[Contribution from the School of Chemistry of the University of Minnesota]

CYCLOPROPANES. XII.[1] THE ACTION OF BASES UPON TERTIARY NITROCYCLOPROPYL KETONES

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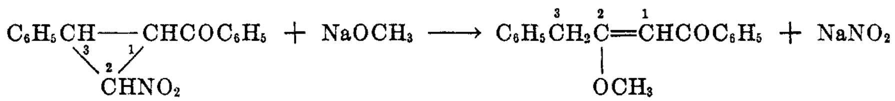
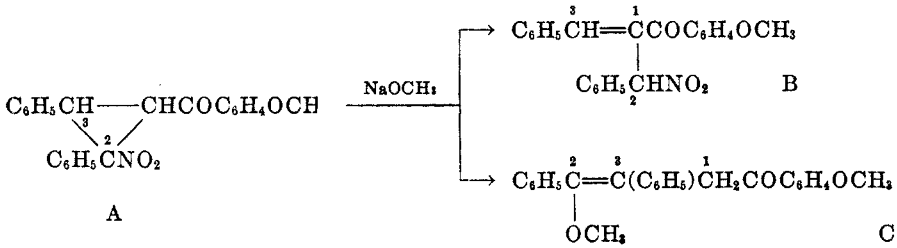
In previous papers of this series[1] the behavior of a number of secondary nitrocyclopropyl ketones toward alkaline reagents has been examined. These compounds all possess an acidic hydrogen atom attached to carbon atom number 2; their reaction with aqueous or alcoholic bases begins with removal of a proton at this point, and the ultimate result is a cleavage of the ring between carbon atoms 1 and 3 with formation of an enol ether of a 1,3-diketone.



The study of this reaction has now been extended to two tertiary nitrocyclopropyl ketones; these compounds are so constituted that removal of a proton from C-2 is impossible, but removal of a proton from C-1, α- to the carbonyl group, is possible. Assuming that the action of bases upon both types of nitrocyclopropyl ketones begins with removal of a proton, it was of some interest to determine the effect of the location of this hydrogen atom upon the course of the over-all reaction and upon the nature of the final product.

Only two tertiary nitrocyclopropyl ketones have been investigated in this respect, and in each of these the group attached to C-2 was phenyl. Kohler and Allen (1) studied the behavior of two (of four possible) stereoisomeric forms of A. When the higher-melting isomer of A reacted with sodium methoxide, the product was the unsaturated nitroketone B (ring cleavage between C-2 and C-3); under the same circumstances, the lower-melting isomer of A was converted into the enol ether C, of a 1,4-diketone (ring cleavage between C-1 and C-2).



Allen and Bridges (2) obtained the cyclopropane D in both (only two possible) stereoisomeric forms; action of sodium methoxide upon either of the stereoisomers

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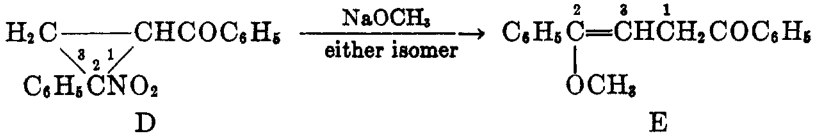
[1] Paper XI, Smith and Kelly, *J. Am. Chem Soc.*, in press.

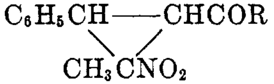
[2] Abstracted from a thesis by John S. Showell, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, November 1951. Monsanto Chemical Fellow, 1950–1951.

gave the same product, the enol ether (E) of a 1,4-diketone (ring cleavage between C-1 and C-2).



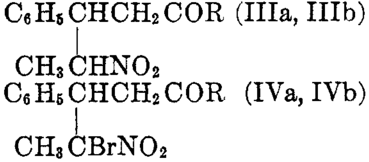
D E

The two nitrocyclopropyl ketones Ia and Ib were synthesized from the corresponding α,β-unsaturated ketones (II) by addition of nitroethane, conversion by alkaline bromination of the resulting nitroketones (III) into the γ-bromo-γ-nitroketones (IV), and cyclization of these by action of methanolic potassium acetate. Addition of nitroethane to benzalacetone (IIa) offered no particular difficulty, although the yield of nitroketone IIIa was low (30–48%). But addition of nitroethane to stryryl cyclopropyl ketone (IIb) failed in that only starting materials and no IIIb could be isolated from the product. However, when the crude alkaline product of the Michael reaction was brominated directly, the bromo compound IVb was produced in 56% yield. Likewise, although the nitroketone IIIa could be isolated in low yields, bromination of the crude alkaline product of the Michael reaction produced the bromo compound IVa in 72% yield. These are two interesting examples of the shifting of a Michael equilibrium by removal of the product *via* a subsequent chemical reaction.



