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

Polycyclic Compounds Containing Nitrogen. III. The Diels-Alder Reaction of Nitroethylene

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Received May 18, 1960

The development of a route to the morphinan and 4-dibenzo[de,g]quinoline nuclei was undertaken by way of the Diels-Alder adduct of nitroethylene with bi-1-cyclohexen-1-yl. The dodecabydro-9-nitrophenanthrene obtained was reduced catalytically to the amine, which was alkylated to give N-carboxymethyl-9-aminododecabydrophenanthrene. Ring closure of this amino acid should provide a convenient route to the above polycyclic compounds containing ring nitrogen.

The ozonolysis of dodecahydro-9-nitrophenanthrene gave 1-nitro-1,2-bis(2-ketocyclohexyl)ethane; the latter was partly converted to 1-keto-1,2-bis(2-ketocyclohexyl)ethane by the Nef reaction on its sodio salt. A pair of isomeric unsaturated ketones, isolated as their 2,4-dinitrophenylhydrazones, were obtained from the Nef reaction on the sodio salt of dodecahy-dro-9-nitrophenanthrene.

Investigation of the Diels-Alder reaction of 1nitro-1-alkenes as dienophiles³ has shown that the nitrocyclohexenes obtained may be converted to heterocyclic substances by way of intermediate aminocyclohexenes.

The reaction of the simplest nitro-olefin, nitroethylene, with bi-1-cyclohexen-1-yl yielded dodecahydro-9-nitrophenanthrene (Ia). This compound, as shown in Chart I, was reduced to the corresponding amine IIa. The reduction was carried out by hydrogenation with palladium on charcoal catalyst. An attempt to reduce the nitro compound using stannous chloride and hydrochloric acid gave a significantly lower yield of the amine. Similar reductions⁴ are reported to fail.

The amine IIa had an infrared spectrum characteristic of a primary amine; the spectrum had strong peaks at 3329, 3284, and 1597 cm.⁻¹ The amine hydrochloride showed a strong band at 1608 cm.⁻¹ (NH₃⁺ deformation, antisymmetric) and a weak band at 1300 cm.⁻¹ (NH₃⁺ deformation, symmetric) in the infrared.⁵

An attempt to hydrogenate dodecahydro-9aminophenanthrene (IIa) to the perhydro compound IIIa failed. The adduct Ib of β -nitrostyrene with bi-1-cyclohexen-1-yl is reported to be inert to exhaustive catalytic hydrogenation,⁶ probably because of the blocking effect of the cyclohexane rings on the olefinic linkage at C₁₅-C₁₃.

The N-substituted amino acid IV was prepared

(6) F. Bergmann, H. Eschinazi, and M. Neeman, J. Org. Chem., 8, 185 (1943).



by the reaction of dodecahydro-9-aminophenanthrene (IIa) with chloroacetic acid. Sodium hydroxide was used as the alkaline condensing agent.⁷ The acid was insoluble in aqueous acids; its sodium salt was soluble.

The infrared spectrum of the compound showed

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⁽⁴⁾ D. V. Nightingale and V. Tweedie, J. Am. Chem. Soc., 66, 1968 (1944).

⁽⁵⁾ L. J. Bellamy, The Infrared Spectra of Complex Molecules, John Wiley & Sons, Inc., New York, 1958 (2nd ed.).

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no absorption above 3200 cm.⁻¹ and strong peaks at 1580 cm.⁻¹ and 1625 cm.⁻¹ No absorption in the region 3500–3300 cm.⁻¹ is shown by amino acids or their hydrochlorides; the ionic carboxyl of amino acids appears as a strong band in the region 1600– 1560 cm.⁻¹ The probable position of the $>NH_2^+$ deformations in acids like sarcosine cannot be predicted. *dl*-Proline absorbs at 1653 cm.⁻¹ and sarcosine at 1625 cm.⁻¹, but *N*-phenylglycine does not absorb in this region.⁵ It seems likely that for compound IV the peak at 1580 cm.⁻¹ is due to ionic carboxyl and that at 1625 cm.⁻¹ to the $>NH_2^+$ group.

Acid IV was characterized as a copper salt,^{7,8} which is thought to be the monohydrate of a basic copper salt V. A salt approaching composition VI was obtained by the reaction of the sodium salt of IV with Benedict's solution.

