that the influence of internal electronic polarizability within the nitriles is not very great in the reaction mechanism. The high space-time yield found with cyanogen is difficult to interpret. It may be accounted for in part by the fact that there are two potential reaction centers present per molecule, and that the delocalization energy within each (C≡N) group is considerably greater than for the cyano groups of the other nitriles in this series.

TABLE II

SPACE-TIME YIELDS FOR THE REACTION OF SOME ORGANIC NITRILES WITH BUTADIENE AT 400° OVER A 12% CHROMIUM OXIDE-ALUMINUM OXIDE CATALYST

Nitrile	Product	Space-time yield,[a] × 10⁴	Reference
NC-CN	2-Cyanopyridine	150	2
H-CN	Pyridine	11	2
CH_3-CN	2-Methylpyridine	16	2
CH_3CH_2-CN	2-Ethylpyridine	7	This work
C_6H_5-CN	2-Phenylpyridine	16	2

[a] Defined as moles of product per hr. per 100 cc. catalyst bed.

As well as the pyridinic product, aniline and ethylbenzene were isolated. The latter is accounted for by the thermal dimerization of butadiene followed by rearrangement to the final product. Shorter reaction times serve to decrease the yield of this simultaneous reaction. This is in accord with the results of related studies using nitriles other than propionitrile. At very short reaction times little or no ethylbenzene was found.

The formation of aniline is understood if there is a rearrangement of the nitrile

$$CH_3{-}CH_2{-}CN \longrightarrow CH_3{-}CH{=}C{=}NH$$

with subsequent cyclization and rearrangement as postulated by Marvel and Hwa.[3] The dissociation energy of the C–H methylene bond is 21 kcal. less than the C–H bond in the methyl group.[6] The thermal stability of propionitrile is thus less than that of acetonitrile.

Acknowledgment.—A grant-in-aid from the American Cyanamid Company in support of this work is gratefully acknowledged.

[6] M. Szwarc, *Chem. Revs.*, **47**, 168 (1950).

TROY, NEW YORK

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Diene Synthesis with Unsymmetrical Butadienes and β-Nitrostyrenes[1]

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The diene synthesis with unsymmetrical butadienes and β-nitrostyrenes has been studied. The adduct formed from 2-ethoxybutadiene and β-nitrostyrene proved to be 1-ethoxy-4-nitro-5-phenylcyclohexene. β-Nitrostyrene and 4-methoxy-β-nitrostyrene each formed two adducts with isoprene. The isomer that possessed the methyl group para to the nitro group was present in the larger amount in each case. Piperylene and β-nitrostyrene formed both possible structural isomers; the isomer in which the methyl group was ortho to the nitro group was predominant.

The diene synthesis with unsymmetrical butadienes and olefins has been studied recently to determine whether any general rules can be formulated for the mode of addition of the components. As a corollary to this type of study, further insight into the mechanism of the Diels–Alder reaction should be gained. These studies have been confined largely to 1- and 2-substituted butadienes and monosubstituted ethylenes. This paper extends the information to include the condensation of a disubstituted olefin, β-nitrostyrene, or its 4-methoxy derivative, with the unsymmetrical dienes, piperylene, isoprene and 2-ethoxybutadiene. The adducts formed in this work are also of value in the projected syntheses of several natural products.

Of the three dienes studied, only 2-ethoxybutadiene formed a single pure adduct with β-nitrostyrene. This adduct possessed the structure IIa. This orientation is in accord with that found for the addition of 2-ethoxybutadiene to methyl 3,4-dihydro-1-naphthoate[3] and to 2,3-dimethoxy-β-nitrostyrene,[4] although no structure proof of the latter adduct was offered.

The condensations with isoprene and piperylene gave high yields of isomeric mixtures of I and II. Only Ic and IIc were completely separable. In series b and d, the isomer ratio could be approximated by the relative amounts of certain transformation products. It is interesting to note that the ratio of Ib to IIb is almost the same as Ic to IIc, indicating that the presence of a 4-methoxyl group does not change the course of addition of isoprene significantly.

Proof that the condensation of 2-ethoxybutadiene and β-nitrostyrene formed IIa involved acid hydrolysis of the enol ether and conversion of the nitroketone to a diketone by the Nef reaction. While the ultraviolet absorption spectrum of this compound was compatible with that of a 1,4-diketone, further proof of structure was offered by conversion to phenylquinone.

