larger ring is more readily formed over chromia-alumina B having low intrinsic acidity. It appears that the catalyst sites leading to the specific ring closures are plural in kind and different in number from one catalyst to another. Besides the acidic properties, the arrangement of chromia on alumina surface may be a more important factor in the dehydrocyclization reaction.

EVANSTON, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Michael Type Additions with Nitroparaffins.[1] A Convenient Route to Nitrocyclohexanols

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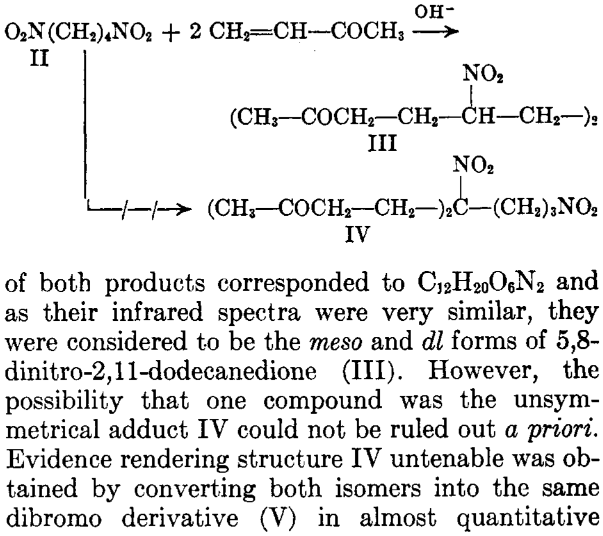
Primary nitroparaffins condense with phenyl vinyl ketone to afford monoaddition adducts. Treatment of these products with an additional equivalent of phenyl vinyl ketone yields predominantly the expected diadducts. Strong bases such as ethoxide and hydroxide cause cyclization of the initial reaction products to form substituted cyclohexanols providing a convenient synthetic route to these structures. When this Michael type reaction is applied to methyl vinyl ketone, the initial diaddition compounds cannot be isolated. Instead, cyclization occurs with the formation of cyclohexanols. The reaction of 2 equivalents of methyl vinyl ketone with α,ω-dinitroalkanes gives the symmetrical addition compound. Four equivalents of methyl vinyl ketone give the tetraaddition product. However, here also cyclization occurs concurrently with reaction so that dicyclohexanol derivatives are obtained. Dehydration of these cyclohexanols, followed by hydrogenation, opens a new route for the preparation of substituted nitrocyclohexanes.

Although the Michael type addition employing primary and secondary nitroparaffins as donors has been investigated by many workers,[2] little attention has been given to the use of α,ω-dinitroparaffins in this reaction. Only two reports[3] dealing with the Michael addition to dinitro compounds have appeared in the literature. Feuer and Leston found that disodium 2,2-dimethyl-1,3-propanedinitronate reacted in an unusual way with methyl acrylate to afford 4,4-dimethyl-5-(2′-carboxyethylidene)isoxazoline oxide, while 1,5-dinitropentane gave a 34% yield of the expected Michael adduct 5,9-dinitro-2,12-tridecanedione (I) when treated with two equivalents of methyl vinyl ketone.[3b]

α,ω-Dinitroparaffins. The present investigation was initiated by studying the reaction between 1,4-dinitrobutane (II) and two equivalents of methyl vinyl ketone. When this reaction was carried out in ethanol and in the presence of a catalytic amount of sodium hydroxide, two products, m.p. 91.5–92.5° and 61–62° were obtained. The same two compounds were secured when the full salt of compound II was employed. As the elemental analyses of both products corresponded to $C_{12}H_{20}O_6N_2$ and as their infrared spectra were very similar, they were considered to be the *meso* and *dl* forms of 5,8-dinitro-2,11-dodecanedione (III). However, the possibility that one compound was the unsymmetrical adduct IV could not be ruled out *a priori*. Evidence rendering structure IV untenable was obtained by converting both isomers into the same dibromo derivative (V) in almost quantitative yield on treatment with two equivalents of base and excess bromine. The infrared spectra of compound V, obtained in both reactions were superimposable and a mixed melting point determination showed no depression.



$$O_2N(CH_2)_4NO_2 + 2\,CH_2{=}CH{-}COCH_3 \xrightarrow{OH^-}$$

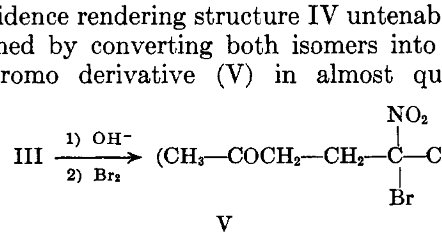
II

$$(CH_3{-}COCH_2{-}CH_2{-}\overset{NO_2}{CH}{-}CH_2{-})_2$$

III

$$\xrightarrow{/\!-\!/} (CH_3{-}COCH_2{-}CH_2{-})_2\overset{NO_2}{C}{-}(CH_2)_3NO_2$$

IV



$$\text{III} \xrightarrow[2)\ Br_2]{1)\ OH^-} (CH_3{-}COCH_2{-}CH_2{-}\overset{NO_2}{\underset{Br}{C}}{-}CH_2{-})_2$$

V

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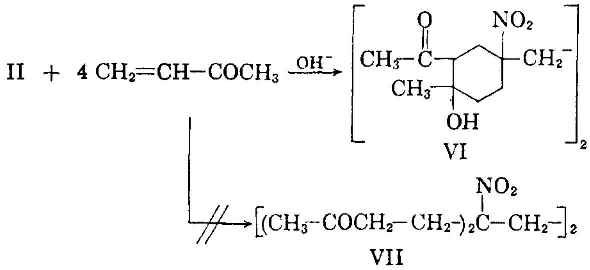
[1] (a) From the Ph.D. thesis of Ronald Harmetz, Purdue University, 1959; (b) presented before the Division of Organic Chemistry at the Cleveland Meeting of the American Chemical Society, April 1960.

[2] (a) M. C. Kloetzel, *J. Am. Chem. Soc.*, **69**, 2271 (1947); (b) D. E. Worrall, and C. J. Bradway, *J. Am. Chem. Soc.*, **58**, 1607 (1936); (c) E. P. Kohler, *J. Am. Chem. Soc.*, **38**, 889 (1916); (d) F. Villani and F. Nord, *J. Am. Chem. Soc.*, **69**, 2608 (1947); (e) E. P. Kohler and H. Engelbrecht, *J. Am. Chem. Soc.*, **41**, 764, 1379 (1919); (f) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **65**, 23 (1943); (g) G. D. Buckley, T. J. Elliott, F. G. Hunt, and A. Lowe, *J. Chem. Soc.*, 1505 (1947); (h) G. D. Buckley, J. L. Charlish, and J. D. Rose, *J. Chem. Soc.*, 1514 (1947); (i) A. Lambert and H. A. Piggott, *J. Chem. Soc.*, **1947**, 1489; (j) for a thorough survey of the literature, reference is made to *The Michael Reaction* by E. D. Bergman, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

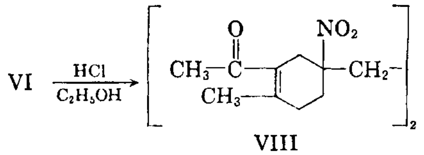
[3] (a) H. Feuer and G. Leston, Abstract of Papers presented at the International Congress of Pure and Applied Chemistry, Paris, July 1957, p. 24; (b) H. Feuer and C. N. Aguilar, *J. Org. Chem.*, **23**, 607 (1958).

When 1,4-dinitrobutane was treated with four equivalents of 85% aqueous methyl vinyl ketone (inhibitor free), an 86% yield of a tetraaddition adduct was secured. Recrystallization of this material from methanol or acetonitrile afforded several fractions, the decomposition point of which ranged from 200–237°. The infrared spectra of the several fractions were similar and all showed a hydroxyl band in the 2.9 μ region. The elemental analyses of two samples, m.p. 223–229° dec. and 236–237° dec., corresponded to a tetraaddition adduct. The presence of a hydroxyl band in the infrared spectrum indicated that the product was not the expected tetraadduct VII but rather the cyclic compound 1,2-bis(1′-nitro-3′-acetyl-4′-hydroxy-4′-methylcyclohexyl)ethane (VI), which probably arose from compound VII *via* an intramolecular aldol condensation.


VI

VII

Compound VI was converted into a dioxime in an 88% yield; this further established its structure. Treatment of the crude derivative with boiling methanol afforded a soluble material, m.p. 248° dec. and an insoluble material, m.p. 254–256° dec. The elemental analyses of both corresponded to that calculated for the dioxime of compound VI and their infrared spectra were void of a carbonyl band, indicating complete reaction of the keto groups. The difference in melting point can be ascribed to the presence of diastereoisomers. Chemical evidence for the presence of a hydroxyl group in compound VI was obtained by dehydrating it to compound VIII. The ultraviolet spectrum of the olefin possessed a band at 232 mμ, indicating that the product was an α,β-unsaturated ketone.[4]


VIII

It was observed that when the preparation of compound VI was carried out with 100% methyl vinyl ketone, containing 0.06 g. of hydroquinone, the yield decreased by about 30%. In order to ascertain whether the absence of water or the presence of hydroquinone in the methyl vinyl ketone was the cause of the lower yield, a series of experiments were performed which are summarized in Table I.

TABLE I

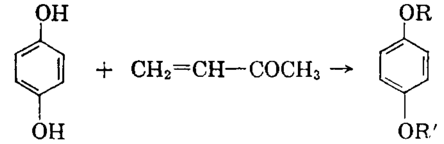
REACTION OF 1,4-DINITROBUTANE WITH FOUR EQUIVALENTS OF METHYL VINYL KETONE[a]

Expt.	Hydroquinone	Catalyst	Added Water[b]	Yield, %
1	None	3 drops of 20% aq. NaOH	3.0 g.	86
2	None	3 drops of 20% aq. NaOH	None	82
3	0.06 g.	3 drops of 20% aq. NaOH	None	59
4	0.06 g.	11 drops of 20% aq. NaOH	None	75
5	0.06 g.	3 drops of 20% aq. NaOH	3.0 g.	56

[a] All experiments were carried out in 95% ethanol at 40° for 24 hours. [b] The water present in the 95% ethanol is not included.

It is seen from the data in Table I that the addition of water did not alter the yield significantly and that the presence of hydroquinone (experiments 3 and 5) had a very detrimental effect on the yield. This effect was largely eliminated when a greater amount of base was employed (Expt. 4). It was obvious then that the hydroquinone or a reaction product between hydroquinone and methyl vinyl ketone, neutralized the base which was necessary to catalyze the desired Michael addition.

In a preliminary investigation it was found that hydroquinone reacted with methyl vinyl ketone to give a product, the elemental analysis of which agreed with both the mono- and diaddition adducts (IXa and IXb). However, the presence of infrared absorption bands at 3.10 and 8.13 μ (aromatic hydroxyl) and 9.02 μ (aromatic ether) established that the product was the monoaddition adduct IXa.


