehydration of both 1-benzylcyclopentanol and cyclopentylphenylcarbinol gives 1-phenylcyclopentene exclusively,[17] it seems probable that the exocyclic double bond initially formed in the dehydration of IX rearranges to an endocyclic double bond before the second hydroxyl group can be dehydrated.

The 1,2-dibenzylidenecyclopentane fluoresces strongly under ultraviolet light, and shows a single, nearly symmetrical band at 336 mμ, ϵ 3.06×10^4 (chloroform); λ_{min} 267 mμ, ϵ 2.53×10^3. *trans-trans*-1,4-Diphenylbutadiene exhibits three closely

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[7] (a) J. M. van der Zanden and G. DeVries, *Rec. trav. chim.*, **75,** 1159 (1956); (b) *Rec. trav. chim.*, **76,** 519 (1957).

[8] I. Tashlick, Ph.D. thesis, Polytechnic Institute of Brooklyn, 1958.

[9] V. Prelog, L. Frenkiel, M. Kobelt, and P. Barman, *Helv. Chim. Acta*, **30,** 1741 (1947).

[10] (a) J. C. Sheehan and R. A. Coderre, *J. Am. Chem. Soc.*, **75,** 3997 (1953). (b) J. C. Sheehan, R. C. Coderre. and P. A. Cruickshank, *J. Am. Chem. Soc.*, **75,** 6231 (1953).

[11] (a) N. J. Leonard, S. Swann, Jr., and G. Fuller, *J. Am. Chem. Soc.*, **76,** 3192 (1954). (b) N. J. Leonard and R. C. Bentz, *J. Am. Chem. Soc.*, **74,** 1704 (1952).

[12] N. J. Leonard and C. W. Schimelpfenig, Jr., *J. Org. Chem.*, **23,** 1708 (1958).

[13] S. G. Cohen, S. Hsiao, E. Saklad, and C. H. Wang, *J. Am. Chem. Soc.*, **79,** 4400 (1957).

[14] A. P. Phillips and J. Mentha, *J. Am. Chem. Soc.*, **78,** 140 (1956).

[15] G. Ohloff, *Ann.*, **627,** 79 (1959).

[16] R. C. Fuson, C. L. Fleming, P. F. Warfield, and D. E. Wolf, *J. Org. Chem.*, **10,** 121 (1945).

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spaced bands in this region[18]; the principal band, $\lambda_{max}^{C_6H_6}$ 334 mμ, ϵ 4.79 × 10^4, closely corresponds to that of 1,2-dibenzylidenecyclopentane. *cis-trans*-1,4-Diphenylbutadiene has only a single band[18a] in this region, $\lambda_{max}^{C_6H_6}$ 319–320 mμ, ϵ 2.61 × 10^4, as has the *cis-cis* isomer,[18b] $\lambda_{max}^{C_6H_6}$ 306 mμ, ϵ 2.67 × 10^4. Neither the *cis-trans* nor the *cis-cis* form fluoresces. 1,2-Dibenzylidenecyclopentane is most probably the *trans-trans* isomer on the basis of the spectral comparisons and the unfavorable steric interactions which must be present in the two *cis* isomers.

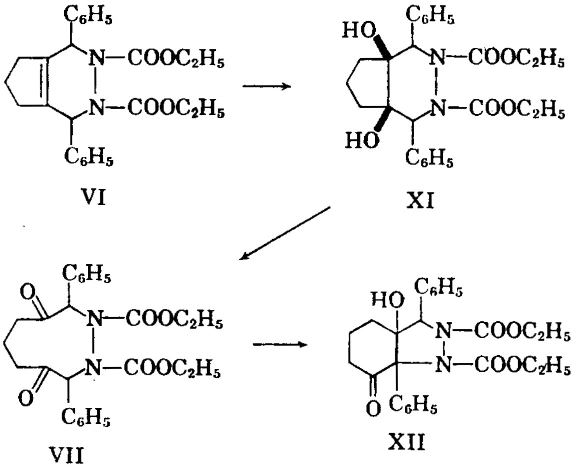
1,2-Dibenzylidenecyclopentane and ethyl azodicarboxylate in refluxing benzene readily gave a Diels-Alder adduct in 93% yield. The adduct, 3,4-dicarbethoxy-2,5-diphenyl-3,4-diaza-$\Delta^{1(6)}$-bicyclo[4.3.0]nonene (VI), exhibited only benzenoid absorption in the ultraviolet region. Ozonolysis of VI was attempted under various conditions.[19a,b] Although ozone was consumed, no identifiable products could be isolated. The diketone, however, was not obtained in crystalline form immediately when prepared later by another route, and may have been present in the crude ozonolysis product; ozonolysis was not reinvestigated.