In a previous paper it was shown that certain 4-nitro-5-phenylcyclohexenes, prepared from *symmetrical* butadienes and β-nitrostyrenes, could be converted by the Nef reaction to 6-phenyl-3-cyclohexen-1-ones and then to 6-phenyl-2-cyclohexen-1-

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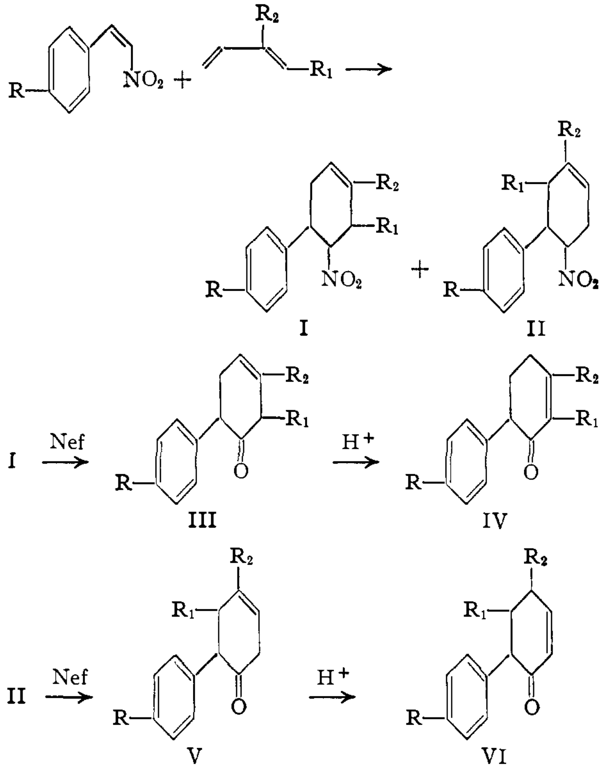
[1] Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1952.

[2] Abstracted in part from a thesis submitted by J. B. Fine in partial fulfillment of the requirements for the degree of Bachelor of Arts, Princeton University, May, 1952.

[3] H. L. Holmes and K. M. Mann, THIS JOURNAL, **69**, 2000 (1947).

[4] J. A. Barltrop and J. S. Nicholson, *J. Chem. Soc.*, 2524 (1951).



Series: a, R, R_1 = H, R_2 = OC_2H_5; b, R, R_1 = H, R_2 = CH_3; c, R = OCH_3, R_1 = H, R_2 = CH_3; d, R, R_2 = H, R_1 = CH_3

ones by isomerization.[5] The ultraviolet absorption spectra of these ketones of known structure were recorded and serve as reference spectra for some of the compounds in the present work. The general plan of structure proof for the unsymmetrical adducts was to assign the position of the alkyl group in accordance with the spectra of the α,β-unsaturated ketones formed from I and II by the method mentioned above.

An inseparable mixture of Ib and IIb was obtained from the diene synthesis with β-nitrostyrene and isoprene. However, it was possible to isolate two isomeric ketones when the adduct mixture was subjected to the Nef reaction. The ketone isolated in the larger amount was formulated as Vb since its ultraviolet absorption spectrum was that of an unconjugated ketone and upon catalytic dehydrogenation it formed the known 4-methyl-2-phenylphenol.[6] Vb could not be converted to VIb by treatment with acid. The ketone present in the smaller amount must have the structure IVb, since it possessed absorption maxima at 234 and 319 mμ in good agreement with maxima of 236 and 321 mμ found previously[5] for the model compound, 3,4-dimethyl-6-phenyl-2-cyclohexen-1-one.

The adducts Ic and IIc were converted to ketones by the Nef reaction. A mixture of IIIc and IVc was formed by the Nef reaction with Ic. Pure IIIc could not be isolated since recrystallization of the crude solid caused further isomerization to IVc. It was possible to isolate the 2,4-dinitrophenylhydrazones of both IIIc and IVc in pure state from the crude Nef reaction mixture. The ultraviolet absorption spectrum of IVc showed a maximum at 228 mμ, a wave length much lower than that predicted by Woodward's rule.[7] To check the validity of this spectrum as a means of structure proof for the compound, a model substance, 3,4-dimethyl-6-(4-methoxyphenyl)-2-cyclohexen-1-one, was prepared. It showed a maximum at 228.5 mμ. This hypsochromic shift from the expected maximum may be due to the exceptionally strong absorption band found for 2-(4-methoxyphenyl)-cyclohexanone and its unsaturated derivatives. The ketone derived from IIc was characterized as a β,γ-unsaturated ketone by its spectrum and, since it could not be conjugated with acid, it was assigned formula Vc in analogy with Vb.