IXa. R = CH_2—CH_2—$COCH_3$; R′ = H
IXb. R = R′ = CH_2—CH_2—$COCH_3$

The reaction of 1,5-dinitropentane (X) with two and four equivalents of methyl vinyl ketone, under conditions which gave good yields in the case of 1,4-dinitrobutane, resulted only in 31–34% yield of the diaddition adduct (I) but gave no tetraaddition product. The crude yield of compound I was increased to 40% when dioxane and "Triton B" were substituted for ethanol and sodium hydroxide. However, this solvent catalyst combination did not give any tetraaddition adduct when four equivalents of methyl vinyl ketone were employed. The tetraaddition adduct, 1,3-bis(1′-nitro-3′-acetyl-4′-hydroxy-4′-methylcyclohexyl)propane (XI), was finally obtained in a 50% yield when the reaction employing ethanol and sodium hydroxide was repeated with compound X which was washed with an aqueous sodium bicarbonate solution. These

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[4] A. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy*, Edward Arnold Ltd., London, 1954, p. 94.

TABLE II

REACTION OF 1,4-DINITROBUTANE WITH METHYL ACRYLATE

Expt.	Solvent	Temp.	Catalyst	Ratio 1,4 D.N.B.[a]/M.A.	Inhibitor	Time in Hours	Yield of XIV, %
1	Abs. CH_3OH	40°	$NaOCH_3$	1/2	None	72	8
2	Abs. CH_3OH	40°	$NaOCH_3$	1/2	Hydroquinone	8	0
3	Abs. CH_3OH	40°	$NaOCH_3$	1/2	Hydroquinone	18	11
4	Abs. CH_3OH	40°	$NaOCH_3$	1/6	*p*-Methoxyphenol	26	34
5	Abs. CH_3OH	40°	Full Na salt	1/2	None	8	0
6	T.H.F.[b]	40°	$NaOCH_3$	1/2	Hydroquinone	8	*ca.* 5
7	T.H.F.	40°	"Triton B"	1/2	Hydroquinone	36	66
8	T.H.F.	28°	Full Na salt	1/2	None	48	0
9	T.H.F.	40°	"Triton B"	1/2	Hydroquinone	8	63-66
10	Abs. CH_3OH	40°	"Triton B"	1/2	Hydroquinone	8	*ca.* 3

[a] $\frac{\text{1,4 D.N.B.}}{\text{M.A.}} = \frac{\text{equivalents of 1,4-dinitrobutane}}{\text{equivalents of methyl acrylate}}$. [b] T.H.F. = tetrahydrofuran.

data indicated that X contained an acidic impurity which neutralized the base necessary to catalyze the desired Michael addition.

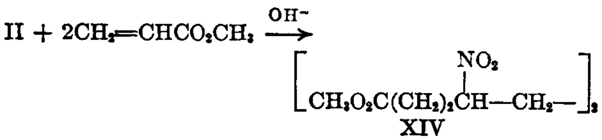
Compound XI was also secured in a 50% yield by treating the diaddition adduct I with two equivalents of methyl vinyl ketone.

The infrared spectrum of the tetraaddition adduct possessed a hydroxyl band a 2.86 μ indicating that cyclization had taken place, resulting in the formation of compound XI. Additional proof for the cyclic structure was obtained by converting compound XI in 71% yield to a dioxime, the infrared spectrum of which was void of a carbonyl absorption.

Treatment of an ethanolic solution of 1,6-dinitrohexane (XII) containing a catalytic amount of sodium hydroxide, with four equivalents of methyl vinyl ketone afforded a 38% yield of 1,4-bis(1′-nitro - 3′ - acetyl - 4′ - hydroxy - 4′ - methylcyclohexyl)butane (XIII). The yield of compound XIII was not increased when the solvent and catalyst were dioxane and Triton B, respectively; treating compound XII with sodium bicarbonate also had no effect on the yield.

The crude product was separated, with isopropyl alcohol, into a higher and lower melting fraction, m.p. 221–221.5° dec., and 180.5–182° dec., the elemental analyses of which were in agreement with structure XIII. The cyclic structure was indicated by their infrared spectra which were similar and showed a hydroxyl band at 2.90 μ. The oximino derivatives of both materials analyzed correctly for the dioxime of compound XIII, indicating that they were diastereoisomers.

The reaction of compound II with two equivalents of methyl acrylate gave the expected product dimethyl 4,7-dinitrodecanedioate (XIV).

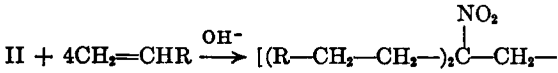

$$\text{II} + 2CH_2{=}CHCO_2CH_3 \xrightarrow{OH^-} \left[CH_3O_2C(CH_2)_2\overset{NO_2}{\overset{|}{C}}H{-}CH_2{-}\right]_2$$

XIV

The highest yield (66%) of compound XIV was obtained when compound II was treated with two equivalents of methyl acrylate for thirty-eight hours at 40° employing tetrahydrofuran and Triton B as solvent and catalyst, respectively. When the reaction was conducted in methanol with the full sodium salt of compound II or with Triton B or sodium methoxide as catalyst, the yields of compound XIV were 0–34%, (Table II).

Two solids, m.p. 60–62° and 91.5–92.5°, were separated from the crude reaction product which represented the diastereomers of compound XIV. The elemental analyses were in agreement with structure XIV and their infrared spectra were very similar.

The tetraaddition adducts dimethyl 4,7-bis(2′-carbomethoxyethyl)-4,7-dinitrodecanedioate (XV) and 4,7-bis(2′-cyanoethyl)-4,7-dinitrodecanedinitrile (XVI) were prepared in excellent yields by treating a solution of compound II in tetrahydrofuran containing a small quantity of Triton B, with four equivalents of methyl acrylate and acrylonitrile, respectively.


$$\text{II} + 4CH_2{=}CHR \xrightarrow{OH^-} [(R{-}CH_2{-}CH_2{-})_2\overset{NO_2}{\overset{|}{C}}{-}CH_2{-}]_2$$

XV. R = CO_2CH_3
XVI. R = CN

By subjecting compound XV to acid hydrolysis a 92% yield of the corresponding tetraacid, 4,7-bis(2′-carboxyethyl)-4,7-dinitrodecanedioic acid was secured.

Mononitroparaffins. In view of the fact that cyclic products were obtained from the reaction of α,ω-dinitroparaffins with four equivalents of methyl vinyl ketone, it appeared desirable to determine the structure of the methyl vinyl ketone diaddition adducts (and triaddition adduct in the case of nitromethane) of primary mononitro paraffins; Shechter, Ley, and Zeldin[5] prepared and

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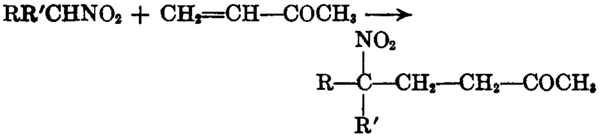
[5] H. Shechter, D. E. Ley, and L. Zeldin, *J. Am. Chem. Soc.*, **74**, 3664 (1952).

characterized the monoaddition adducts XVIIa and XVIIb. These authors stated that besides

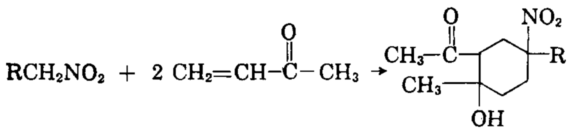


$$RR'CHNO_2 + CH_2{=}CH{-}COCH_3 \longrightarrow R{-}\overset{\displaystyle NO_2}{\underset{\displaystyle R'}{C}}{-}CH_2{-}CH_2{-}COCH_3$$

XVIIa. R = R′ = H
XVIIb. R = H; R′ = CH_3
XVIIc. R = H; R′ = $CH_3{-}CH_2{-}CH_2$

these products "... nitroethane and nitromethane also yield 1:2 and 1:2 and 1:3 adducts respectively...." However, no attempts to isolate and characterize these materials were reported.

When nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane were treated with two equivalents of methyl vinyl ketone (three equivalents in the case of nitromethane), cyclization of the Michael adducts took place with the formation of 1-methyl 2-acetyl-4-alkyl-4-nitro-1-cyclohexanols (XVIII).



XVIII

XVIIIa. R = CH_3; XVIIIb. R = $CH_2{-}CH_3$; XVIIIc. R = $CH_2{-}CH_2{-}CH_3$; XVIIId. R = $CH_2{-}CH_2{-}COCH_3$; XVIIIe. R = H.

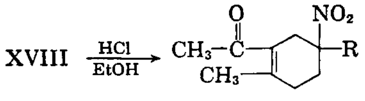
The structure of these products was established by (1) elemental analyses, (2) infrared data, (3) oxime and/or semicarbazone formations, and (4) dehydration to cyclic olefins (XIX). In Table III are summarized the yields of the cyclic alcohols (XVIII) and their derivatives.

TABLE III

Compound	Yield, %	Oxime, Yield, %	Olefin, Yield, %
XVIIIa	93	92	85
XVIIIb	65	90	73
XVIIIc	73	80, 97[a]	86
XVIIId	64	85	—
XVIIIe	5	—	—

[a] Semicarbazone.

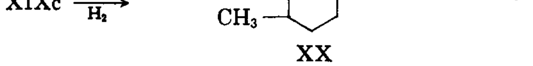
The infrared spectra of compounds XVIII possessed hydroxyl bands in the region of 2.85–3.0 μ and their oxime derivatives showed the correct analysis for monoximes, except compound XVIIId which showed the correct analysis for a dioxime. Complete oximation was established by the absence of a carbonyl band in the infrared spectra of these derivatives.



XIXa. R = CH_3
XIXb. R = $CH_2{-}CH_3$
XIXc. R = $CH_2{-}CH_2{-}CH_3$

The dehydration of compounds XVIII to XIX was carried out in refluxing ethanol saturated with hydrogen chloride. The olefins were shown to be α,β-unsaturated ketones by the presence of a peak in the 242–243 mμ region of their ultraviolet spectra.

Catalytic hydrogenation of compound XIXc with palladium chloride gave an 89% yield of compound XX, b.p. 90–120° (0.2 mm). The wide boiling point range can be ascribed to the presence



XX

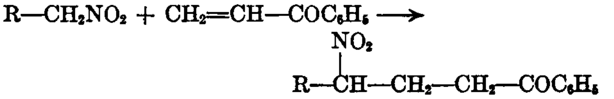
of diastereoisomers since the infrared spectra of the several fractions obtained were all very similar. The isomers were partially separated by dissolving the distillate in hexane and cooling the resulting solution to −78°. Filtration afforded a solid isomer, which after several recrystallizations from hexane melted at 54–55°. The hexane filtrate was distilled and a fraction boiling at 90–95° (0.2 mm.) as well as the above solid, were subjected to elemental analyses. Both samples showed the correct analysis for $C_{12}H_{21}O_3N$ which was in agreement with structure XX.