Cope and Kagan[20] hydroxylated 3,3,7,7-tetracarbethoxy-$\Delta^{1(5)}$-bicyclo[3.3.0]octene with potassium permanganate and with Milas' reagent (*t*-butyl hydroperoxide with osmium tetroxide catalyst)[21] to give the *cis*-diol and with performic acid to give the *trans*-diol. Both diols were cleaved with lead tetraacetate to the cyclooctanedione.

Treatment of the adduct (VI) with performic acid and then with ammonium hydroxide[20] gave a product of rather broad melting range in 85% yield. The analysis of a sample, m.p. 123.4–126.8°, most closely correspondeded to the oxide. The infrared spectrum showed no hydroxyl bands, but had bands at 1250, 898, and 825 cm.$^{-1}$, in agreement with tentative correlations for the epoxy group.[22] Attempted hydrolysis of the product to the *trans*-diol with dilute periodic acid[23a] was unsuccessful. There are several steroidal oxides resistant to acid hydrolysis.[23b]

Hydroxylation of the adduct (VI) with *t*-butyl hydroperoxide containing a catalytic amount of osmium tetroxide (Milas' reagent)[20,21] gave a diol (X) which proved to be resistant to cleavage with lead tetraacetate. The latter result was unexpected since Milas' reagent is a *cis* hydroxylating reagent[21,24] and *cis*-1,2-diols are rapidly cleaved by lead tetraacetate. The infrared spectrum is similar to that of the *cis*-diol obtained by hydroxylation of the adduct with osmium tetroxide. The product would seem to be either a *trans*-diol or a very hindered *cis*-diol.

Treatment of VI with osmium tetroxide, catalyzed with pyridine, resulted in a mildly exothermic reaction; the osmate ester formed was cleaved with hydrogen sulfide[25,26] to give a diol (XI) in 96% yield (crude), 76.7% after two recrystallizations. A product melting at 166.6–167.6° was obtained in the initial hydroxylation experiment; a mixed melting point with X was depressed. Seeding experiments indicated that X and XI are not different crystalline forms of the same compound; furthermore, XI is rapidly cleaved by lead tetraacetate. When the recrystallization solvent was changed from benzene to aqueous ethanol, a different crystalline form of XI was obtained, m.p. 151.8–153.1°, followed by resolidification, and finally melting at 179.0–180.0°. The high-melting form was the only one obtained in subsequent hydroxylations. Infrared spectra of the two forms are very similar.



cis-1,6-Dihydroxy-2,5-diphenyl-3,4-diazabicyclo[4.3.0]nonane (XI) was cleaved with lead tetraacetate to give the diketone, 1,2-dicarbethoxy-3,9-diphenyl-1,2-diaza-4,8-cyclononanedione (VII), in 70.8% yield. The infrared spectrum had a carbonyl absorption at 1725 cm.$^{-1}$ with a shoulder at 1740

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(18) (a) A. Sandoval and L. Zechmeister, *J. Am. Chem. Soc.*, **69**, 553 (1947). (b) J. H. Pinkard, B. Wille, and L. Zechmeister, *J. Am. Chem. Soc.*, **70**, 1938 (1948).

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(20) A. C. Cope and F. Kagan, *J. Am. Chem. Soc.*, **80**, 5499 (1958).

(21) (a) N. A. Milas and S. Sussman, *J. Am. Chem. Soc.*, 58, 1302 (1936). (b) N. A. Milas, J. H. Trepagnier, J. T. Nolan, Jr., and M. I. Iliopulos, *J. Am. Chem. Soc.*, **81**, 4730 (1959).

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(23) (a) L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **71**, 3938 (1949). (b) M. Davis and V. Petrow, *J. Chem. Soc.*, 2973 (1949); G. Stork, J. Romo, G. Rosenkranz, and C. Djerassi, *J. Am. Chem. Soc.*, **73**, 3546 (1951).