Conversion of acid IV to its acyl chloride, followed by a Friedel-Crafts attack on the olefinic bond⁹ might provide a feasible route to the morphinan nucleus VII. Alternatively, ring closure to a hydro-4-dibenzo[de,g]quinoline VIII might be accomplished.

The position of the double bond in adduct Ia is of interest in determining the site of Friedel-Crafts reaction if compounds like VII are prepared by this route. The infrared spectrum of Ia showed a very strong peak at 1541 cm.⁻¹ and lesser peaks at 1379 and 1358 cm.⁻¹ This arrangement is found in 4nitrocyclohexene and in nitrocyclohexane.¹⁰ The absence of a peak in the olefinic region is probably due to molecular symmetry, since this band is weak for compounds having a symmetrically or pseudosymmetrically substituted ethylenic linkage.^{5,11} The lack of olefinic band tends to exclude an α or β -nitroolefin structure for Ia, since these compounds show enhanced olefinic absorption.¹⁰

The ozonolysis¹² of adduct Ia (Chart II) yielded a nitrodiketone IXa, which had strong peaks in the infrared at 1558 cm.⁻¹ ($-NO_2$) and 1720–30 cm.⁻¹

C = 0). Partial conversion to triketone X was

accomplished by Nef reaction on the sodio salt of IXa. The infrared spectrum of the mixture of diketone IXa and triketone X showed a strong band

at 1707 cm.⁻¹ (C=0) and weaker bands at 1542 cm.⁻¹ ($-NO_2$) and 1605 cm.⁻¹ (β -diketone).



Diketone IXa was characterized by its bisphenylhydrazone and its bis-2,4-dinitrophenylhydrazone.

Ozonolysis of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 14-dodecahydrophenanthrene (Ic) is reported to yield diketone IXc, whereas a conjugated monoketone XIV is obtained by ozonolysis of 1, 2, 3, 4, 5, 6, 7,-8, 9, 10, 11, 12-dodecahydrophenanthrene (XIII).¹⁸

The Nef reaction on the sodio salt of Ia yielded a pair of isomeric ketones, XI and XII, isolated as 2,4-dinitrophenylhydrazones. In each case the primary ketonic product was slightly contaminated by the other isomer. Ketone XI had a strong infrared absorption band at 1705 cm.⁻¹ (uncon-

jugated C=0 and weaker peaks at 1542 cm.⁻¹

(-NO₂) and 1660 cm.⁻¹ (conjugated
$$C=0$$
)

Its ultraviolet spectrum showed a plateau at 265-290 m μ . The yellow-orange 2,4-dinitrophenylhydrazone obtained showed a slight inflection at 260 m μ in the ultraviolet. Oil containing ketone XI was converted to the 2,4-dinitrophenylhydrazone of XII by prolonged exposure to acidic 2,4-dinitrophenylhydrazine solution.

Conjugated ketone XII was obtained by heating the Nef reaction product of Ia in an acidic medium. The infrared spectrum of XII showed a strong peak

at 1660 cm.⁻¹ (conjugated C=O) and weaker

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(11) H. Jones and C. Sandorfy, Chemical Applications of Spectroscopy, W. West, ed., (Techniques of Organic Chemistry, Vol. IX, A. Weissberger, ed.), Interscience Publishers, Inc., New York, 1956, p. 368.

⁽¹²⁾ W. J. Bailey and H. Golden, J. Am. Chem. Soc., 79, 6516 (1957).

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bands at 1545 cm.⁻¹ and 1707 cm.⁻¹ The ultraviolet spectrum showed maxima at 235 m μ (ϵ 3,880) and 280 m μ (ϵ 940). This is not inconsistent with a conjugated ketone.¹⁴ The red 2,4-dinitrophenylhydrazone of XII had a maximum at 260 m μ (ϵ 20,400) and an inflection at 293 m μ in the ultraviolet. Conversion of 1,2-dimethyl-4-nitro-5-phenylcyclohexene to 1,6-dimethyl-4-phenylcyclohexen-3-one via 1,2-dimethyl-5-phenylcyclohexen-4-one has been reported.¹⁶ For the 2,4-dinitrophenylhydrazones of certain α , β -unsaturated cyclohexenones, ultraviolet absorption maxima in the region 256–263 m μ (ϵ 15,580–16,400) are cited^{15,16}; the corresponding β , γ -unsaturated cyclohexenone derivatives do not absorb in this region.