It is interesting to note that the diaddition adduct XVIIIa prepared from nitroethane and two equivalents of methyl vinyl ketone was not obtained unless the nitroparaffin was washed with an aqueous sodium bicarbonate solution. This indicated that an acidic impurity was present in the nitroethane which neutralized the catalytic amount of sodium hydroxide employed. These results are analogous to those obtained in the reaction of compound X with methyl vinyl ketone (*vide supra*). The product XVIIIa consisted of a solid and a liquid. As the infrared spectra of both were very similar, it was surmised that the liquid was either very crude or a product of a mixture of diastereoisomers of compound XVIIIa. The latter assumption was verified by dehydrating the oil in 77% yield to the same olefin (XIXa) which was also obtained from the solid product.

During the course of this investigation the monoaddition adduct, 5-nitro-2-octanone (XVIIc), which has not been previously reported, was prepared in 83% yield by treating 1-nitrobutane with one equivalent of methyl vinyl ketone.

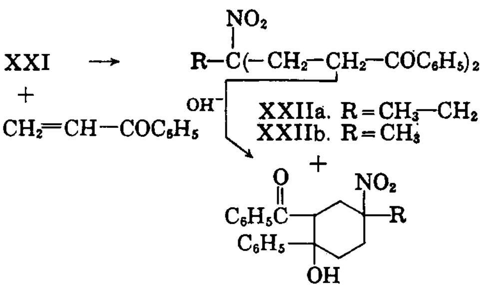
In view of the cyclic products resulting from the Michael addition with methyl vinyl ketone and primary nitroparaffins, it was interesting to extend the investigation to phenyl vinyl ketone.

The monoaddition adducts XXIa and XXIb were prepared in 92% yield by treating nitropropane and nitroethane with one equivalent of phenyl vinyl ketone, prepared *in situ* from β-chloropropiophenone and the salt of the nitroparaffin. The diaddition adducts were prepared in almost quantitative yield by treating compounds XXIa and



$$R{-}CH_2NO_2 + CH_2{=}CH{-}COC_6H_5 \longrightarrow R{-}\overset{NO_2}{\overset{|}{C}H}{-}CH_2{-}CH_2{-}COC_6H_5$$

XXIa. R = $CH_3{-}CH_2$
XXIb. R = CH_3



XXIIIa. R = CH_3CH_2
XXIIIb. R = CH_3

XXIb with another equivalent of phenyl vinyl ketone.

The infrared spectrum of the crude reaction product obtained by treating XXIa, at 0–5°, with phenyl vinyl ketone, possessed a hydroxyl band at 2.90 μ, two carbonyl bands of similar intensity at 5.97 and 6.02 μ and aromatic absorption bands at 13.16, 13.45, 14.32, and 14.42 μ. Fractional recrystallization of this material from isopropyl ether afforded several fractions the infrared spectra of which were similar to that of the crude product. However, two fractions were obtained which possessed only one carbonyl band. One of these, m.p. 132–132.5°, had absorption peaks at 2.90 (hydroxyl), 6.02 (aromatic ketone), 13.16 and 14.32 μ (aromatic), while the other, m.p. 128–129°, had bands at 5.97 μ (aromatic ketone), 13.45 and 14.42 μ (aromatic), but was void of a hydroxyl band. Both showed correct analyses for a diaddition adduct. As the infrared spectrum of the higher melting material possessed a hydroxyl band, it was assigned the cyclic structure XXIIIa while the lower melting product, which did not contain a hydroxyl band, was assigned structure XXIIa. To verify this assignment, compound XXIIa was converted to its corresponding oximino derivative, in 95% yield. The elemental analysis of this material was in agreement with that calculated for the dioxime of compound XXIIa. In addition, compound XXIIa gave compound XXIIIa in almost quantitative yield, by refluxing in ethanol containing a catalytic amount of sodium hydroxide.

The yield of compound XXIIIa from the monoaddition adduct XXIa was increased to 90% by refluxing for five hours an aqueous ethanolic solution of XXIa with phenyl vinyl ketone.

When an attempt was made to convert compound XXIIIa to its corresponding oximino derivative, 93% of the starting material was recovered. The resistance to oximation might be rationalized from a study of the Fisher-Taylor-Hirschfelder model of XXIIIa, which showed that the carbonyl carbon is shielded by the substituents on the cyclohexane ring.

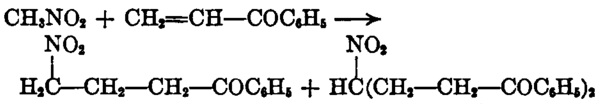
The phenyl vinyl ketone diaddition adduct of nitroethane was obtained in a 99% yield by treating an aqueous ethanolic solution of the sodium salt of compound XXIb with β-chloropropiophenone at 40° for four hours. The infrared spectrum of the product possessed a hydroxyl band at 2.90 μ and a strong carbonyl band at 6.01 μ with a weak shoulder at 5.95 μ, indicating that the product was predominantly compound XXIIIb containing a small amount of compound XXIIb. This assumption was based on the presence of the hydroxyl band and the fact that it was previously found (*vide supra*) that compound XXIIIa possessed a carbonyl band at 6.01 μ while its open chain structural isomer XXIIa showed a carbonyl band at a lower wave length (5.97 μ).

The small amount of compound XXIIb in the crude product was converted to the cyclic structure XXIIIb by refluxing it for eleven hours in ethanol containing a catalytic amount of sodium hydroxide. The total yield of compound XXIIIb was 93%. The infrared spectrum contained a hydroxyl band at 2.90 μ and only one carbonyl band at 6.01 μ. Attempted reaction of this compound with hydroxylamine was fruitless and only starting material (92% recovery) was obtained. The unreactivity of the carbonyl group is analogous to the results obtained with compound XXIIIa and again can be attributed to shielding of the carbonyl carbon.

When the reaction with compound XXIb and β-chloropropiophenone was carried out under anhydrous conditions, by replacing the aqueous ethanol with dry methanol and the sodium hydroxide with sodium methoxide, a 97% crude yield of product was obtained which consisted mostly of the noncyclic product XXIIb (weak hydroxyl band at 2.90 μ and a strong carbonyl band at 5.95 μ with a shoulder at 6.01 μ). By treating the crude product with hot ethanol, followed by recrystallization of the insoluble material from acetonitrile a solid, m.p. 153.5–154°, was secured. This material was identified as compound XXIIb by (1) its elemental analysis which corresponded to $C_{20}H_{21}O_4N$ (2) its infrared spectrum, which was void of a hydroxyl band but contained a carbonyl band at 5.95 μ, and (3) the elemental analysis of its dioximino derivative which agreed with that calculated for compound XXIIb.

The previous experiments indicated that the formation of the cyclic product XXIIIb was favored when aqueous ethanol was employed as the solvent, while mostly noncyclic material (XXIIb) resulted when dry methanol was used. These results may be explained on the basis of the strength of the base present in the reaction mixture. Hine and Hine[6] have reported that the relative base strength of methoxide, ethoxide, and hydroxide ion increases in the order given. Thus, in the reaction employing dry methanol the base, methoxide ion, did not catalyze the internal aldol condensation as well as ethoxide or hydroxide, which were present in the experiment performed in aqueous ethanol.

The investigation of the reaction of mononitroparaffins with phenyl vinyl ketone was extended to nitromethane by treating an aqueous methanolic solution containing 0.2 mole of sodium methanenitronate with 0.19 mole of β-chloropropiophenone at 0–20° for an hour and a half. Two products, m.p. 131–132° and 62.5–63.5°, were obtained, the infrared spectra of which were void of a hydroxyl absorption, indicating that neither compound was cyclic in structure. The elemental analysis of the lower melting product and its corresponding semicarbazone, prepared in 96% yield, agreed with that calculated for the monoaddition adduct, γ-nitrobutyrophenone (XXIV). Sonn[7] who had prepared this compound by a similar procedure, reported a melting point of 102° dec. The yield of compound XXIV was increased to 78% by employing a 10:1 ratio of nitromethane to phenyl vinyl ketone.



$$CH_3NO_2 + CH_2{=}CH{-}COC_6H_5 \longrightarrow H_2\overset{NO_2}{\overset{|}{C}}{-}CH_2{-}CH_2{-}COC_6H_5 + H\overset{NO_2}{\overset{|}{C}}(CH_2{-}CH_2{-}COC_6H_5)_2$$

XXIV XXV

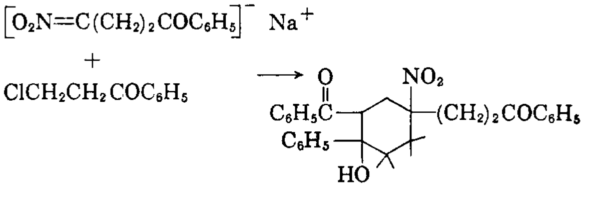
The elemental analysis of the higher melting product, m.p. 131–132°, corresponded only to that calculated for the diaddition adduct (XXV). Its structure was established by its conversion to a mono-bromo product, 1,5-dibenzoyl-3-bromo-3-nitropentane,[8] which in its turn showed the correct analysis.

As Allen and Bell[9] had reported the preparation of the triaddition adduct (XXVI) of phenyl vinyl ketone to nitromethane by treating β-chloropropiophenone and nitromethane in the presence of potassium acetate and a sufficient quantity of sodium methoxide to keep the reaction medium basic, we duplicated their reaction conditions. A product, m.p. 131–132° was obtained which was not XXVI but was identical with the diadduct XXV.

$$O_2NC[(CH_2)_2CO]_3$$

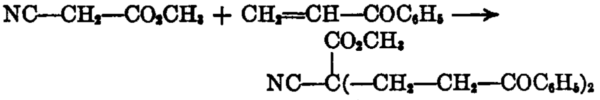
XXVI

Treatment[8] of the sodium salt of XXV with β-chloropropiophenone in dimethyl sulfoxide gave the cyclic triadduct XXVII. The structure assignment was based on (1) its elemental analysis, (2) its infrared spectrum, which possessed a hydroxyl band at 2.91 μ and a carbonyl band at 6.05 μ with a shoulder at 5.98 μ, and (3) the elemental analysis of its monooxime derivative. The infrared spectrum of this derivative showed a hydroxyl band at 2.90 μ and a carbonyl band at 6.08 μ. The failure of compound XXVII to give a dioxime can be again attributed (*vide supra* compound XXIIIa) to the highly hindered carbonyl group attached to the cyclohexane ring.



XXVII

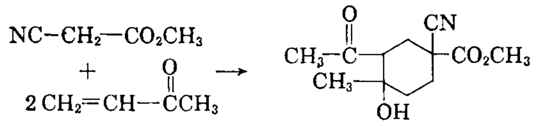
The reaction between methyl cyanoacetate and phenyl vinyl ketone was also investigated because Allen and Bell[9] claimed that the product was the open chain diaddition adduct XXVIII. Our findings were in agreement with their structure assignment, as the elemental analysis of the product corresponded to $C_{22}H_{21}O_4N$ and its infrared spectrum was void of a hydroxyl absorption.



$$NC{-}CH_2{-}CO_2CH_3 + CH_2{=}CH{-}COC_6H_5 \longrightarrow NC{-}\overset{CO_2CH_3}{\overset{|}{C}}({-}CH_2{-}CH_2{-}COC_6H_5)_2$$

XXVIII

It is interesting to note that the reaction between methyl cyanoacetate and two equivalents of methyl vinyl ketone, in the presence of a catalytic amount of sodium methoxide gave the cyclic product XXIX. The structure assignment was based on (1) the elemental analysis which corresponded to $C_{12}H_{17}O_4N$, (2) its infrared spectrum which possessed a hydroxyl band at 2.89 μ, and (3) its corresponding semicarbazone, prepared in 90% yield which showed the correct analysis for structure XXIX.