(24) F. D. Gunstone in *Advances in Organic Chemistry; Methods and Results*. Interscience Publishers, New York, N. Y., 1960, p. 103.

(25) D. H. R. Barton and D. Elad, *J. Chem. Soc.*, 2085 (1956).

(26) R. Hirschmann, G. A. Bailey, R. Walker, and J. M. Chermerda, *J. Am. Chem. Soc.*, **81**, 2822 (1959).

cm.$^{-1}$, but no hydroxyl absorption. The diketone gave a positive carbonyl test with 2,4-dinitrophenyl hydrazine reagent.

The diketone (VII) readily undergoes an intramolecular aldol condensation to give a bicyclic hydroxyketone, 1-hydroxy-7,8-dicarbethoxy-6,9-diphenyl-7,8-diaza-5-bicyclo[4.3.0]nonanone (XII). Attempts to prepare the mono- or bissemicarbazone, or the thioketal with 1,3-propanedithiol and boron trifluoride etherate at room temperature gave only XII. In one instance the hydroxy ketone was obtained during recrystallization of the diketone from 75% ethanol. The infrared spectrum (Nujol) had a sharp hydroxyl absorption at 3540 cm.$^{-1}$, and two carbonyl absorptions, one at 1733 cm.$^{-1}$ and a split absorption at 1710 and 1720 cm.$^{-1}$ The absence of conjugation was indicated by the ultraviolet spectrum. Dehydration usually occurs to give an α,β-unsaturated bicyclic ketone in intramolecular aldol condensations.[27] An α,β-unsaturated ketone could be obtained in this case only if the condensation occurred on an unsubstituted methylene group to give a fused four- and seven-membered ring system.

Reduction of the keto groups of the diketone (VII) to methylene groups to give VIII proved unsuccessful. The Clemmensen reduction was not considered because of the strong acid employed. The low reactivity of medium ring ketones and the likelihood of base-catalyzed intramolecular condensation ruled against the usual Wolff-Kishner reduction. It was hoped that the semicarbazone could be prepared under mild acidic catalysis and reduced by the Wolff-Kishner method,[28] with simultaneous saponification and decarboxylation of the carbethoxy groups; however, only the aldol condensation product (XII) was obtained.

Raney nickel desulfurization of thioketals has proved an excellent method of reducing ketones to methylene compounds and has been used extensively in the steroid field.[29] Although the preparation of cyclic thioketals from ethane or propanedithiol requires a strong acid catalyst which should cause aldol condensation, it was hoped that the condensation would be sufficiently reversible to allow formation of the thioketal. However, numerous attempts to prepare the cyclic thioketal from propanedithiol and boron trifluoride etherate at various temperatures (room temperature to 125°) led either to XII (room temperature) or various oils. The oils could not be purified by crystallization, chromatography, or molecular distillation; all showed hydroxyl and carbonyl groups in the infrared. Raney nickel desulfurization and saponification with potassium hydroxide in refluxing ethylene glycol[13] gave a viscous oil which had a broad hydroxyl band and a carbonyl band of reduced intensity. The oil did not crystallize and did not evolve nitrogen upon heating.

In an attempt to prepare 4,8-dihydroxy-1,2-dicarbethoxy-3,9-diphenyl-1,2-diazacyclononane, the diketone was reduced with sodium borohydride. Although the product showed a hydroxyl band, attempts at purification met with little success. High-pressure hydrogenation of the diketone with W-5 Raney nickel gave a semisolid which showed a strong hydroxyl absorption. A small amount of sharp melting solid was isolated and, although the spectrum showed a hydroxyl band, the analytical data correspond more closely to $C_{25}H_{26}N_2O_6$ instead of the expected $C_{25}H_{32}N_2O_6$. Catalytic hydrogenation of 1,5-cyclooctanediones[20] and 1,6-cyclodecanediones[27] often results in transannular bridging to give a bicyclic *cis*-diol. The *cis*-diol, XI, was not obtained in this case.

The *cis* configuration can be safely assigned to the hydroxyl groups of XI since hydroxylation with osmium tetroxide involves a cyclic intermediate and invariably results in a *cis*-1,2-diol[30]; furthermore, XI is rapidly cleaved by lead tetraacetate.[31] Although hydroxylation with Milas' reagent has always given *cis*-1,2-diols,[24] X is resistant to cleavage with lead tetraacetate. One of the two possible *cis*-diols is more hindered than the other, according to examination of models, but tests with potassium triacetylosmate, a reagent for *cis*-1,2-diols, indicate that X is probably the *trans* isomer. This matter is still unresolved.