Partial regeneration of Ia from its sodio salt by addition to hydroxylamine hydrochloride solution¹⁷ suggests inconclusively that the sodio salt of Ia does not isomerize prior to the Nef treatment.

A consideration of the stereochemistry of adduct Ia indicates that formation of two diastereoisomeric racemates (XV and XVI) is possible. Vapor-phase chromatographic analysis of the adduct indicates the presence of only one racemate. This may be explained, if both racemates were formed initially, by epimerization of the more unstable adduct *via* the aci form of the nitro group. No attempt was made to separate the racemate probably obtained.

EXPERIMENTAL

Melting points were determined in a Hershberg apparatus and are corrected; boiling points are uncorrected. The microanalyses and molecular weight determinations were performed by the Misses M. K. Gerdeman and J. Swan. Ultraviolet spectra were obtained on a Beckman DK-1 spectrophotometer with quartz cells. Infrared spectra were obtained, unless otherwise noted, in Nujol mulls on a Beckman IR-4 spectrophotometer by Mr. W. R. Feairheller, Jr. Vapor-phase chromatograms were obtained on a Model 17A Gas Chromatograph (K. and M. Scientific Glassware Co.).

2-Nitroethanol. The nitroalcohol was prepared from nitromethane and paraformaldehyde by a published method.¹⁸

2-Nitroethyl acetate. The acetate was prepared by sulfuric acid-catalyzed esterification with acetic anhydride.^{3a} The acetate boiled at 90° (5 mm.); n_D^{27} , 1.4275.

Nitroethylene. The olefin was obtained by pyrolysis of 2-nitroethyl acetate over glass helices¹⁹ at 350° or by the dehydration of 2-nitroethanol with phthalic anhydride.²⁰

Bicyclohexyl-1,1'-diol. The bimolecular reduction of cyclohexanone with aluminum amalgam gave 28-48% yields of the desired diol.²¹

Bi-1-cyclohexen-1-yl. The diene was obtained by the dehydration of bicyclohexyl-1,1'-diol with dilute sulfuric acid, 22

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(15) W. Wildman and R. Wildman, J. Org. Chem., 17, 581 (1952).

(16) A. J. Birch, J. Chem. Soc., 593 (1946).

(17) N. Kornblum and G. Graham, J. Am. Chem. Soc., 73, 4041 (1951).

(18) I. Gorski and S. Makarov, Ber., 67B, 996 (1934).

(19) M. Gold, J. Am. Chem. Soc., 68, 2544 (1946).

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potassium aluminum sulfate,²³ and phosphorus oxychloride and pyridine.²⁴ Only the latter procedure gave diene free of ketonic contaminants.

Dehydration of bicyclohexyl-1,1'-diol was also carried out at 350° on a column packed with 8-14 mesh activated alumina. The material obtained by this method apparently contained various isomers of the desired diene; its reactivity with β -nitrostyrene⁶ and with nitroethylene was poor.

The adduct with tetracyanoethylene, described below, was made in an attempt to develop an assay method for bi-1-cyclohexen-1-yl and other dienes.

The dehydration of 10 g. of the diol with 0.5 g. of *p*-toluenesulfonic acid in 50 ml. of benzene gave 95% of the water theoretically possible after 4 hr. of heating under reflux. The catalyst was removed by filtration and the benzene solution was washed thoroughly with cold saturated aqueous sodium carbonate. Fractional distillation of the dry benzene solution yielded no diene; the distillation residue was a viscous liquid to yellow-brown glass. Distillation over an open flame afforded two major fractions, which boiled at 340-360° $(n_D^{24.5}, 1.5480)$ and 370-372° $(n_D^{24.5}, 1.5524)$. Vaporphase chromatograms run at 245-250° indicated the presence of at least seven components in each fraction.

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-nitrophenanthrene (Ia). In a typical experiment, 67.5 g. (0.75 mole) of 2-nitroethanol was dehydrated with 108.1 g. (0.69 mole) of phthalic anhydride. The nitroethylene produced was collected in 15 ml. of acetic anhydride. The nitroethylene solution was added drop by drop to 38.3 g. (0.24 mole) of bi-1-cyclohexen-1-yl in a 250-ml. three-necked flask equipped with a reflux condenser, thermometer, and dropping funnel. Stirring was provided by a magnetic stirring bar; the reaction flask was purged with nitrogen before the addition of nitroethylene was begun; during the remainder of the reaction period nitrogen was swept over the condenser outlet.