XXIX

EXPERIMENTAL

Reagents and solvents. Methyl vinyl ketone (85% water azeotrope), b.p. 76°, was obtained from Monomer and Polymers. Methyl vinyl ketone (100%), b.p. 79.5–81°, n_D^{20} 1.4108 was secured by rectification of technical grade methyl vinyl ketone produced by Matheson, Coleman and Bell. Unless otherwise specified the methyl vinyl ketone employed in this investigation did not contain any inhibitor. Methyl acrylate was Eastman yellow label, distilled prior to use, b.p. 80°, n_D^{20} 1.4018. Acrylonitrile, b.p. 78–79°, n_D^{20} 1.3908, was an American Cyanamid product. Methyl cyanoacetate, b.p. 115–116° (35 mm.), n_D^{20} 1.4182 was obtained from Matheson, Coleman and Bell.

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(6) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(7) A. Sonn, *Chem. Ber.*, **68**, 150 (1935).

(8) We are indebted to Maria L. G. Limson, Purdue University, for carrying out this experiment.

(9) C. F. H. Allen and A. B. Bell, *Can. J. Research*, **11**, 40 (1934).

Mononitroparaffins were secured from Commercial Solvents Corporation and distilled over boric acid prior to use. The α,ω-dinitroparaffins were prepared according to the procedure of Feuer and Leston.[10]

Tetrahydrofuran was DuPont's technical grade, purified according to the procedure of Feuer and Savides.[11] Purified dioxane and absolute methanol were prepared according to the procedure of Fieser.[12]

Spectral measurements. All ultraviolet spectral measurements were carried out with a Cary Model 10-11 spectrophotometer. The solvent employed was commercial 95% ethanol.

All infrared spectral-measurements were performed with a Perkin-Elmer Recording Infrared Spectrophotometer Model 21. The solid compounds were measured in a Nujol mull.

5,8-Dinitro-2,11-dodecanedione (III). A solution of 14.8 g. (0.1 mole) of 1,4-dinitrobutane, 100 ml. of 95% ethanol, 3 drops of 20% aqueous sodium hydroxide, and 16.5 g. (0.2 mole) of 85% aqueous methyl vinyl ketone, contained in a 200 ml. round bottom flask equipped with a mechanical stirrer and thermometer, was heated at 40° for 24 hr. After cooling the solution to 0–5°, 3 drops of glacial acetic acid was added. Further cooling to −78° and subsequent filtration afforded 24.2 g. (83% yield) of 5,8-dinitro-2,11-dodecanedione (III), m.p. 56–85°. After three recrystallizations from 95% ethanol the melting point rose to 91.5–92.5°. The filtrates from these recrystallizations were combined and evaporated to dryness. The residue was triturated with a small quantity (*ca.* 75 ml.) of methanol at room temperature and the insoluble material, high melting isomer, removed by filtration. Cooling the filtrate to −15° afforded a solid enriched with the low melting isomer. After repeating this procedure three times the melting point, 61–62°, remained constant.

The infrared spectra of the two isomers were very similar. The high melting isomer possessed a carbonyl band at 5.85 μ and nitro bands at 6.48 and 7.32 μ, while the lower melting diastereoisomer showed a carbonyl absorption at 5.83 μ and nitro bands at 6.48 and 7.32 μ.

Anal. Calcd. for $C_{12}H_{20}O_6N_2$: C, 49.99; H, 6.99; N, 9.72. Found for higher melting solid: C, 50.02; H, 7.17; N, 9.96. Found for lower melting solid: C, 49.88; H, 7.00; N, 9.53.

5,8-Dibromo-5,8-dinitro-2,11-dodecanedione (V). To a mixture of 8.64 g. (0.03 mole) of compound III, m.p. 61–62° and 70 ml. of methanol was added dropwise, with stirring, a solution of 2.48 g. (0.06 mole) 97% sodium hydroxide dissolved in 20 ml. of water. The addition was regulated so that the temperature did not exceed 9°. The ice bath was then removed and the solution warmed to 25° and stirred until a *p*H of 8–9 was attained (*ca.* 20 min.). After cooling to 0–5°, 11.5 g. (0.072 mole) of bromine was added dropwise at such a rate that the temperature did not exceed 9°. Stirring for an additional 0.5 hr. at room temperature, followed by filtration and washing of the precipitate with 100 ml. of distilled water gave 13.5 g. (100% yield) of product, m.p. 120–121°. Recrystallization from aqueous methanol yielded 12.4 g. (92% yield) of pure *5,8-dibromo-5,8-dinitro-2,11-dodecanedione* (V), m.p. 121–122°.

The infrared spectrum possessed a carbonyl band at 5.85 μ and nitro bands at 6.46 and 7.46 μ.

Anal. Calcd. for $C_{12}H_{18}O_6N_2Br_2$: C, 32.28; H, 4.04; N, 6.28; Br, 35.87. Found: C, 32.18; H, 3.96; N, 6.10; Br, 36.15.

When the previous experiment was repeated employing 8.64 g. (0.03 mole) of the higher melting diastereoisomer of compound III a 97% yield of the same dibromo derivative (V) was obtained.

1,2-Bis(1′-nitro-3′-acetyl-4′-hydroxy-4′-methylcyclohexyl)-ethane (VI). In a 200-ml. round bottom flask equipped with a mechanical stirrer and thermometer were placed 7.4 g. (0.05 mole) of 1,4-dinitrobutane, 125 ml. of 95% ethanol, 3 drops of 20% aqueous sodium hydroxide, and 19.8 g. (0.24 mole) of 85% aqueous methyl vinyl ketone. The solution was stirred at room temperature for 1 hr. and then heated at 40° for an additional 24 hr. After cooling to 0–5°, 3 drops of glacial acetic acid was added. Filtration afforded 18.6 g. (86% yield) of a mixture of diastereoisomers possessing the structure, *1,2-bis(1′-nitro-3′-acetyl-4′-hydroxy-4′-methylcyclohexyl)ethane* (VI), m.p. 200–203° dec. Two recrystallizations from methanol raised the melting point to 223–229° dec., while several recrystallizations from acetonitrile afforded a solid, melting at 236–237° dec.

The infrared spectra of the high and low melting samples were very similar. The high melting solid possessed a hydroxyl band at 2.92 μ, a carbonyl band at 5.94 μ, and a nitro band at 6.52 μ, while the lower melting solid showed absorptions for these groups at 2.90, 5.92, and 6.51 μ, respectively.

Anal. Calcd. for $C_{20}H_{32}O_8N_2$: C, 56.06; H, 7.53; N, 6.54. Found for higher melting solid: C, 56.11; H, 7.75; N, 6.51. Found for lower melting solid: C, 56.50; H, 7.92; N, 6.20.

The dioxime of compound VI was prepared in the usual manner[13] except that the reaction mixture was refluxed for 17 hr. An 88% yield of product was obtained which on treatment with boiling methanol afforded an insoluble material, m.p. 254–256° dec., and a soluble material, m.p. 244–245° dec., which precipitated from the filtrate on the addition of water. Recrystallization of the lower melting material from 50% aqueous methanol raised the melting point to 248° dec.

Anal. Calcd. for $C_{20}H_{34}O_8N_4$: C, 52.39; H, 7.47; N, 12.22. Found for lower melting solid: C, 52.32; H, 7.75; N, 12.22. Found for higher melting solid: C, 52.69; H, 7.53; N, 12.33.

1,2-Bis(1′-nitro-3′-acetyl-4′-methyl-1′-cyclohexenyl)ethane (VIII). A mixture of 8.56 g. (0.02 mole) of compound VI, m.p. 230–231°, and 175 ml. of absolute ethanol was cooled in an ice bath at 0–5°, while 41.5 g. (1.13 moles) of gaseous hydrogen chloride was bubbled into the reaction mixture. The flask was fitted with a condenser, refluxed for 24 hr., and then cooled to 0–5°. Filtration afforded 3.57 g. (46% yield) of compound VIII, m.p. 167–169°. Recrystallization from isopropyl alcohol afforded pure *1,2-bis(1′-nitro-3′-acetyl-4′-methyl-1′-cyclohexenyl)ethane* (VIII), m.p. 173.5–174.5°.

The infrared spectrum possessed an olefinic band at 6.02 μ, a shoulder at 5.94 μ (carbonyl), and nitro bands at 6.54 and 7.42 μ while the ultraviolet spectrum showed a peak at 232 mμ, log ϵ 4.02.

Anal. Calcd. for $C_{20}H_{28}O_6N_2$: C, 61.21; H, 7.19; N, 7.14. Found: C, 61.12; H, 7.21; N, 7.24.

p-(1′-Oxa-4′-oxopentyl)phenol (IXa). In a 200-ml. round bottom flask were placed 11.0 g. (0.1 mole) of hydroquinone, 100 ml. of 95% ethanol, 3 drops of 20% aqueous sodium hydroxide, and 19.8 g. (0.24 mole) of 85% aqueous methyl vinyl ketone. The mixture was heated at 40° with stirring for 24 hr., cooled to 0–5°, and acidified with 3 drops of glacial acetic acid. Evaporation of the solution to dryness, *in vacuo*, and recrystallization of the residue from water afforded 8.3 g. of product, m.p. 115–119°. Subsequent recrystallization from carbon tetrachloride raised the melting point to 124.5–125.5°.

The infrared spectrum contained a carbonyl band at 5.92 μ, an ether band at 9.02 μ, and aromatic hydroxyl bands at 3.10 and 8.13 μ.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.89; H, 6.71.

5,9-Dinitro-2,12-tridecanedione (I). The procedure em-

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(10) H. Feuer and G. Leston, *Org. Syntheses*, **34**, 37 (1954).

(11) H. Feuer and C. Savides, *J. Am. Chem. Soc.*, **81**, 5826 (1959).

(12) L. F. Fieser, *Experiments in Organic Chemistry*, D. C. Heath, New York, 1941, pp. 359 and 368.

(13) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, Third Ed., Wiley, New York, 1948, pp. 202 and 170.

ployed was similar to that used for the preparation of compound III except that 16.2 g. (0.1 mole) 1,5-dinitropentane was employed, which was mixed with 10 ml. of a 6.5% aqueous sodium bicarbonate solution.

Filtration of the cooled (−78°) reaction mixture afforded an oily solid which on treatment with a small quantity of 95% ethanol at room temperature afforded a 40–50% yield of 5,9-dinitro-2,12-tridecanedione (I), m.p. 75–76° (lit. value,[8b] m.p. 77.5–78.5°).