EXPERIMENTAL[32]

1,2-Dibenzylidenecyclopentane. A solution of benzylmagnesium chloride[33] was prepared from 54.7 g. (2.25 g.-atoms) of magnesium turnings and 284.4 g. (2.25 moles) of benzyl chloride (freshly vacuum distilled). 2-Benzylidenecyclopentanone,[14] 258.3 g. (1.50 moles), in 1.67 l. of ether was added during 2.5 hr. The mixture was refluxed for 0.5 hr., 1 kg. of 25% sulfuric acid was added with cooling, and refluxing was continued for 40 min. The ether layer was washed with water, 10% sodium carbonate solution, water, and dried briefly over sodium sulfate. The ether was evaporated, 700 ml. of hexane added to the residue and the solution cooled. The crude product, 210 g., m.p. 75–151°, was recrystallized from 1.5 l. of hexane-benzene to give 91.8 g. (24.7%) of 1,2-dibenzylidenecyclopentane, m.p. 153.8–161.3°. Another recrystallization gave 76.3 g. of pale yellow crystals, m.p. 157.4–162.1°, which was combined with 14 g. of product extracted from the drying agent and recrystallized from benzene and a small amount of hexane to give 83.5 g. (22.5%) of white crystals with a pale greenish yellow cast, m.p. 158–162.7°.

The material was strongly fluorescent; the ultraviolet spectrum had a single peak, $\lambda_{max}^{CHCl_3}$ 336 mμ (3.06×10^4), $\lambda_{min} \sim 267$ mμ (2.53×10^3). The infrared spectrum showed an absorption at 840 cm.$^{-1}$ (m), considered to be indicative

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[27] P. A. Plattner and J. Hulstkamp, *Helv. Chim. Acta*, **27**, 211 (1944).

[28] D. Todd, *Org. Reactions*, **IV**, 378 (1948).

[29] L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

(30) R. Criegee, B. Marchand, and H. Wannowis, *Ann.*, **550**, 99 (1942).

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(32) All melting points were uncorrected; analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(33) H. Gilman and W. E. Catlin, *Org. Syntheses*, **Coll. Vol. I**, 471 (1941).

of $R_1R_2C—CHR_3$.[22] An analytical sample melted at 153.4–156.1°.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.71; H, 7.30.

1-Benzyl-2-benzylidenecyclopentanol. The above procedure was followed, using 17.6 g. (0.726 g.-atom) of magnesium, 91.8 g. (0.726 mole) of benzyl chloride, and 99.4 g. (0.577 mole) of 2-benzylidenecyclopentanone, except that instead of sulfuric acid, 90–100 ml. of saturated ammonium chloride solution was used to hydrolyze the Grignard complex. The precipitate was filtered off and washed with ether, the combined solution was evaporated at 45–70° under vacuum. The residue crystallized upon the addition of 200 ml. of hexane and cooling. The yellowish solid, 84 g. (54%), m.p. 52.1–53.5°, was recrystallized from a mixture of 300 ml. of hexane and 50 ml. of benzene to give 63 g. (40.4%), m.p. 55.0–56.0°; a second recrystallization, from 220 ml. of heptane and 35 ml. of benzene yielded 52.6 g. (33.7%), m.p. 56.0–57.1°. An analytical sample, from several recrystallizations from hexane and then from dilute ethanol, melted at 56.9–57.6°; the infrared spectrum (melt) exhibited absorptions at 3570, 3440, 3060, and 3030 cm.$^{-1}$

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.65; H, 7.74.

trans-Cyclopentane-1,2-di(phenylcarbinol) (IX). *trans*-1,2-Dibenzoylcyclopentane[17] was prepared from cyclopentanedicarboxylic acid.[34] The diketone, 49 g. (0.176 mole), was dissolved in a mixture of 250 ml. of ether and 100 ml. of tetrahydrofuran and slowly added to 6.73 g. (0.177 mole) of lithium aluminum hydride in 400 ml. of ether. The mixture was refluxed for 1.5 hr., 2025 ml. of ethyl acetate was added, and the mixture treated with dilute sulfuric acid to a *p*H of 4–5. The ether extract was washed and dried and the solvent removed. Upon addition of a little benzene, the residue crystallized, 45.6 g. (91.4%), m.p. 118–144.6°. Recrystallization twice from benzene raised the melting point to 119.2–119.6°. Four recrystallizations from benzene-hexane gave an analytical sample, m.p. 120.6–121.8°.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 81.06; H, 8.03.