During the initial stages of the olefin addition, the temperature of the reaction mixture reached 120°; the reaction was moderated by adjusting the rate of addition and by the application of external cooling. The mixture was stirred at room temperature for 24 hr. after the addition of nitroethylene was complete. The mixture, to which was added about twice its volume of 95% ethanol, was decolorized with Darco and filtered from the decolorizing charcoal. Water was added to the clear filtrate until the cloud point was reached; crystallization was induced by the addition of a seed crystal. The weight of adduct was 33.7 g. (61%). The adduct, recrystallized from aqueous ethanol, melted at 74.0-74.8°.

Anal. Calcd. for $C_{14}H_{21}NO_2$: C, 71.47; H, 9.00; N, 5.81; mol. wt., 235. Found: C, 71.40, 71.31; H, 9.07, 8.84; N, 5.81, 5.95; mol. wt. (Rast method; camphene solvent), 260, 282.

A sample sublimed at the temperature of boiling acetone under 1.5 mm. pressure showed peaks at 1541 cm.⁻¹, 1379 cm.⁻¹, and 1358 cm.⁻¹ in the infrared (potassium bromide pellet); no peak was present in the 1600 cm.⁻¹ region.

Vapor-phase chromatograms run at 260° and 280° (bromobenzene solvent) indicated that the adduct was one substance (or racemate) by the appearance of only one peak.

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9,9,10,10-tetracyanophenanthrene. A solution of 0.40 g. (0.0025 mole) of bi-1cyclohexen-1-yl and 0.32 g. (0.0025 mole) of tetracyanoethylene^{25a,b} in 5 ml. of benzene was allowed to stand at room temperature for 2 days. The olefin produced a green

(22) E. Gruber and R. Adams, J. Am. Chem. Soc., 57, 2555 (1935).

(23) E. Barnett and C. Lawrence, J. Chem. Soc., 1104 (1935).

(24) D. Greidinger and D. Ginsburg, J. Org. Chem., 22, 1406 (1957).

(25)(a) W. Middleton, R. Heckert, E. Little, and C. Krespan, J. Am. Chem. Soc., 80, 2784 (1958). (b) The tetracyanoethylene was kindly supplied by Dr. B. C. McCusick of E. I. du Pont de Nemours & Co.

complex in the presence of diene and solvent. The color faded to yellow-orange after one day; it did not change further. Removal of the solvent yielded a brown mass which was recrystallized twice from aqueous ethanol. The yield was 0.55 g. (76%) of adduct. Further recrystallizations improved the color of the pale brown solid and gave a product melting at 146.3-148.8°.

Anal. Caled. for C₁₄H₁₈N₄: C, 74.44; H, 6.25. Found: C, 74.81, 74.87; H, 6.34, 6.12.

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-aminophenanthrene (IIa).

(a) Catalytic hydrogenation. A solution of 10.0 g. of dodecahydro-9-nitrophenanthrene in 100 ml. of 95% ethanol was placed in a 500-ml. pressure bottle. To this was added 4 g. of 10% palladium on charcoal catalyst (Fisher catalyst; lot 4452). The reduction was conducted in a Parr hydrogenation apparatus with an initial hydrogen pressure of 50 p.s.i. At the end of 13 hr., 90% of the 3 moles of hydrogen needed to reduce the nitro group had been absorbed.

The suspension of amine was warmed to dissolve the amine, the solution of which was removed by filtration from the catalyst. The catalyst was washed three times with hot 95% ethanol. The amine (2.63 g.; 30%) was recovered from the combined filtrate and washings by removal of most of the solvent under reduced pressure. An additional 4.87 g. (47%) of amine hydrochloride was recovered from the amine mother liquors by the addition of concd. hydrochloric acid to them. The hydrochloride, washed once with 1:4 aqueous hydrochloric acid and four times with ether, decomposed at 271.8-272.3°.

Anal. Caled. for C₁₄H₂₄ClN: C, 69.55; H, 10.00. Found: C, 69.24, 69.52; H, 9.80, 9.87.

The *benzoyl derivative*, prepared by the Schotten-Baumann procedure, melted at 218.4–219.2° after recrystallization from aqueous ethanol.

Anal. Calcd. for C_nH_nNO: C, 81.51; H, 8.80. Found: C, 81.83, 81.68; H, 8.95, 8.82.