1,3-Bis(1'-nitro-3'-acetyl-4'-hydroxy-4'-methylcyclohexyl)-propane (XI). (a) *From 1,5-dinitropentane.* The procedure employed was similar to that used for the preparation of compound VI except that 8.1 g. (0.05 mole) 1,5-dinitropentane was employed which had been washed with an aqueous sodium bicarbonate solution and dried by filtering through anhydrous sodium sulfate. A 50% yield (11.0 g.) of a mixture of diastereoisomers of compound XI, m.p. 153–160° was obtained. Recrystallization from isopropyl alcohol afforded a solid, m.p. 167–177°, the infrared spectrum of which possessed a hydroxyl band at 2.86 μ, a carbonyl band at 5.90 μ, and a nitro band at 6.50 μ.

Anal. Calcd. for $C_{21}H_{34}O_8N_2$: C, 57.00; H, 7.75; N, 6.33. Found: C, 56.85; H, 7.59; N, 6.27.

(b) *From compound I.* A mixture consisting of 9.06 g. (0.03 mole) of compound I, 150 ml. of 95% ethanol, 2 drops of 20% aqueous sodium hydroxide, and 4.62 g. (0.066 mole) of 85% aqueous methyl vinyl ketone was mechanically stirred at 40° for 24 hr. Cooling to 0–5° followed by acidification with 3 drops of glacial acetic acid and subsequent filtration afforded 6.5 g. (50% yield) of compound XI, m.p. 165–175°.

The dioxime of compound XI was prepared in the usual manner[13] except that the reaction mixture was refluxed for 24 hr. A 71% yield of product, m.p. 168–171°, was obtained. Recrystallization from aqueous methanol raised the melting point to 180–187°.

Anal. Calcd. for $C_{21}H_{36}O_8N_4$: C, 53.38; H, 7.68; N, 11.86. Found: C, 53.09; H, 7.79; N, 12.05.

1,4-Bis(1'-nitro-3'-acetyl-4'-hydroxy-4'-methylcyclohexyl)-butane (XIII). The procedure employed was similar to that used for the preparation of compound VI except that 8.80 g. (0.05 mole) of 1,6-dinitrohexane was employed. A 39% yield (8.90 g.) of 1,4-bis(1'nitro-3'-acetyl-4'-hydroxy-4'-methylcyclohexyl)butane (XIII), m.p. 188–198° dec., was obtained. The diastereoisomers of compound XIII were partially separated by treating the product with 300 ml. of boiling isopropyl alcohol. The insoluble material melted at 219–221° dec. Concentration and cooling of the filtrate to −15° afforded a lower melting solid, m.p. 170–174° dec. Recrystallization of the higher melting solid from acetonitrile and the lower from isopropyl alcohol raised the melting points to 221–221.5° dec. and 180.5–182° dec., respectively.

The infrared spectra of both materials were similar and possessed a strong hydroxyl band at 2.90 μ.

Anal. Calcd. for $C_{22}H_{36}O_8N_2$: C, 57.88; H, 7.95; N, 6.14. Found for lower melting solid: C, 57.79; H, 7.89; N, 6.16. Found for higher melting solid: C, 57.84; H, 8.10; N, 6.16.

The *dioxime* of the lower melting mixture of the diastereoisomers of compound XIII was prepared in the usual manner[13] except that the reaction mixture was refluxed for 27 hr. A 90% yield of product was obtained, which after recrystallization from acetonitrile melted at 190–193°. The infrared spectrum of this material was void of a carbonyl absorption.

Anal. Calcd. for $C_{22}H_{38}O_8N_4$: C, 54.30; 7.87; N, 11.52. Found: C, 54.48; H, 7.98; N, 11.23.

The *dioxime* of the higher melting mixture of diastereoisomers of compound XIII was obtained in a 92% yield. Recrystallization from isopropyl alcohol raised the melting point to 239.5–240°.

Anal. Calcd. for $C_{22}H_{38}O_8N_4$: C, 54.30; H, 7.87; N, 11.52. Found: C, 54.41; H, 8.12; N, 11.69.

Dimethyl 4,7-dinitrodecanedioate (XIV). In a 200-ml. round bottom flask, equipped with a mechanical stirrer, dropping funnel, and thermometer were placed 120 ml. of tetrahydrofuran, 14.8 g. (0.1 mole) of 1,4-dinitrobutane and 2 ml. of an 85% methanolic solution of Triton B. The flask was placed in an ice bath and 17.2 g. (0.2 mole) of methyl acrylate, containing 0.05 g. of hydroquinone, was added dropwise, so that the temperature did not exceed 35°. After stirring the solution at 40° for 36 hr. it was cooled to 0–5° and acidified with 7*N* hydrochloric acid. Evaporation *in vacuo* afforded an oil. Dissolution of the oil in a mixture containing 125 ml. of diethyl ether and 50 ml. of purified tetrahydrofuran and subsequent cooling to −78° gave on filtration 21.2 g. (66% yield) of a mixture of the two diastereoisomers of dimethyl 4,7-dinitrodecanedioate (XIV), m.p. 65–75°.

The isomers were separated by dissolving the product in hot methanol and allowing the resulting solution to cool to room temperature. Filtration afforded a solid enriched with the high melting isomer, m.p. 70–89°. Several recrystallizations from methanol raised the melting point to 91.5°–92.5°. The filtrates from the above recrystallizations were combined, evaporated *in vacuo* to one quarter of the original volume, frozen in Dry Ice, and filtered. The solid obtained was treated with warm methanol (30–35°) and filtered to remove the undissolved high melting isomer. Slow cooling of the filtrate to −15° and subsequent filtration yielded material enriched with the low melting isomer, m.p. 59–71°. After several recrystallizations in this manner a solid melting at 60–62° was secured.

The infrared spectra of the high and low melting isomers were similar and possessed a carbonyl band at 5.80 μ and a nitro band at 6.46 μ.

Anal. Calcd. for $C_{12}H_{20}O_8N_2$: C, 45.00; H, 6.29; N, 8.75. Found for higher melting solid: C, 45.34; H, 6.60; N, 8.64. Found for lower melting solid: C, 44.79; H, 6.32; N, 8.81.

Dimethyl 4,7-bis(2'-carbomethoxyethyl)-4,7-dinitrodecanedioate (XV). The procedure employed was similar to that used in the preparation of compound XIV except that 7.4 g. (0.05 mole) of 1,4-dinitrobutane and a reaction time of 60 hr. was employed. After acidification, the reaction mixture was filtered and afforded 22.9 g. (93% yield) of dimethyl 4,7-bis(2'-carbomethoxyethyl)-4,7-dinitrodecanedioate (XV), m.p. 120–122°. Recrystallization from acetonitrile raised the melting point to 122.5–123.5°.

The infrared spectrum possessed an ester carbonyl band at 5.74 μ and nitro bands at 6.48 and 7.37 μ.

Anal. Calcd. for $C_{20}H_{32}O_{12}N_2$: C, 48.77; H, 6.55; N, 5.69. Found: C, 48.91; H, 6.34; N, 5.62.

4,7-Bis(2'-carboxyethyl)-4,7-dinitrodecanedioic acid. In a 500-ml. round bottom flask were placed 18.4 g. (0.0374 mole) of compound XV and 300 ml. of 6*N* hydrochloric acid. The flask was fitted with a condenser and the mixture refluxed for 24 hr. Cooling to 5° and filtration afforded 15.1 g. (92% yield) of 4,7-bis(2'-carboxyethyl)-4,7-dinitrodecanedioic acid, m.p. 219.5°. Recrystallization from water did not raise the melting point.

The infrared spectrum possessed a carbonyl band at 5.88 μ and a nitro band at 6.52 μ.

Anal. Calcd. for $C_{16}H_{24}O_{12}N_2$: C, 44.03; H, 5.54; N, 6.42. Found: C, 43.90; H, 5.66; N, 6.40.

4,7-Bis(2'-cyanoethyl)-4,7-dinitrodecanedinitrile (XVI). The procedure employed was similar to that used for the preparation of compound XV except that the methyl acrylate was replaced with 11.7 g. (0.22 mole) of acrylonitrile and the reaction time was decreased to 24 hr. A 68% yield of compound XVI, m.p. 153–156°, was obtained. Recrystallization from acetonitrile raised the melting point to 162–164°.

The infrared spectrum possessed a nitrile band at 4.46 μ and nitro bands at 6.47 and 7.36 μ.

Anal. Calcd. for $C_{16}H_{20}O_4N_6$: C, 53.32; H, 5.59; N, 23.32. Found: C, 53.20; H, 5.81; N, 23.65.

5-Nitro-2-octanone (XVIIc). In a 300-ml. round bottom flask, equipped with a mechanical stirrer and thermometer, were placed 20.6 g. (0.2 mole) of freshly distilled 1-nitrobutane, 150 ml. of 95% ethanol, and 4 drops of 20% aqueous sodium hydroxide. The mixture was cooled to 0–5° and 14.0

g. (0.2 mole) of methyl vinyl ketone (containing 0.05 g. of hydroquinone) was added. After heating the mixture with stirring at 40° for 24 hr., it was cooled to 0–5° and acidified with 3 drops of glacial acetic acid. The ethanol was removed *in vacuo* and the residue distilled to afford 28.8 g. (83% yield) of product, b.p. 67–71° (0.2 mm.); n_{D}^{20} 1.4414–1.4428. Redistillation afforded pure *5-nitro-2-octanone* (XVIIc), b.p. 62° (0.12 mm.); n_{D}^{20} 1.4418.

The infrared spectrum possessed a ketone band at 5.82 μ and nitro bands at 6.46 and 7.36 μ.,

Anal. Calcd. for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.80; H, 8.69; N, 8.43.

The semicarbazone of compound XVIIc was prepared in 88% yield by the usual method[13] and recrystallized from 25% aqueous ethanol, m.p. 112–112.5°.

Anal. Calcd. for $C_9H_{18}O_3N_4$: C, 46.94; H, 7.88; N, 24.33. Found: C, 46.77; H, 7.88; N, 24.40.

1,4-Dimethyl-2-acetyl-4-nitro-1-cyclohexanol (XVIIIa). A 300-ml. round bottom flask, equipped with a mechanical stirrer was charged with 150 ml. 95% ethanol, 15.0 g. (0.2 mole) freshly distilled nitroethane (which had been washed with a 6% aqueous sodium bicarbonate solution and dried by filtering through anhydrous sodium sulfate) and 4 drops of 20% aqueous sodium hydroxide. The mixture was cooled to 0–5° and 36.2 g. (0.44 mole) of 85% aqueous methyl vinyl ketone was added. The mixture was then stirred at room temperature (28°) for 1 hr. and at 40° for an additional 24 hr. After cooling the solution to 0–5°, acidification with 3 drops of glacial acetic acid, and evaporation of the solvent *in vacuo* a semisolid was obtained which upon dissolution in warm (60°) 40% aqueous methanol and slow cooling to −15° afforded 25.3 g. of crude product (XVIIIa), m.p. 66–76°. Removing the methanol, *in vacuo*, extracting with three 100-ml. portions of ether, drying with magnesium sulfate followed by filtration and distillation gave 14.5 g., b.p. 70–140° (0.2 mm.) of liquid, the infrared spectrum of which was similar to the solid previously obtained. Thus the total crude yield of 1,4-dimethyl-2-acetyl-4-nitro-1-cyclohexanol (XVIIIa) was 93%.