3,4-Dicarbethoxy-2,5-diphenyl-3,4-diaza-$\Delta^{1(6)}$*-bicyclo[4.3.0] nonene* (VI). 1,2-Dibenzylidenecyclopentane, 73.8 g. (0.30 mole) and 52.3 g. (0.30 mole) of ethyl azodicarboxylate[35] in 600 ml. of benzene were refluxed for 3 hr. After 1 hr. the orange color faded to a pale yellow. The solvent was removed and 150 ml. of ether and 200 ml. of hexane were added; cooling gave 117.7 g. (93.3%) of white powder, m.p. 95.5–98.1°. Recrystallization from 360 ml. of 1:1 ether-hexane gave 99.9 g. (79.2%) of product, m.p. 96.1°–99.6°. The ultraviolet spectrum showed end absorption at 213 mμ, ϵ 8570, $\lambda_{max}^{CH_3OH}$ 258 mμ, ϵ 260.

Anal. Calcd. for $C_{25}H_{28}N_2O_4$: C, 71.41; H, 6.71; N, 6.66. Found: C, 71.10; H, 6.59; N, 6.61.

Attempted trans-hydroxylation of adduct (VI) *with performic acid*[2]*; epoxide formation.* Ten grams (0.0238 mole) of VI was suspended in 100 ml. of 88% formic acid and 5 ml. of 30% hydrogen peroxide. The mixture was heated with stirring at 45° for 1 hr. and VI dissolved. The mixture was allowed to stand for 23 hr. and then was concentrated to a small volume and washed with water to give a plastic mass. The residue was dissolved in ethanol, 100 ml. of concd. ammonium hydroxide was added, and the mixture stirred for 4–5 hr. The white precipitate was crystallized from 25 ml. of ethanol to give 8.94 g. (86.2%) of product, m.p. 119–127.4°, clear at 128.0°. Recrystallization from ethanol gave 6.20 g. (59.8%), m.p. 123–126°, clear at 127.6°. The infrared spectrum (potassium bromide pellet) showed absorptions at 1750–1730 cm.$^{-1}$ (s, sl. split), in the 1330–1230-cm.$^{-1}$ region, including one at 1250 cm.$^{-1}$ (s), at 898 (m) and 825 cm.$^{-1}$ (m), but no absorption in the hydroxyl region. A sample was recrystallized for analysis, m.p. 123.4–126.8°. The analytical data correspond to the unhydrolyzed oxide.

Anal. Calcd. for $C_{25}H_{28}N_2O_5$: C, 68.79; H, 6.47; N, 6.42. Found: C, 69.21; H, 6.56; N, 6.07.

Hydroxylation of VI *with Milas' reagent.*[20,21] Adduct VI, 19.0 g. (0.0452 mole), and 12 ml. of 0.5% osmium tetroxide were added to a solution (previously dried for several hours over sodium sulfate) of 18 ml. of 90% hydrogen peroxide in 450 ml. of *t*-butyl alcohol. The mixture was refluxed for 20 hr. The excess peroxide was destroyed with sodium bisulfite solution and the solvent removed under vacuum. The residue was dissolved in methylene chloride and washed with dilute ammonium hydroxide. The dried solution was evaporated to an amorphous solid which showed absorption at 3670 and 1730 cm.$^{-1}$ (broad).

In an attempt to cleave the diol (X), 7.8 g. of the crude product and 8 g. of lead tetraacetate in 200 ml. of methylene chloride were allowed to stand for 3 hr., heated for several hours, and then allowed to stand overnight. Little or no reaction took place. The unchanged lead tetraacetate was destroyed with ethylene glycol in ethanol. The recovered material was crystallized from ethanol, m.p. 173.0–174.4°, by seeding with crystalline X (see below). Several recrystallizations from benzene-hexane gave a product melting at 181.4–183.1°; the infrared spectrum (Nujol) showed absorptions at 3470, 1730 and 1680 (split), 1600, and 1500 cm.$^{-1}$

Anal. Calcd. for $C_{25}H_{30}N_2O_6$: C, 66.06; H, 6.65; N, 6.16. Found: C, 65.73, 65.78, H, 6.26, 6.32; N, 6.47.