The infrared spectrum of the amine³⁸ had strong peaks at 3329 cm.^{-1} , 3284 cm.^{-1} , and 1597 cm.^{-1} The amine hydrochloride showed no absorption above 3000 cm.^{-1} ; there was absorption at 1608 cm.^{-1} (strong) and 1300 cm.^{-1} (weak).

(b) Exhaustive hydrogenation. A solution of 2.0 g. of dodecahydro-9-nitrophenanthrene in 100 ml. of 95% ethanol was shaken with 0.4 g. of 10% palladium on charcoal catalyst (Matheson catalyst; lot 311373) in the Parr apparatus for 5 hr., at the end of which the amount of hydrogen necessary to reduce the nitro group to the amine had been taken up. No further hydrogen was absorbed during 61 hr. more of shaking in the hydrogenation apparatus.

(c) Stannous chloride reduction. A solution of 7.5 g. (0.0322 mole) of stannous chloride dihydrate⁴ in 15 ml. of concd. hydrochloric acid was warmed on a steam bath prior to the addition of a solution of 2.5 g. (0.0105 mole) of dodecahydro-9-nitrophenanthrene in 15 ml. of ethanol. The mixture was heated under reflux until all of the nitro compound had redissolved; 3 hr. of heating were required. The ethanol was removed from the solution under reduced pressure.

The precipitated double salt, after removal by filtration, was suspended in ether and washed repeatedly with 5% sodium carbonate solution. The ether extracts of the amine were washed once with potassium carbonate and three times with water, and then dried over magnesium sulfate. The oil remaining after removal of the ether from the dried extracts was suspended in 15 ml. of water; the addition of 10 ml. of coned. hydrochloric acid resulted in the precipitation of 0.26 g. (13%) of amine hydrochloride.

N-Carboxymethyl-1,2,3,4,5,6,7,8,9,10,11,14-dodecahydro-9aminophenanthrene (IV). A suspension of 4.90 g. (0.024 mole) of dodecahydro-9-aminophenanthrene, 0.96 g. (0.024 mole) of sodium hydroxide, and 2.28 g. (0.024 mole) of chloroacetic acid in 25 ml. of water was heated on a steam bath for 18 hr. To the hot mixture was added an additional 0.96 g. of sodium hydroxide.

The cooled alkaline solution was extracted three times with ether; aqueous hydrochloric acid was added to these extracts for the recovery of 2.08 g. (36%) of the amine hydrochloride.

The alkaline solution of amino acid was heated and filtered hot; the acid was precipitated by the addition of 1:1 hydrochloric acid to the clear filtrate (to pH 6). The amino acid (2.05 g.; 49% based on unrecovered amine) was separated by filtration from the resulting gelatinous mass. It was reprecipitated by way of its sodium salt to give material which decomposed at 225.7-226.5°.

Anal. Calcd. for $C_{16}H_{28}NO_2$: C, 72.95; H, 9.57; N, 5.32. Found: C, 72.73, 72.84; H, 9.50, 9.40; N, 5.65, 5.85. Its infrared spectrum showed no band above 3200 cm.⁻¹; strong peaks occurred at 1625 cm.⁻¹ and 1580 cm.⁻¹

Copper salt (V). A solution of 0.25 g. (0.001 mole) of Ncarboxymethyldodecahydro-9-aminophenanthrene in 10 ml. of 0.1N sodium hydroxide was added to a solution of 0.25 g. (0.001 mole) of copper sulfate pentahydrate⁸ in 5 ml. of water. The resulting blue precipitate was removed by filtration and washed with 125 ml. of hot water. The solid melted at 186.7-187.7°.

About 100 mg. of this solid was suspended in 5 ml. of water containing 3 ml. of ammonium hydroxide. After digestion on a steam bath for several hours, the solid was bluegrey in color and decomposed from 187.0 to 195.0°. The analytical sample was dried under 0.4 mm. pressure at the temperature of refluxing xylene.

temperature of refluxing xylene. Anal. Calcd. for $C_{14}H_{11}NHCH_2COOCu(OH).H_2O = C_{16}H_{27}CuNO_4$: C, 53.25; H, 7.54; N, 3.88; Cu, 17.61. Found: C, 53.53, 53.72; H, 7.69, 7.52; N, 3.93; Cu (as residual CuO), 18.05, 17.85.

An attempt to remove water of hydration by heating 25 mg. of the salt overnight under 0.2 mm. pressure at the temperature of refluxing cymene changed the color of the salt to grey; the sample decomposed at 190-200°.