Recrystallization of the solid product from hexane raised the melting point to 78–79°.

The infrared spectrum showed bands at 2.89 (hydroxyl), 5.88 (carbonyl), 6.53 and 7.46 μ (nitro).

Anal. Calcd. for $C_{10}H_{17}O_4N$: C, 55.80; H, 7.96; N, 6.51. Found: C, 55.70: H, 8.06; N, 6.46.

The *monoöxime of compound* XVIIIa was prepared in 92% yield by the usual method.[13] Recrystallization from aqueous ethanol raised the melting point to 165.5–166°.

Anal. Calcd. for $C_{10}H_{18}O_4N_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.01; H, 8.14; N, 12.28.

1,4-Dimethyl-2-acetyl-4-nitro-1-cyclohexene (XIXa). A mixture of 21.5 g. (0.1 mole) of solid 1,4-dimethyl-2-acetyl-4-nitro-1-cyclohexanol (XVIIIa) and 300 ml. of absolute ethanol, contained in a 500 ml. round bottom flask, was cooled in an ice bath to 0–5°, while 50 g. (1.4 moles) gaseous hydrogen chloride was bubbled into the mixture. The flask was fitted with a condenser and the reaction mixture refluxed for 24 hr. Removing the ethanol *in vacuo*, diluting the residue with 100 ml. of water, extracting with four 100-ml. portions of ether, washing the combined extracts with 100 ml. of a saturated sodium bicarbonate solution, drying over magnesium sulfate, filtering and distilling gave 16.8 g. (85% yield) of product, b.p. 100–104° (0.3 mm.). Redistillation afforded pure 1,4-dimethyl-2-acetyl-4-nitro-1-cyclohexene (XIXa), b.p. 82° (0.1 mm.), n_{D}^{20} 1.4998.

The infrared spectrum possessed a ketone band at 5.92 μ, an olefinic band at 6.15 μ, and nitro bands at 6.50 and 7.41 μ, while the ultraviolet spectrum showed a peak at 242 mμ, log ε 3.72.

Anal. Calcd. for $C_{10}H_{15}O_3N$: C, 60.89; H, 7.67; N, 7.10: Found: C, 61.08; H, 7.64; N, 7.27.

When the liquid fraction, b.p. 70–140° (0.2 mm.), of 1,4-dimethyl-2-acetyl-1-cyclohexanol (XVIIIa) was dehydrated, a 77% yield of compound XIXa was obtained.

1-Methyl-2-acetyl-4-ethyl-4-nitro-1-cyclohexanol (XVIIIb). The procedure employed was similar to that used for the preparation of compound XVIIIa except that 17.8 g. (0.2 mole) of 1-nitropropane was employed.

After evaporation of the solvent *in vacuo*, a heavy oil was obtained which partially solidified when cooled to −78°. Filtration afforded 13.2 g. of crude product (XVIIIb), m.p. 49–55°. Distillation of the filtrate afforded three fractions. The first, 3.43 g., b.p. 103–108° (5 mm.), n_{D}^{20} 1.4418 was identified as 5-nitro-2-heptanone [lit. value[14] b.p. 102° (4.8 mm.), n_{D}^{20} 1.4410]. Fraction two, 6.80 g. b.p. 80–110° (0.1 mm.) consisted of a solid suspended in a liquid. Filtration gave 1.35 g. of product (XVIIIb), m.p. 53–56°. The filtrate consisted of crude 5-nitro-2-heptanone (XVIIc) as indicated by comparison of its infrared spectrum with that of an authentic sample of compound XVIIc. Fraction three, solidified completely affording 15.1 g. of compound XVIIIb, m.p. 50–56°. Thus the total crude yield of 1-methyl-2-acetyl-4-nitro-4-ethyl-1-cyclohexanone (XVIIIb) was 65%. Recrystallization from 40% aqueous ethanol raised the melting point to 58–58.5°.

The infrared spectrum possessed bands at 2.97 (hydroxyl), 5.92 (carbonyl), 6.52 and 7.37 μ (nitro).

Anal. Calcd. for $C_{11}H_{19}O_4N$: C, 57.62; H, 8.35; N, 6.11. Found: C, 57.79; H, 8.36; N, 6.18.

The *monoöxime of compound* XVIIIb which was prepared by the usual manner[13] in 90% yield and recrystallized from aqueous ethanol, melted at 169–169.5°.

Anal. Calcd. for $C_{11}H_{20}O_4N_2$: C, 54.08; H, 8.25; N, 11.47. Found: C, 54.34; H, 8.36; N, 11.44.

1-Methyl-2-acetyl-4-ethyl-4-nitro-1-cyclohexene (XIXb). The procedure employed was similar to that used in the preparation of compound XIXa except that 22.9 g. (0.1 mole) of compound XVIIIb was employed.

Distillation afforded 18.8 g. (86% crude yield) of liquid product, b.p. 110–115° (0.5 mm.). Dissolving this liquid in 95% ethanol and cooling to −78°, gave 15.4 g. (73% yield) of 1-methyl-2-acetyl-4-ethyl-4-nitro-1-cyclohexene (XIXb), m.p. 41–44°. Dissolving XIXb in isopropyl ether at room temperature and slow cooling to 10° raised the melting point to 44.5–46°.

The infrared spectrum possessed a ketone band at 5.95 μ, an olefinic band at 6.13 μ, nitro bands at 6.53 and 7.37 μ, while the ultraviolet spectrum showed a peak at 242 mμ, log ε 3.47.

Anal. Calcd. for $C_{11}H_{17}O_3N$: C, 62.54; H, 8.11; N, 6.65. Found: C, 62.37; H, 8.27; N, 6.59.

1-Methyl-2-acetyl-4-propyl-4-nitro-1-cyclohexanol (XVIIIc). In a 300-ml. round bottom flask, equipped with a mechanical stirrer and thermometer, were placed 20.6 g. (0.2 mole) of freshly distilled 1-nitrobutane, 150 ml. of purified dioxane, and 2 ml. of a 35% methanolic solution of Triton B. The flask was immersed in a cold water bath (18°) and 36.3 g. (0.44 mole) of 85% aqueous methyl vinyl ketone (containing 0.1 g. of hydroquinone) was added dropwise so that the temperature did not exceed 30°. The solution was stirred at 40° for an additional 15 hr., cooled to 0–5°, acidified with dilute hydrochloric acid, diluted with 900 ml. of water, and extracted with three 250-ml. portions of ether. The ether extracts were combined, dried over magnesium sulfate, filtered, and evaporated *in vacuo* to afford a semisolid. Recrystallization of this material from 50% aqueous methanol afforded 29.1 g. of product (XVIIIc), m.p. 89.5–90.5°. By warming the filtrate, from the recrystallization, to 60° followed by the addition of 100 ml. of water and slow cooling to 10°, an additional 6.8 g. of product (XVIIIc), m.p. 74–84° was obtained. Thus the total yield of 1-methyl-2-acetyl-4-propyl-4-nitro-1-cyclohexanol (XVIIIc) was 73%. Recrystallization from 50% aqueous ethanol or hexane raised the melting point to 89.5–90°.

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(14) Unpublished data from the Ph.D. thesis of R. Miller, Purdue University January 1959.

The infrared spectrum showed bands at 2.92 (hydroxyl), 5.93 (carbonyl), 6.51 and 7.41 μ (nitro).

Anal. Calcd. for $C_{12}H_{21}O_4N$: C, 59.24; H, 8.70; N, 5.76. Found: C, 59.18; H, 8.74; N, 5.73.

The monoöxime, m.p. 153–154°, and *monosemicarbazone*, m.p. 190.5–191.5° of compound XVIIIc were prepared by the usual method[13] in 80% and 97% yields, respectively. Both compounds were purified by recrystallization from aqueous ethanol.

Anal. Caled. for $C_{12}H_{24}O_4N_4$: C, 55.79; H, 8.58; N, 10.85. Found: C, 55.64; H, 8.83; N, 10.99.

Anal. Calcd. for $C_{13}H_{24}O_4N_4$: C, 51.98; H, 8.05; N, 18.66: Found: C, 52.11; H, 8.14; N, 18.66.

1-Methyl-2-acetyl-4-nitro-4-propyl-1-cyclohexene (XIXc). The procedure employed was similar to that used in the preparation of compound XIXa except that 31.6 g. (0.13 mole) of compound XVIIIc was employed.

Distillation afforded 25.3 g. (86% yield) of liquid product, b.p. 124° (1.0 mm.). Dissolving the distillate in methanol at room temperature and cooling the solution to −78°, gave 24.1 g. (81% yield) of 1-methyl-2-acetyl-4-nitro-4-propyl-1-cyclohexene (XIXc), m.p. 55.5–56.5°. Dissolving XIXc in methanol and slowly cooling to −15°, raised the melting point to 57.5–58.5°.

The infrared spectrum possessed a ketone band at 5.90 μ, an olefinic band at 6.10 μ and nitro bands at 6.49 and 7.39 μ while the ultraviolet spectrum showed a peak at 243 mμ, log ε 3.75.

Anal. Calcd. for $C_{12}H_{19}O_3N$: C, 63.97; H, 8.50; N, 6.22. Found: C, 63.98; H, 8.71; N, 5.97.

1-Methyl-2-acetyl-4-nitro-4-(3′-oxobutyl)-1-cyclohexanol (XVIIId). The procedure employed was similar to that used for the preparation of compound XVIIIa except that 6.1 g. (0.1 mole) of nitromethane and 27.2 g. (0.33 mole) of 85% aqueous methyl vinyl ketone were used.

After acidification, the reaction mixture was cooled to −78° and filtered to afford 14.0 g. of compound XVIIId, m.p. 104–105°. Distillation of the filtrate at 0.001 mm. afforded several fractions boiling at 80–160°. By dissolving the distillates in 95% ethanol and slowly cooling to −15° an additional 3.45 g. of product (XVIIId), m.p. 102–104°, was obtained. The total yield of 1-methyl-2-acetyl-4-nitro-4-(3′-oxobutyl)-1-cyclohexanol (XVIIId) was 94%. Recrystallization from isopropyl alcohol raised the melting point to 107–108°.

The infrared spectrum possessed a hydroxyl band at 2.89 μ, a carbonyl band at 5.88 μ with a shoulder at 5.82 μ and nitro bands at 6.50 and 7.36μ.

Anal. Calcd. for $C_{13}H_{21}O_5N$: C, 57.55; H, 7.80; N, 5.16. Found; C, 57.52; H, 7.81; N, 5.18.

The *dioxime* of compound XVIIId was prepared in 85% yield by the usual method.[13] It melted at 95–97° after recrystallization from water and drying on a clay plate. Drying it for 4 days at 28° and 0.1 mm. increased the melting point to 155–156°, but the analysis indicated that water of crystallization was still present.

Anal. Calcd. for $C_{13}H_{23}O_5N_3$: $^3/_4H_2O$: C, 49.60; H, 7.80; N, 13.35. Found: C, 49.65; H, 8.15; N, 13.43.