Two geometrical forms of Id and one of IId were isolated from the condensation of piperylene and β-nitrostyrene. The isolated material amounted to less than 50% of the crude adduct. Each form of Id, when converted to the ketone by the Nef reaction and conjugated with acid, gave the same ketone, m.p. 37–38°. Since this ketone showed an absorption maximum at 236 mμ, it was assigned formula IVd. One pure form of IId, m.p. 98–99°, was isolated in 3% yield and converted to an α,β-unsaturated ketone that showed an absorption plateau at 221–223 mμ. In keeping with the spectra of model compounds,[5] this ketone was assigned formula VId.

Finally, one interesting observation should be mentioned. The ease of conjugation of the β,γ-unsaturated ketones varied from those that could not be isomerized at all (Vb and Vc) to those that isomerized spontaneously (IIIb and IIIc). A possible explanation may be obtained from a consideration of the hyperconjugation forms of the isomers. Vb and Vc each possess seven possible hyperconjugation forms, while the conjugated ketones VIb and VIc possess only one form each. In IIIb and IIIc seven hyperconjugation forms are possible, while in IVb and IVc there are five. Two factors are operative in establishing the position of equilibrium in the conversion of a β,γ-unsaturated ketone to an α,β-unsaturated ketone. One is the tendency for the double bond to become conjugated with the largest number of α-hydrogen atoms; the other is the tendency for the double bond to become conjugated with the carbonyl group. In the case of Vb and Vc these two factors oppose each other with the result that the conversion to VIb and VIc, respectively, does not occur to any significant extent. In the case of IIIb and IIIc the first factor, although in opposition to the second, is not of the same magnitude and conversion to IVb and IVc goes to completion readily. Alexander[8] cites many examples of this type of equilibrium which substantiate this explanation.

Experimental[9]

1-Ethoxy-4-nitro-5-phenylcyclohexene (IIa).—A solution of 12.0 g. (0.12 mole) of 2-ethoxybutadiene and 10.0 g.

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[5] W. C. Wildman and R. B. Wildman, *J. Org. Chem.*, **17**, 581 (1952).

[6] M. Anchel and A. H. Blatt, THIS JOURNAL, **63**, 1948 (1941).

[7] R. B. Woodward, *ibid.*, **63**, 1123 (1941).

[8] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 281–286.

[9] All melting points are corrected. All boiling points are uncorrected. All ultraviolet absorption spectra were determined in 95% ethanol solution with a Model DU Beckman spectrophotometer in 1-cm. cells.

(0.08 mole) of β-nitrostyrene was refluxed for three hours. The adduct crystallized on cooling and was separated by filtration, 11.0 g. (66%), m.p. 96–96.5°. A sample was recrystallized from methanol for analysis, m.p. 96.5–97°.

Anal.[10] Calcd. for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.66. Found: C, 68.03; H, 7.03; N, 5.91.

4-Nitro-3-phenylcyclohexanone.—A hot solution of 4.66 g. (0.019 mole) of the enol ether in 20 ml. of ethanol was treated with 2 ml. of concentrated hydrochloric acid and 4 ml. of water. The solution was allowed to cool in the refrigerator over a period of three hours. The solid was isolated by filtration, and the filtrate was diluted with water and allowed to stand at 0° overnight. A second crop of crystals was obtained; total yield 3.92 g. (99%), m.p. 104–104.5°. A sample was recrystallized from benzene–petroleum ether for analysis, m.p. 105.5–106.5°.

Anal.[10] Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.67; H, 5.94; N, 6.56.

The 2,4-dinitrophenylhydrazone was prepared in quantitative yield by the method of Shriner and Fuson,[11] m.p. 213.5–214° (dec.).

Anal.[12] Calcd. for $C_{18}H_{17}N_5O_6$: C, 54.13; H, 4.29; N, 17.54. Found: C. 54.38; H, 4.33; N, 17.78.

2-Phenylcyclohexanedione-1,4.—Prepared from 6.0 g. (0.027 mole) of 4-nitro-3-phenylcyclohexanone by the method of Wildman and Wildman[5]; yield 2.23 g. (43%), m.p. 89–92°. A sample was recrystallized from petroleum ether for analysis, m.p. 91–92°.