Anal. Calcd. for C₁₆H₂₅CuNO₅: C, 56.07; H, 7.35; N, 4.09; Cu 18.54. Found: C, 54.12, H, 7.62; Cu, 20.56.

Copper salt (VI). A solution of 0.25 g. of the amino acid in 5 ml. of 0.24N sodium hydroxide was added to 5 ml. of Benedict's solution. A blue-grey salt, decomposing at 180-181°, was isolated in small yield. A blank yielded neither turbidity nor precipitate.

Anal. Caled. for $(C_{14}H_{11}NHCH_{2}COO)_{2}Cu=C_{12}H_{48}CuN_{2}O_{4}$: C, 65.33; H, 8.22; Cu, 10.80. Cale. for $(C_{14}H_{11}NHCH_{2}COO)_{2}$ -Cu.H₂O=C₁₂H₄₀CuN₂O₆: C, 63.37; H, 8.31; Cu, 10.49. Found: C, 63.13, 63.31; H, 8.63, 8.89; Cu, 11.49, 11.35.

1-Nitro 1,2-bis (2-ketocyclohexyl) ethane (IXa). The ozone generator employed was substantially that described in the literature.²⁷ A solution of 2.0 g. of dodecahydro-9-nitrophenanthrene in 100 ml. of dry ethyl acetate was exposed to a stream of oxygen containing ozone for slightly longer than the time required to complete the ozonization. The reaction vessel was immersed in an ice-salt water bath. Ozone not absorbed by the compound was allowed to pass through 2% potassium iodide solution; the liberated iodine was titrated with standard potassium thiosulfate.

The ozonide solution was transferred to a 500-ml. threenecked flask fitted with dropping funnel, reflux condenser, and mechanical stirring.¹³ During the drop by drop addition of 100 ml. of water, the mixture was cooled in an ice bath. At the end of the addition, the mixture was allowed to warm to room temperature. The ethyl acetate was removed by distillation. The product, recrystallized from aqueous acetone, weighed 2.01 g. (89%) and melted at 107.5–108.1°. It was stable on storage.

(27) L. Smith, F. Greenwood, and O. Hurdick, Org. Syntheses, Coll. Vol. III, 673 (1955).

⁽²⁶⁾ This spectrum was obtained on a Beckman IR-3 spectrophotometer with the assistance of Dr. H. W. Schamp, Jr., and Dr. W. G. Maisch of the Institute for Molecular Physics.

The bisphenylhydrazone, prepared in the usual manner,³⁸ melted at 151.8–154.8° after thorough washing with 95% ethanol.

Anal. Caled. for C₂₅H₂₂N₅O₃: C, 69.76; H, 7.43. Found: C, 69.41, 69.51; H, 7.37, 7.52.

The bis-2,4-dimitrophenylhydrazone was prepared by allowing 0.05 g. of the ketone to react with 5.4 ml. of 2,4-dimitrophenylhydrazine solution (5% sulfuric acid in ethanol; 66 ml. contain 1 g. of 2,4-dimitrophenylhydrazine) at room temperature for 18 hours. The red-orange solid, washed three times with cold 95% ethanol, melted at 117.5-119.5°. Anal. Calcd. for C₂₅H₂₉N₉O₁₀: C, 49.74; H, 4.66. Found:

C, 50.12, 50.20; H, 4.78, 5.06.

1-Keto-1,2-bis(2-ketocyclohexyl)ethane (X). A suspension of 1.0 g. (0.0038 mole) of 1-nitro-1,2-bis(2-ketocyclohexyl)ethane (IXa) in 20 ml. of absolute ethanol was cooled under a nitrogen atmosphere. To the magnetically stirred suspension was added over a period of 30 min. a solution resulting from the reaction of 0.15 g. (0.0075 mole) of sodium with 15 ml. of absolute ethanol.¹⁶ The resulting yellow sodio-salt solution was stirred for 1 hr. with cooling under the nitrogen atmosphere.