Drying the compound for 36 hr. at about 1.0 mm. removed all the water.

Anal. Calcd. for $C_{13}H_{23}O_5N_3$: C, 51.81; N, 7.69; N, 13.95. Found: C, 51.47; H, 7.72; N, 14.32.

1-Methyl-2-ethyl-4-nitro-1-cyclohexanol (XVIIIe). In a 200-ml. round bottom flask, equipped with a mechanical stirrer and thermometer, were placed 100 ml. of methanol and 16.6 g. (0.2 mole) of sodium methanenitronate. The reaction mixture was cooled in an ice bath and 50 ml. of water and 28.0 g. (0.4 mole) of methyl vinyl ketone were added dropwise, not allowing the temperature to exceed 10°. After stirring at 0–5° for 0.5 hr. the solution was acidified with 13.4 g. (0.26 mole) of glacial acetic acid, evaporated *in vacuo* to remove the methanol and the aqueous residue diluted with 100 ml. of water and extracted with four 100-ml. portions of ether. Drying the combined extracts with magnesium sulfate, filtering, and distilling gave 6.8 g. (27% yield), b.p. 67–73° (0.25 mm.), n^{20}_{D} 1.4442–1.4463 of crude 5-nitro-2-pentanone (XIa) [lit. value,[6] b.p. 117–120° (10 mm.), n^{20}_{D} 1.4441] and 14.7 g., b.p. 93–150° (0.001 mm.) of a heavy oil. By dissolving the oil in 95% ethanol and cooling to −78° a 5% yield (3.3 g.) of crude 1-methyl-2-acetyl-4-nitro-1-cyclohexanol (XVIIIe) was obtained. Recrystallization from isopropyl ether afforded pure product, m.p. 85–85.5°.

The infrared spectrum possessed bands at 2.89 (hydroxyl), 5.91 (carbonyl), 6.45 and 7.43 μ (nitro).

Anal. Calcd. for $C_9H_{15}O_4N$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.89; H, 7.75; 7.02.

2-Acetyl-4-nitro-4-propyl-1-methylcyclohexane (XX). A solution of 38.3 g. (0.17 mole) of compound XIXc in 175 ml. of 95% ethanol was placed in a low pressure Parr Hydrogenator and shaken with 3 g. of 5% palladium chloride on Darco G-60,[15] at an initial hydrogen pressure of 30 p.s.i. A total of 14.3 lbs. (0.17 mole) of hydrogen was absorbed in 3 hr. The solution was filtered and the filtrate evaporated *in vacuo*. Vacuum distillation of the residue afforded 34.2 g. (89% yield) of product (XX), b.p. 90–120° (0.2 mm.), which consisted of a mixture of solid and liquid isomers. Partial separation of the isomers was achieved by dissolving the distillate at room temperature in hexane and cooling the resulting solution to −78°. Filtration gave a small amount of solid which was recrystallized by dissolving it in a minimum amount of hexane at room temperature and slowly cooling to −15°. In this manner a solid isomer of 2-acetyl-4-nitro-4-propyl-1-methylcyclohexane (XX), m.p. 54–55° was secured.

Anal. Calcd. for $C_{12}H_{21}O_3N$: C, 63.41; H, 9.31; N, 6.16. Found: C, 63.15; H, 9.35; N, 6.05.

The filtrate from the original separation of isomers was redistilled and a fraction boiling at 90–95° (0.2 mm.) was subjected to elemental analysis.

Anal. Calcd. for $C_{12}H_{21}O_3N$: C, 63.41; H, 9.31; N, 6.16. Found: C, 63.65; H, 9.10; N, 6.38.

γ-Nitrocaprophenone (XXIa). To a cold (0–5°) solution of 21.1 g. (0.19 mole) sodium 1-propanenitronate in 220 ml. of 85% aqueous methanol, was added 30.42 g. (0.18 mole) of β-chloropropiophenone prepared according to the procedure of Allen and Barker.[16] The mixture was stirred at room temperature 30 min. and then at 40° for an additional 24 hr. After cooling to 0–5° it was acidified with 11 drops of glacial acetic acid, evaporated *in vacuo* to remove the methanol, diluted with 400 ml. of water, and extracted with four 100-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate, filtered, and evaporated. The residue (38 g.) was dissolved in a minimum amount of 95% ethanol and slowly cooled to −15°. Filtration afforded 32.5 g. of product (XXIa), m.p. 33–34°. An additional 4.0 g. of compound XXIa, m.p. 32–33°, was secured by cooling the filtrate to −78°. Thus the total yield of γ-nitrocaprophenone (XXIa) was 92%. Dissolving the product in a minimum amount of 95% ethanol at room temperature and slowly cooling to −15°, raised the melting point to 33.5–34.5°.

The infrared spectrum of this material possessed a carbonyl band at 5.92 μ, nitro bands at 6.47 and 7.35 μ, and aromatic bands at 6.27, 6.33, 13.27, and 14.49 μ.

Anal. Calcd. for $C_{12}H_{15}O_3N$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.88; H, 6.84; N, 6.34.

The *bromo-derivative of compound* XXIa was prepared in 95% yield by treating XXIa with one equivalent of base and excess bromine. Recrystallization of the product from 95% ethanol raised the melting point to 59–60°.

Anal. Calcd. for $C_{12}H_{14}O_3NBr$: C, 48.00; H, 4.67; N, 4.67; Br, 26.67. Found: C, 47.93; H, 4.67; N, 4.61; Br, 26.92.

γ-Nitrovalerophenone (XXIb). The procedure employed

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(15) R. Mozingo, *Org. Syntheses*, Coll. Vol. III, 685 (1955).

(16) C. F. H. Allen and W. E. Barker, *J. Am. Chem. Soc.*, 54, 736 (1932).

was similar to that used for the preparation of compound XXIa except that 19.4 g. (0.2 mole) of sodium ethanenitronate was employed.

The reaction mixture was heated 4 hr. at 40°, cooled to 0–5°, acidified with glacial acetic acid, diluted with 1700 ml. of water, and kept at 10° for 10 hr. Filtration afforded 36.1 g. (93% yield) of product, m.p. 54.5–56.5°, which was readily recrystallized from warm (50°) isopropyl ether or 85% aqueous methanol to yield pure γ-nitrovalerophenone (XXIb), m.p. 58.5–59°.

The infrared spectrum possessed a carbonyl band at 5.95 μ, nitro bands at 6.52 and 7.40 μ, and aromatic bands at 6.26, 6.31, 13.40, and 14.46 μ.

Anal. Calcd. for $C_{11}H_{13}O_3N$: C, 63.75; H, 6.32; N, 6.76. Found: C, 64.01; H, 6.37; N, 6.70.

3-Ethyl-3-nitro-1,5-dibenzoylpentane (XXIIa) *and 1-phenyl-2-benzoyl-4-ethyl-4-nitro-1-cyclohexanol* (XXIIIa). In a 300 ml. round bottom flask, equipped with a mechanical stirrer and thermometer, were placed 24.3 g. (0.11 mole) of γ-nitrocaprophenone (XXIa) and 170 ml. of methanol. The flask was cooled in an ice bath while a solution of 4.52 g. (0.11 mole) 97% sodium hydroxide, dissolved in 30 ml. of water was added dropwise, with stirring, so that the temperature did not exceed 9°. After complete addition, the ice bath was removed and the solution stirred until a *p*H of 8–9 (Hydrion paper) was attained (*ca.* 0.5 hr.). The flask was again immersed in an ice bath and 16.9 g. (0.10 mole) of β-chloropropiophenone was added. Within 5 min. the reaction mixture set into a solid cake. The contents of the flask were diluted with 1800 ml. of water and manually stirred for approximately 10 min. Filtration afforded 34.3 g. (94% yield) of a mixture, m.p. 118–120°, of compounds XXIIa and XXIIIa. The infrared spectrum of this mixture possessed two carbonyl bands (5.97 μ and 6.02 μ) and a hydroxyl band (2.90 μ). Separation of the structural isomers was accomplished by fractional recrystallization from isopropyl ether, compound XXIIa being more soluble. A 31 and 46% yield of compounds XXIIa, m.p. 128–129°, and XXIIIa, m.p. 128–132°, respectively, were obtained. Recrystallization of compound XXIIIa from hexane raised the melting point to 132–132.5°.

The infrared spectrum of compound XXIIa possessed bands at 5.97 (carbonyl), 6.55 (nitro), 6.26, 6.34, 13.45, and 14.42 μ (aromatic), but was void of a hydroxyl band. The spectrum of compound XXIIIa possessed bands at 2.90 (hydroxyl), 6.02 (carbonyl), 6.53 and 7.45 (nitro), 6.26, 6.34, 13.16, and 14.32 μ (aromatic).

Anal. Calcd. for $C_{21}H_{23}O_4N$: C, 71.37; H, 6.56; N, 3.96. Found for XXIIa: C, 71.27; H, 6.45; N, 3.83. Found for XXIIIa: C, 71.15; H, 6.74; N, 4.22.

When the previous reaction was repeated with the following modifications, 500 ml. of 95% ethanol and a reflux time of 5 hr., a 90% yield of compound XXIIIa was obtained.

The *dioxime* of compound XXIIa was prepared in 95% yield by the usual method.[13] The product, m.p. 139.5–140° was purified by recrystallization from 50% aqueous ethanol.

Anal. Calcd. for $C_{21}H_{25}O_4N_3$: C, 65.78; H, 6.57; N, 10.96. Found: C, 65.82; H, 6.65; N, 11.02.

1-Phenyl-2-benzoyl-4-methyl-4-nitro-1-cyclohexanol (XXIIIb). A 500-ml. round bottom flask, immersed in an ice bath and equipped with a mechanical stirrer, dropping funnel, and thermometer, was charged with 10.4 g. (0.05 mole) of γ-nitropentanophenone (XXIb) and 250 ml. of 95% ethanol. A solution of 2.05 g. (0.05 mole) of 97% sodium hydroxide dissolved in 25 ml. of water was added dropwise with stirring at such a rate that the temperature did not exceed 9°. The ice bath was removed and the solution stirred until a *p*H of 8–9 (Hydrion paper) was attained (*ca.* 20 min.). The solution was again cooled to 0–5° and 7.61 g. (0.045 mole) of β-chloropropiophenone was added. The mixture was then heated with stirring at 40° for 4 hr., cooled to 0–5°, acidified with glacial acetic acid, and poured into 1500 ml. of water. Filtration afforded 15.0 g. of product, m.p. 127–137°, the infrared spectrum of which showed that it was mostly XXIIIb containing a small amount of noncyclic product XXIIb. To cyclize the product completely it was refluxed further for 11 hr. in ethanol containing 4 drops of 20% aqueous sodium hydroxide. Slow cooling to −78° and subsequent filtration afforded 14.2 g. (93% yield) of 1-phenyl-2-benzoyl-4-methyl-4-nitrocyclohexanol (XXIIIb), m.p. 138–142°. Recrystallization from 95% ethanol raised the melting point to 139–143°.