Attempted preparation of the diozalane from crude X and benzaldehyde with *p*-toluenesulfonic acid catalyst led to crystallization of the crude X, m.p. 138–160°. Purification gave a m.p. of 173.7–174.8°.

cis-Hydroxylation of VI *with osmium tetroxide.*[25,26] A solution of 0.496 g. (0.25 mmole) of osmium tetroxide in 15 ml. of dry dioxane was added, with cooling, to 0.656 g. (0.25 mmole) of the adduct VI in 19 ml. of dioxane, and 5 drops of pyridine was added; the solution became brown after a few minutes. After 5 days at room temperature, the reaction mixture was saturated with hydrogen sulfide with cooling and the fine black precipitate filtered. The combined filtrate was evaporated and the residue taken up in ether; the solution deposited crystals, m.p. 152–179°, 0.46 g. (64.8%). After two recrystallizations from benzene, the diol, XI, melted at 166.6–167.6°. The infrared spectrum (Nujol) showed absorptions at 3530, 1735, and 1700 cm.$^{-1}$

That the two diols, X and XI, are not different crystalline forms of the same compound was shown by seeding benzene solutions of each diol with the other; only crystals of the original diol were obtained in either case.

The product, XI, was recrystallized twice more from benzene containing a little hexane, m.p. 166.2–167.4°. A final recrystallization from aqueous ethanol gave a different crystalline form which showed a phase change at 151.8–153.1°, then resolidification, followed by final melting at 179.0–180.0°. The infrared spectrum (Nujol) of the new form showed absorptions at 3520, 1730, and 1685 cm.$^{-1}$, differing from the lower melting form mainly in the relative strength of several peaks and in the 8–15 μ region.

An analytical sample prepared by recrystallization of several second crops of the lower melting form, m.p. 165.8–167.1°, did not give a completely satisfactory analysis; further attempts to obtain the lower-melting form were unsuccessful. A sample of the higher melting form was recrystallized several times from aqueous ethanol; phase change 153.0–154.1°, m.p. 182.0–183.5°.

Anal. Calcd. for $C_{25}H_{30}N_2O_6$: C, 66.06; H, 6.65; N, 6.16. Found: C, 66.40; H, 6.96; N, 6.46.

In a larger experiment, 33.3 g. (0.0793 mole) of the Diels-Alder adduct was hydroxylated with 20.15 g. (0.0793 mole) of osmium tetroxide in 600 ml. of dry ether in the presence of 13 ml. of dry pyridine. The mixture was kept in the dark for 3 days; the dark crust was dissolved in methylene chlo-

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(34) W. J. Bailey and W. R. Sorenson, *J. Am. Chem. Soc.*, **76**, 5421 (1954).

(35) N. Rabjohn, *Org. Syntheses*, Coll. Vol. III, 375 (1955).

ride and the osmate ester cleared as before with hydrogen sulfide. The crude product crystallized from ether, 34.6 g. (96%), m.p. 152°, then 178°. Two recrystallizations from aqueous ethanol gave 27.6 g. (76.7%), m.p. 152°, then 178.6–180.1°.

1,2-Dicarbethoxy-3,9-diphenyl-1,2-diaza-4,8-cyclononanedione (VII). The *cis*-diol (XI), 4.10 g. (9.03 mmoles), and 4.00 g. (9.03 mmoles) of freshly recrystallized lead tetraacetate were dissolved separately in warm methylene chloride (total, 110 ml.) and the solutions mixed. An immediate precipitate formed. The mixture was allowed to stand for 0.5 hr., refluxed for 4 hr., and finally allowed to stand for 1.5 days until a negative test was obtained with starch-iodide paper.