The cold sodio-salt solution was added, over a period of 30 min., to a chilled solution of 0.5 ml. (0.008 mole) of concd. hydrochloric acid in 5 ml. of water and 4 ml. of ethanol. Stirring of the yellow solution was continued for 1 hr., after which 50 ml. of water was added. The organic material was recovered by four extractions with 35-ml. portions of ether. The ether extracts were washed twice with 5% sodium carbonate solution and four times with water. The residual yellow oil obtained from the dried ether extracts could not be crystallized. The infrared spectrum of the oil showed a very strong carbonyl band at 1707 cm.⁻¹, a less strong band at 1542 cm.⁻¹, and a weak band at 1605 cm.⁻¹

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-ketophenanthrene (XI). The same procedure¹⁵ used above to obtain triketone X was followed, using 2.0 g. of dodecahydro-9-nitrophenanthrene (Ia). The ether was removed from the dry extracts without heat; a stream of nitrogen aided the process. The infrared spectrum of the residual oil had strong bands at 1705 cm.⁻¹ and 1542 cm.⁻¹; there was a weak band at 1660 cm.⁻¹ An ultraviolet spectrum (in iso-octane) showed a plateau at 265-290 m μ (ϵ 147).

(28) R. Shriner and R. Fuson, The Systematic Identification of Organic Compounds, John Wiley & Sons, Inc., New York, 1948 (3rd ed.), p. 116. Reaction of some of the ethereal extracts with chilled 2,4-dinitrophenylhydrazine solution for 20 min. at 0° produced a yellow-orange precipitate which was removed by filtration and washed once with 5% potassium carbonate solution and three times with water.¹⁶ This yellow 2,4-dinitrophenylhydrazone melted at $\{158.0-158.6^\circ$ after recrystallization from ethyl acetate and ethanol.

Anal. Calcd. for C₂₀H₂₄N₄O₄: C, 62.48; H, 6.29. Found: C, 62.16, 62.40; H, 6.27, 6.02. The ultraviolet spectrum (in chloroform) had a slight inflection at 260 m μ .

A red 2,4-dinitrophenylhydrazone, identical with that obtained below, was isolated by allowing the ketonic oil to react with acidic 2,4-dinitrophenylhydrazine solution at room temperature for several hours.

1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-9-ketophenanthrene (XII). A solution of 2.5 g. (0.01 mole) of dodecahydro-9nitrophenanthrene and 1 g. (0.025 mole) of sodium hydroxide in 40 ml. of ethanol was cooled for 30 min.³⁹ The yellow solution was poured rapidly into 70 ml. of cold 1:6 hydrochloric acid. The resulting mixture was stirred with cooling for 1.5 hr.; it was allowed to warm to room temperature overnight.

The organic material was extracted from the solution with ether; the ether was removed from the dry extracts by heating on a steam bath. The residual brown oil could not be crystallized; its infrared spectrum had a strong band at 1660 cm.⁻¹ and weak peaks at 1707 and 1545 cm.⁻¹ Its ultraviolet spectrum (in isooctane) showed maxima at 235 m μ (ϵ 3,880) and 280 m μ (ϵ 940).

A brick-red 2,4-dinitrophenylhydrazone, melting at 233.5-234.1° after recrystallization from ethyl acetate and ethanol (1:1), was isolated.

Anal. Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.48; H, 6.29. Found: C, 62.37, 62.33; H, 6.17, 6.44. Its chloroform solution showed an inflection at 293 m μ and a maximum at 260 m μ (ϵ 20,400) in the ultraviolet.

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-nitrophenanthrene (Ia) from its sodio salt. Sodio salt was prepared from 2.0 g. of dodecahydro-9-nitrophenanthrene (Ia) by reaction with ethanolic sodium ethoxide at 0° under a nitrogen atmosphere. To the sodio-salt solution was added over a period of 20 min. a chilled solution of 1.25 g. (0.018 mole) of hydroxylamine hydrochloride¹⁷ in 25 ml. of water. The mixture was stirred with cooling.

The weight of recovered product (from aqueous ethanol) was 0.82 g. (41%); it was identical with the adduct in melting point, mixed melting point, and infrared spectrum.

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A Study of the Alkylation of β , β , β -Trialkylpropionitriles

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Received May 9, 1960

A study has been made of the alkylation of β,β,β -trialkylpropionitriles (I) by means of alkyl halides and sodamide. It has been found that α -alkylated nitriles (II), N- α -dialkyl substituted ketenimines (III) and α, α -dialkylated nitriles (IV) are formed in varying proportions depending upon conditions.

In view of the recent report² of the isolation of ketenimines from the alkylation of dialkylacetonitriles, we wish to describe our results on the alkylation of β,β,β -trialkylpropionitriles (I) which confirm and

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