The infrared spectrum possessed bands at 2.89 (hydroxyl), 6.01 (carbonyl), 6.52, 7.41 (nitro), 6.25, 6.31, 13.14, and 13.33 μ (aromatic).

Anal. Calcd. for $C_{20}H_{21}O_4N$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.64; H, 6.37; N, 4.05.

1,5-Dibenzoyl-3-methyl-3-nitropentane (XXIIb). The procedure employed was similar to that used for the preparation of XXIIIb except that the ethanol and sodium hydroxide were replaced with absolute methanol and 1.15 g. (0.05 mole) of sodium dissolved in 100 ml. of absolute methanol. After acidification, the reaction mixture was poured into 1500 ml. of cold distilled water. Filtration afforded 14.8 g. (97% yield) of product, m.p. 131–141°, the infrared spectrum of which indicated by the presence of a weak hydroxyl band at 2.89 μ and a strong carbonyl band at 5.95 μ with a shoulder at 6.01 μ that it was mostly the open chain compound XXIIb containing a small amount of the cyclic compound XXIIIb. Partial separation of these structural isomers was accomplished by triturating the crude product with 200 ml. of boiling 95% ethanol and filtering. The infrared spectrum of the insoluble material (10.0 g.), m.p. 150–151°, did not contain a hydroxyl band and had only a single carbonyl absorption at 5.95 μ. Recrystallization of this material from acetonitrile afforded pure 1,5-dibenzoyl-3-methyl-3-nitropentane (XXIIb), m.p. 153.5–154°.

Cooling of the ethanol filtrate to −10°, and subsequent filtration afforded 4.5 g. of a mixture, m.p. 132–140°, of compounds XXIIb and XXIIIb.

The infrared spectrum of compound XXIIb possessed bands at 5.95 (carbonyl), 6.54, 7.40 (nitro), 6.26, 6.32, 13.45, and 14.48 μ (aromatic).

Anal. Calcd. for $C_{20}H_{21}O_4N$ (XXIIb): C, 70.78; H, 6.24; N, 4.13. Found: C, 70.86; H, 6.05; N, 4.02.

The *dioxime* of compound XXIIb was prepared by the usual method.[13] A 98% yield of product, m.p. 157.5–158.5°, was obtained. Recrystallization from aqueous methanol or benzene did not change the melting point.

Anal. Calcd. for $C_{20}H_{23}O_4N_3$: C, 65.02; H, 6.28; N, 11.38. Found: C, 64.92; H, 6.31; N, 11.05.

1,5-Dibenzoyl-3-nitropentane (XXV) *and γ-nitrobutyrophenone* (XXIV). A 500-ml. round bottom flask, immersed in an ice bath and equipped with a mechanical stirrer, thermometer, and dropping funnel, was charged with 12.2 g. (0.2 mole) of freshly distilled nitromethane and 200 ml. of methanol. A solution of 8.24 g. (0.2 mole) of 97% sodium hydroxide dissolved in 90 ml. of water was added dropwise, not allowing the temperature to exceed 8°. The reaction mixture was stirred for 20 min., followed by the addition of 32.1 g. (0.19 mole) of β-chloropropiophenone. After the initial exothermic reaction had subsided, the ice bath was removed and the mixture was stirred for an additional 1.5 hr. The mixture was again cooled to 0–5°, acidified with glacial acetic acid and poured into 600 ml. of cold distilled water. Filtration afforded 29.4 g. of product, m.p. 98–114°, which was dissolved in 2100 ml. of boiling methanol. The resulting solution was slowly cooled to 10° and kept at this temperature for 10 hr. Filtration afforded 18.7 g. (61% yield) of 1,5-dibenzoyl-3-nitropentane (XXV) m.p. 131–132°. Evaporation of the filtrate *in vacuo* afforded a semisolid residue which was dissolved in a minimum amount of boiling methanol and slowly cooled to room temperature. Filtration gave 7.3 g. (20% yield) of γ-nitrobutyrophenone (XXIV), m.p. 57–61°.

Recrystallization of compounds XXIV and XXV from acetonitrile and 95% ethanol respectively, raised the melting point of the former compound to 62.5–63.5° and that of the latter compound to 132.5–133.5°.

The infrared spectrum of compound XXIV possessed a carbonyl band at 5.95 μ, a nitro band at 6.46 μ and aromatic bands at 13.44 and 14.44 μ. The spectrum of compound XXV showed these bands at 5.95, 6.47, 13.24, and 14.49 μ.

Anal. Calcd. for $C_{10}H_{11}O_3N$ (XXIV): C, 62.16; H, 5.74; N, 7.25. Found: C, 62.51; H, 5.70; N, 7.17.

Anal. Calcd. for $C_{19}H_{19}O_4N$ (XXV): C, 70.14; H, 5.89; N, 4.31. Found: C, 70.35; H, 6.05; N, 4.31.

The yield of compound XXIV was increased to 78% by repeating the above reaction using 122 g. (2.0 moles) of nitromethane and reducing the reaction time to 0.5 hr. at 10–15°.

The *semicarbazone of* compound XXIV was prepared by the usual method.[13] A 96% yield of product, m.p. 150–152° dec., was obtained. Recrystallization from isopropyl alcohol raised the melting point to 155.5–156° dec.

Anal. Calcd. for $C_{10}H_{14}O_3N_4$: C, 52.79; H, 5.64; N, 22.39. Found: C, 53.07; H, 5.74; N, 22.38.

1,5-Dibenzoyl-3-bromo-3-nitropentane.[8] A solution of 12 g. (0.037 mole) of compound XXV in 100 ml. of dimethyl sulfoxide was cooled to 0–5°. To this solution was added 1.53 g. (0.037 mole) of sodium hydroxide (97% assay) dissolved in 25 ml. of water. The reaction mixture was stirred at room temperature until a *p*H of 8–9 was obtained. Bromine (6.5 g., 0.041 mole) was then added dropwise below 9° and the mixture was stirred at room temperature for 1.5 hr. Suction filtration afforded 6.08 g. (40.7% yield), m.p. 143–157°. This crude material was recrystallized by dissolving it in acetonitrile and reprecipitating with water. After four recrystallizations, 1,5-dibenzoyl-3-bromo-3-nitropentane melted at 166°.

Anal. Calcd. for $C_{19}H_{18}O_4NBr$: C, 56.43; H, 4.45; N, 3.47; Br, 19.80. Found: C, 56.57; H, 4.61; N, 3.56; Br, 19.58.

1-Phenyl-2-benzoyl-4-(2'-benzoylethyl)-4-nitro-1-cyclohexanol (XXVII). In a 200-ml. round bottom flask, equipped with a mechanical stirrer and reflux condenser, were placed 14.6 g. (0.045 mole) of compound XXV and 100 ml. of dimethyl sulfoxide. The flask was immersed in an ice bath at 0–5° and a solution of 1.85 g. (0.045 mole) of 97% sodium hydroxide, dissolved in 75 ml. of water was added dropwise with stirring at such a rate that the temperature did not exceed 9°. The ice bath was removed and the solution stirred until a *p*H of 8–9 (Hydrion paper) was attained (in *ca.* 20 min.). The solution was again cooled to 0–5° and 6.72 g. (0.040 mole) of β-chloropropiophenone was added. The mixture was heated with stirring for 2 hr. at 60–70°, then cooled to 0–5°, acidified with glacial acetic acid and diluted with 600 ml. of water. Filtration afforded 17.6 g. (97% yield) of crude 1-phenyl-2-benzoyl-4-(2'-benzoylethyl)-4-nitro-1-cyclohexanol (XXVII), m.p. 135–143°, which on recrystallization from aqueous acetonitrile melted at 151–151.5°.

The infrared spectrum possessed a hydroxyl band at 2.91 μ, a carbonyl band at 6.05 μ with a shoulder at 5.98 μ and nitro bands at 6.55 and 7.43 μ.

Anal. Calcd. for $C_{28}H_{27}O_4N$: C, 73.50; H, 5.95; N, 3.06. Found: C, 73.72; H, 5.82; N, 3.09.

The *monoöxime* of compound XXVII was prepared in 88.6% yield by the usual method.[13] The product, m.p. 182–183° was purified by dissolving it in hot 95% ethanol and reprecipitating it with water.

Anal. Calcd. for $C_{28}H_{28}O_5N_2$: C, 71.17; H, 5.97; H, 5.93. Found: C, 71.46; H, 6.00; N, 5.95.

3-Carbomethoxy-3-cyano-1,5-dibenzoylpentane (XXVIII). The procedure employed was similar to that used for the preparation of compound XXIIIb except that the following solvent and reagents were used: 19.8 g. (0.2 mole) of methyl cyanoacetate, 150 ml. of absolute methanol, 4.6 g. (0.2 mole) of sodium dissolved in 200 ml. of absolute methanol, and 32.1 g. (0.19 mole) of β-chloropropiophenone.

A 96% yield (33.2 g.) of compound XXVIII, m.p. 132.5–138°, was obtained. Recrystallization from acetonitrile raised the melting point to 145–146° (lit. value,[9] m.p. 144°).

The infrared spectrum possessed an ester carbonyl band at 5.74 μ, a cyano band at 4.45 μ, a ketone carbonyl band at 5.95 μ and aromatic absorptions at 6.26, 6.32, and 14.47 μ.

Anal. Calcd. for $C_{22}H_{21}O_4N$: C, 72.71; H, 5.82; N, 3.85: Found: C, 72.50; H, 6.04; N, 3.88.

1-Methyl-2-acetyl-4-carbomethoxy-4-cyano-1-cyclohexanol (XXIX). In a 300-ml. round bottom flask, fitted with a mechanical stirrer, thermometer and drying tube were placed 17 ml. of absolute methanol and 0.15 g. (6.52 mmoles) of sodium. After dissolution was complete, 14.85 g. (0.15 mole) of methyl cyanoacetate was added. The solution was cooled to 0–5° and 23.1 g. (0.33 mole) of methyl vinyl ketone was added portionwise with stirring so that the temperature did not exceed 10°. The mixture was then heated at 40° for 11 hr. After cooling to 0–5° and neutralization with 0.39 g. of glacial acetic acid, the solution was evaporated *in vacuo* to afford an oil which on dissolution in 65 ml. of isopropyl alcohol and cooling to −10° gave 15.5 g. (46% yield) of 1-methyl-2-acetyl-4-carbomethoxy-4-cyano-1-cyclohexanol (XXIX), m.p. 75–80°. Recrystallization from isopropyl alcohol raised the melting point to 84–85°.

The infrared spectrum possessed bands at 2.89 μ (hydroxyl), 4.48 (cyano), 5.74 (ester carbonyl) and 5.90 μ (ketone carbonyl).

Anal. Calcd. for $C_{12}H_{17}O_4N$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.30; H, 7.07; N, 6.02.

The *monosemicarbazone* of compound XXIX, m.p. 197–197.5°, was obtained by the usual method.[13]

Anal. Calcd. for $C_{13}H_{20}O_4N_4$: C, 52.69; H, 6.80; N, 18.91. Found: C, 52.68; H, 6.79; N, 19.26.

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