The lead acetate was filtered off and the residue from the filtrate was taken up in a small volume of ether and hexane added. A first crop, 2.19 g., m.p. 94.7–97.6° and a second crop, 0.70 g., m.p. 94.0–96.8° were obtained; total, 2.89 g. (70.8%). The combined product was recrystallized from 27 ml. of 75% ethanol to give 2.19 g. of VII, m.p. 96.2–100.2°. Recrystallization, once from methylcyclohexane and four times from 75% ethanol, gave an analytical sample, m.p. 97.5–102.2° (cloudy), clear at 103.3°. The ultraviolet spectrum showed $\lambda_{max}^{CH_3OH}$ 261 mμ, ε 478, λ_{max} 297, ε 398. An infrared spectrum showed absorptions at 1725 (s, shoulder at 1740), 1300–1200 (several peaks, m-s), and 1110 cm.$^{-1}$ (m).

Although the diketone VII gave a positive test for carbonyl upon standing with 2,4-dinitrophenylhydrazine reagent, attempts to obtain a pure derivative were unsuccessful. Attempts to prepare the mono- or bissemicarbazone gave XII, m.p. 178–180° (see next section).

Anal. Calcd. for $C_{25}H_{28}N_2O_6$: C, 66.36; H, 6.24; N, 6.19. Found: C, 66.13; H, 6.47; N, 6.38.

Earlier attempts to cleave VI by ozonolysis[1a] gave products which could not be purified. Ozonolysis of the adduct at −30° in chloroform led to rapid and nearly quantitative ozone absorption; the product could not be crystallized.

1-Hydroxy-7,8-dicarbethoxy-6,9-diphenyl-7,8-diaza-5-bicyclo[4.3.0]nonanone (XII). The diketone, VII, readily underwent an acid-catalyzed intramolecular aldol condensation to give XII (see next section). The ease with which the reaction occurs is illustrated by the transformation of the diketone to XII in 20% yield, in one instance, merely upon recrystallization from 75% ethanol. An analytical sample of XII was prepared by several recrystallizations from 75% ethanol, m.p. 177.6–179.8°. The ultraviolet spectrum indicated the absence of conjugation: $\lambda_{max}^{CH_3OH}$ 213 mμ, log ε 4.20; λ_{max} 257 mμ, log ε 2.67; λ_{max} 296 mμ, log ε 2.45. An infrared spectrum (Nujol) showed an extremely narrow hydroxyl band at 3540 cm.$^{-1}$ (m) and a split carbonyl absorption at 1733, 1720, and 1710 cm.$^{-1}$ (s).

Anal. Calcd. for $C_{25}H_{28}N_2O_6$: C, 66.36; H, 6.24; N, 6.19. Found: C, 66.64, 66.76; H, 6.71, 6.53; N, 6.11.

Attempted preparation of the thioketal of diketone VII. A mixture of 0.5 g. (0.0011 mole) of VII and 0.9 ml. (~0.008 mole) of 1,3-propanedithiol was treated with 0.8 ml. of boron trifluoride etherate. After standing for several hours, the mixture was cooled and 20 ml. of 10% sodium hydroxide added, followed by 30 ml. of ether. The ether layer was extracted several times with sodium hydroxide to remove excess mercaptan. Concentration of the dried solution gave white crystals, m.p. 174.8–177.0°. The product did not contain sulfur, and was shown to be XII.

In several experiments, the mixture was heated at various temperatures, up to 125°, under nitrogen or in sealed tubes for periods of up to several days. All resulted in oils which could not be crystallized or purified by molecular distillation. Desulfurization[10b] was unsuccessful.

Comparison of the two diols, X *and* XI. A test solution of potassium triacetylosmate[20] in acetic acid was prepared. The deep blue color of the reagent faded to brownish yellow upon the addition of a few drops of a solution of XI in acetic acid. The blue color of the reagent could not be regenerated by the addition of water or potassium acetate in acetic acid, indicating the formation of a stable complex between Os^{+6} and a *cis*-diol.[21] The addition of a solution of X to potassium triacetylosmate solution produced no immediate change; upon standing for approximately 8–12 hr., the solution slowly became dark purple. The color change was not greatly affected by the addition of water or potassium acetate. However, the blank developed a similar purple color upon standing several days.

The infrared spectra of X and XI in methylene chloride were determined over a several-fold concentration range, using a Perkin-Elmer Model 21 recording spectrophotometer with sodium chloride optics. Comparison of the hydroxyl region of the spectra indicates more intermolecular hydrogen bonding for X than XI, although the results are not conclusive.

Acknowledgment. We wish gratefully to acknowledge the support of this work by the National Science Foundation, Grant NSF-G2427.

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