Anal.[10] Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.37; H, 6.45.

Phenylquinone.—A stirred solution of 1.05 g. (0.056 mole) of 2-phenylcyclohexanedione-1.4 in 20 ml. of chloroform at 0° was treated with 0.89 g. (0.056 mole) of bromine in 7 ml. of chloroform. The solution was allowed to come to room temperature without reaction and then suddenly lost color with the evolution of hydrogen bromide. The solution was concentrated immediately under reduced pressure to half its original volume and then treated with 13 ml. of pyridine and further concentrated. The light orange oil was dissolved in ether and extracted with several portions of dilute hydrochloric acid. The ethereal extract was washed with water, dried over magnesium sulfate, and concentrated to 1.18 g. of brown oil that would not crystallize. This material was oxidized with sodium dichromate as described in reference 13. The yellow quinone was recrystallized from ethanol, m.p. 113.5–114°. A mixed melting point with a sample, m.p. 114°, prepared by the method of Kvalnes[14] was not depressed.

1-(and 2)-Methyl-4-nitro-5-phenylcyclohexene (IIb and Ib).—Prepared by the method of Wildman and Wildman[5] from 15.0 g. (0.10 mole) of β-nitrostyrene and 15.0 g. (0.22 mole) of freshly-distilled isoprene; yield 18.70 g. (86%) of colorless needles, m.p. 53.5–54.5° (reported[15] 52°). A sample was recrystallized from ethanol for analysis, m.p. 53.5–55.5°. The mixture of isomers could not be separated by distillation, fractional crystallization or chromatography on alumina.

Anal.[10] Calcd. for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 72.04: H, 7.07; N, 6.70.

Nef Reaction with 1-(and 2)-Methyl-4-nitro-5-phenylcyclohexene.—A portion, 10.85 g. (0.05 mole), of the mixture of nitro isomers was converted to a mixture of the isomeric ketones by the Nef reaction.[5] The orange oil was distilled to give two fractions.

(a) **Isolation of 4-Methyl-6-phenyl-3-cyclohexen-1-one (Vb).**—The first fraction, b.p. 104–106° (0.1 mm.), proved to be 4-methyl-6-phenyl-3-cyclohexen-1-one (Vb). The pale yellow oil, $n^{20}\text{D}$ 1.5544, solidified in the refrigerator to give 6.00 g. (65%) of nearly colorless solid, m.p. 39–43°. A portion was recrystallized twice from petroleum ether to give colorless plates, m.p. 46°.

Anal.[16] Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.99; H, 7.68.

The 2,4-dinitrophenylhydrazone of Vb was prepared by the method of Birch[17] in two polymorphic forms, (A) m.p. 132–133° and (B) m.p. 146.5–147.5°.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.29; H, 4.95; N, 15.29. Found (A)[16]: C, 62.44; H, 5.14; N, 15.40. (B)[10]: C, 62.22; H, 4.75; N, 15.28.

4-Methyl-2-phenylphenol.—A sample of 4-methyl-6-phenyl-3-cyclohexen-1-one weighing 0.439 g. (2.36 millimoles) was dehydrogenated with 100 mg. of 30% palladium-on-charcoal at 270°. After 1.5 hours the theoretical amount of hydrogen had been evolved and hydrogen evolution stopped. The cooled reaction mixture was suspended in ethanol, and the catalyst was removed by filtration. Concentration of the filtrate gave 0.418 g. (96%) of slightly yellow solid, m.p. 62.5–64.5°. Two recrystallizations from petroleum ether gave colorless plates, m.p. 67.5–68.5° (reported[6] 67–68°). A 10% yield of the same phenol was obtained by dehydrobromination of 4,5-dibromo-4-methyl-2-phenylcyclohexanone (formed by the addition of bromine to Vb) with alcoholic potassium hydroxide. **The benzoate** was prepared by the Schotten–Baumann method, m.p. 94–94.5° (reported[6] 94–94.5°). **4-Methoxy-3-phenylbenzoic acid** was prepared by the method of Anchel and Blatt[6] as a further proof of structure, m.p. 215–217° (reported[6] 215–218°).

(b) **Isolation of 3-Methyl-6-phenyl-2-cyclohexen-1-one (IVb).**—The second fraction, 1.37 g., b.p. 121–123° (0.1 mm.), $n^{20}\text{D}$ 1.5643, solidified in the refrigerator. Two recrystallizations from ethyl acetate–petroleum ether gave 0.266 g. of colorless prisms, m.p. 60–61.5°, λ_{max} 234 mμ (log ϵ 4.19) and λ_{max} 319 mμ (log ϵ 1.82).

Anal.[16] Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.52; H, 7.72.

The semicarbazone was prepared in quantitative yield, m.p. 202.5–204° (dec.), λ_{max} 268 mμ (log ϵ 4.39).

Anal.[12] Calcd. for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.05; N. 17.27. Found: C, 69.35; H, 7.20; N, 17.68.

Diene Synthesis with Isoprene and 4-Methoxy-β-nitrostyrene.—By the method previously described,[5] 20.0 g. (0.112 mole) of 4-methoxy-β-nitrostyrene and 25.0 g. (0.367 mole) of freshly-distilled isoprene gave 24.5 g. (89%) of a mixture of adducts from which Ic and IIc were isolated.

(a) **5-(4-Methoxyphenyl)-1-methyl-4-nitrocyclohexene (IIc).**—Fractional crystallization of the mixture from methanol gave 17.5 g. (63%) of IIc, m.p. 97.5–98.5°.

Anal.[10] Calcd. for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.67. Found: C, 68.21; H, 7.00; N, 5.62.

(b) **4-(4-Methoxyphenyl)-1-methyl-5-nitrocyclohexene (Ic).**—Fractional crystallization of the mother liquors from IIc using petroleum ether gave 3.34 g. (12%) of Ic, m.p. 74–75°.

Anal.[10] Calcd. for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.67. Found: C, 68.30; H, 6.73; N, 5.73.

6-(4-Methoxyphenyl)-4-methyl-3-cyclohexen-1-one (Vc).—By the procedure previously reported, 6.57 g. (0.026 mole) of IIc was converted to the ketone. The product was obtained in 69% yield, 3.97 g., as a pale yellow oil, b.p. 138-140° (0.4 mm.). A small amount was redistilled for analysis, b.p. 133–135° (0.6 mm.), $n^{20}\text{D}$ 1.5357.

Anal.[10] Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.03; H, 7.56.

The 2,4-dinitrophenylhydrazone of Vc was prepared in quantitative yield by the method of Birch[17] and recrystallized three times from ethanol to yield light orange needles, m.p. 160.5–161.5°.

Anal.[10] Calcd. for $C_{20}H_{20}N_4O_5$: C, 60.60; H, 5.09; N, 14.14. Found: C, 60.88; H, 5.35; N, 14.33.

6-(4-Methoxyphenyl)-3-methyl-2-cyclohexen-1-one (IVc).—A sample of 2.50 g. (0.01 mole) of Ic was converted by the Nef reaction to 2.16 g. (99%) of orange oil which was a mixture of IIIc and IVc. To ensure complete conjugation, the oil was refluxed for two hours in a solution of 25 ml. of ethanol and 3 ml. of concentrated hydrochloric acid. The

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[10] Analyzed by J. F. Alicino, Metuchen, N. J.

[11] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170.

[12] Analyzed by Clark Microanalytical Laboratory, Urbana, Illinois.

[13] H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 482.

[14] D. E. Kvalnes, THIS JOURNAL, **56**, 2478 (1934).

[15] C. H. F. Allen, A. Bell and J. W. Gates, *J. Org. Chem.*, **8**, 373 (1943).

[16] Analyzed by Tiedcke Laboratory of Microchemistry, Teaneck, N. J.

[17] A. J. Birch, *J. Chem. Soc.*, 593 (1946).

product was treated as previously described to give 2.15 g. (99%) of tan solid, m.p. 67–90°. Recrystallization from ethanol gave 1.98 g. (90%) of colorless needles, m.p. 91–93.5°. A small sample was further recrystallized for analysis, m.p. 92.5–93.5°, λ_{max} 228 mu (log ϵ 4.34), λ_{max} 275 mμ (log ϵ 3.23), λ_{max} 282 mμ (log ϵ 3.15), λ_{max} 312–320 mμ (log ϵ 1.97).

Anal.[12] Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.91; H, 7.34.

The 2,4-dinitrophenylhydrazone of IVc was prepared in quantitative yield by the method of Shriner and Fuson[11] and recrystallized three times from ethanol to give red needles, m.p. 191.5–192.5°.

Anal.[12] Calcd. for $C_{20}H_{20}N_4O_5$: C, 60.60; H, 5.09; N, 14.14. Found: C, 60.82; H, 5.24; N, 13.92.

The 2,4-Dinitrophenylhydrazone of 6-(4-Methoxyphenyl)-3-methyl-3-cyclohexen-1-one (IIIc).—A small sample of the crude orange oil obtained as the product of the Nef reaction in the preparation of IVc was converted by the method of Birch[17] into a 67% yield of a light orange derivative, m.p. 134–145°. The filtrate on cooling gave 19% of a red solid, m.p. 161–175°, which on recrystallization from ethanol melted at 191–192° and showed no depression of melting point when mixed with a sample of the 2,4-dinitrophenylhydrazone of IVc. The light orange solid was recrystallized three times from ethanol to give orange-yellow needles, m.p. 162–163°.

Anal.[12] Calcd. for $C_{20}H_{20}N_4O_5$: C, 60.60; H, 5.09; N, 14.14. Found: C, 60.71; H, 5.38; N, 13.95.

To further establish the identity of this orange-yellow derivative, a small sample was converted in quantitative yield to a red solid, m.p. 187–190°, by refluxing in a solution of benzene–ethanol and two drops of concentrated sulfuric acid. A mixed melting point proved this red solid to be identical with the 2,4-dinitrophenylhydrazone of IVc.

1,2-Dimethyl-5-(4-methoxyphenyl)-4-nitrocyclohexene.—By the method previously described,[6] 8.92 g. (0.049 mole) of 4-methoxy-β-nitrostyrene and 12.00 g. (0.146 mole) of 2,3-dimethylbutadiene-1,3 gave 11.94 g. (92%) of colorless needles, m.p. 103.5–104°.

Anal.[10] Calcd. for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.74; H, 7.28; N, 5.58.

3,4-Dimethyl-6-(4-methoxyphenyl)-3-cyclohexen-1-one.—Obtained in 89% yield from 1,2-dimethyl-5-(4-methoxyphenyl)-4-nitrocyclohexene by the Nef reaction, m.p. 38–41°. Recrystallization from ethanol gave colorless needles, m.p. 43–43.5°.

The 2,4-dinitrophenylhydrazone was prepared by the method of Birch,[17] m.p. 137–137.5°.

Anal.[10] Calcd. for $C_{21}H_{22}N_4O_5$: C, 61.45; H, 5.40; N, 13.65. Found: C, 61.40; H, 5.31; N, 13.91.

3,4-Dimethyl-6-(4-methoxyphenyl)-2-cyclohexen-1-one.—A mixture of geometrical isomers weighing 3.37 g. (72%), m.p. 48–50°, was obtained by acid isomerization of 4.68 g. (0.02 mole) of 3,4-dimethyl-6-(4-methoxyphenyl)-3-cyclohexen-1-one. Fractional crystallization of the mixture from petroleum ether gave one isomer in pure condition, m.p. 77–77.5°, λ_{max} 228.5 mμ (log ϵ 4.34), λ_{max} 275 mμ (log ϵ 3.22), λ_{max} 282 mμ (log ϵ 3.14).

Anal.[10] Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.19; H, 7.89.

The 2,4-dinitrophenylhydrazone of the pure isomer was prepared in quantitative yield by the procedure of Shriner and Fuson[11] and recrystallized three times from ethanol, m.p. 167.5–168°.

Anal.[10] Calcd. for $C_{21}H_{22}N_4O_5$: C, 61.45; H, 5.40; N, 13.65. Found: C, 61.45; H, 5.02; N, 13.85.

Diene Synthesis with Piperylene and β-Nitrostyrene.—A mixture of isomers weighing 7.60 g. (90%), b.p. 127° (0.15 mm.), m.p. 72–80°, was obtained from 5.81 g. (0.085 mole) of piperylene and 5.81 g. (0.039 mole) of β-nitrostyrene. Fractional crystallization of this mixture from ethanol gave a solid, m.p. 80–82°, which was still a mixture of isomers.

(a) **3-Methyl-4-nitro-5-phenylcyclohexene (Id).**—Chromatography of 4.00 g. of this mixture on alumina gave 0.96 g. of nearly pure Id, m.p. 93–93.5°. A sample was crystallized from petroleum ether for analysis, m.p. 94–95°.

Anal.[10] Calcd. for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 72.09; H, 7.01; N, 6.53.

A second isomer, Id_1, m.p. 85–85.5°, was obtained in trace amounts from the mixture melting 80–82° by rechromatographing the residue from the isolation of isomer Id on 60 g. of alumina.

Anal.[10] Calcd. for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.57; H, 6.88; N, 6.40.

(b) **3-Methyl-5-nitro-4-phenylcyclohexene (IId).**—From the mother liquors of the isomer mixture melting 80–82°, 250 mg. of IId, m.p. 98–99°, was obtained by fractional crystallization from petroleum ether. A mixed melting point with Id was depressed to 72°.

Anal.[10] Calcd. for $C_{13}H_{15}NO_2$: C, 71.86; H. 6.96; N, 6.45. Found: C, 72.13; H, 6.81; N, 6.55.

2-Methyl-6-phenyl-2-cyclohexen-1-one (IVd).—A solution of sodium ethoxide prepared from 0.219 g. (9.5 milligram-atoms) of sodium and 10 ml. of ethanol was added to a solution of 0.970 g. (4.5 millimoles) of Id, m.p. 94–95°, in 10 ml. of ethanol, allowed to stand covered with nitrogen for 11 hours, and added over five minutes to a well-stirred solution of 9 ml. of concentrated hydrochloric acid, 125 ml. of water and 75 ml. of acetone at 0°. A blue color developed after 20 minutes, and the ice-bath was replaced with a warm water-bath (50°). The solution was stirred at 50° for one hour and then at room temperature for six hours. The solution then was refluxed for four hours with 10 ml. of concentrated hydrochloric acid and cooled overnight. The yellow solution was diluted with twice its volume of water and extracted with ether. The ethereal extracts were washed with water, dried and concentrated to give an 88% yield of a crude brown oil that was chromatographed on 40 g. of alumina. Elution with petroleum ether (60–70°)–benzene (2:1) gave 0.292 g. (35%) of pink oil which solidified on trituration with petroleum ether. The analytical sample was prepared by crystallization from petroleum ether; m.p. 37–38°, λ_{max} 236 mμ (log ϵ 4.02), λ_{max} 311 mμ (log ϵ 1.96).

Anal.[12] Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.03; H, 7.33.

The 2,4-dinitrophenylhydrazone of IVd was prepared in quantitative yield by the method of Shriner and Fuson[11] and recrystallized from ethanol–ethyl acetate to give red prisms, m.p. 184.5–185.5°.

Anal.[12] Calcd. for $C_{19}H_{18}N_4O_4$: C. 62.29; H, 4.95; N, 15.29. Found: C, 62.53; H, 4.85; N, 15.20.

By the same technique, 87 mg. of Id_1, m.p. 85–85.5°, was converted to IVd in 42% yield. It was identified by ultraviolet absorption spectrum and melting point (36–37°).

5-Methyl-6-phenyl-2-cyclohexen-1-one (VId).—By the same method as described for IVd, 160 mg. of IId, m.p. 98–99°, was converted quantitatively by the Nef reaction to a brown oil. The oil was chromatographed on 20 g. of alumina. Elution with benzene gave a 33% yield of solid, m.p. 64–65°. A sample was recrystallized from ethanol–water to give colorless needles, m.p. 64.5–65°. The compound showed a plateau at 222–223 mμ (log ϵ 4.09) and a maximum at 324 mμ (log ϵ 1.62).

Anal.[10] Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.16; H, 7.64.

The 2,4-dinitrophenylhydrazone was prepared according to the method of Shriner and Fuson[11] and recrystallized twice from ethanol, m.p. 143–144°.

Anal.[10] Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.29; H, 4.95; N, 15.29. Found: C. 61.93; H, 5.12; N, 15.52.

To determine more accurately the ratio of Id to IId a mixture of the conjugated ketones IVd and VId was obtained directly by subjecting the crude distillate of nitro adducts to the Nef reaction. A solution of 6.96 g. (0.032 mole) of the distilled adducts in 50 ml. of ethanol was converted to a mixture of conjugated ketones by the same method that was used to prepare the ketones from the pure nitro compounds. The product 3.6 g. (53%), b.p. 112–116° (0.2 mm.), $n^{20}D$ 1.5711, was chromatographed on 40 g. of alumina. Elution with petroleum ether gave 2.0 g. (34%) of IVd that crystallized on trituration with petroleum ether, m.p. 37–38°. Elution with benzene gave 0.3 g. (5%) of pale yellow oil from which 100 mg. of VId, m.p. 62–64°, was obtained.

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