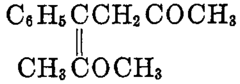
Ia, R = CH_3
Ib, R = cyclopropyl

$C_6H_5CH{=}CHCOR$ (IIa, IIb)



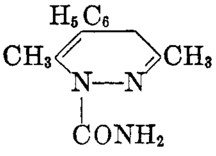
$C_6H_5CH(CH_3CHNO_2)CH_2COR$ (IIIa, IIIb)
$C_6H_5CH(CH_3CBrNO_2)CH_2COR$ (IVa, IVb)

As previous work had indicated that the configuration of the substituents in a nitrocyclopropyl ketone was of importance in determining the course of the reaction with alkali, it was hoped to study some of the individual isomers of Ia and Ib, but unfortunately only one pure isomer of each could be isolated. Even so, the one pure isomer of Ia (m.p. 59.5–60°) behaved toward alkali in a different manner from that shown by the liquid mixture of isomers left after removal of Ia. The solid isomer of Ia, by action of sodium methoxide, was converted in quantitative yield into a neutral liquid $C_{12}H_{16}O_2$ (V). This liquid V was also produced by action of sodium methoxide upon the bromonitroketone IVa—probably *via* the cyclopropane. Compound V contained one methoxyl group, was

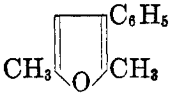


$C_6H_5C(=CCH_3OCH_3)CH_2COCH_3$

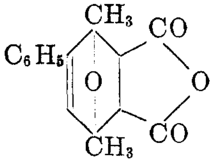
V



VI



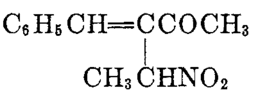
VII



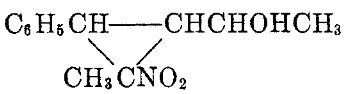
VIII

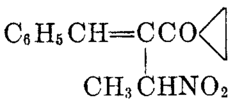
unsaturated toward permanganate and bromine, gave a positive iodoform reaction, formed a dehydropyridazine (VI) by action of semicarbazide, and upon ozonolysis, was converted into benzoylacetone. Action of hydrochloric acid upon V led to 2,5-dimethyl-3-phenylfuran (VII), which likewise was formed (8%) when the sodium derivative of the nitroketone IIIa was refluxed with methanolic hydrochloric acid. The furan formed a Diels-Alder adduct VIII with maleic anhydride. These facts are sufficient to establish the structure of V as the methyl enol ether of a 1,4-diketone.

Thus, action of sodium methoxide upon the solid isomer of Ia resulted in cleavage of the cyclopropane ring between C-1 and C-2. As mentioned before, only the one pure stereoisomer of Ia was isolated, but after removal of this solid, there remained a liquid having the same composition as the solid and possessing properties which showed that it was a mixture of stereoisomeric nitrocyclopropanes. When this liquid was subjected to action of sodium methoxide, there resulted two products. One of these, obtained in 23% yield, was a neutral liquid identified as V. The remainder of the product was a liquid soluble in base, unsaturated toward permanganate, giving a positive test for the nitro group with ferrous sulfate, and a precipitate with 2,4-dinitrophenylhydrazine. This liquid could not be purified, and so was not definitely identified, but the properties indicated that it had structure IX. Thus, in the synthesis of cyclopropane Ia, at least two stereoisomers were formed, one of which (the solid) was converted into V by action of sodium methoxide, whereas the other was converted into IX, a reaction involving cleavage of the ring between C-2 and C-3.


$C_6H_5CH{=}\underset{\substack{|\\ CH_3CHNO_2}}{C}COCH_3$

IX


X


XI

The solid nitrocyclopropane Ia was reduced, by action of aluminum isopropoxide, to the carbinol X. This carbinol, a viscous liquid (mixture of stereoisomeric forms?) gave the solid Ia when subjected to action of sodium dichromate and sulfuric acid. The carbinol X was inert to the action of sodium methoxide. Thus, exactly as has been found for the secondary nitrocyclopropyl ketones of this series, the carbonyl group in the tertiary compound Ia is necessary for any reaction between the cyclopropane and bases.

The nitrocyclopropyl ketone Ib was obtained in only one form, a solid melting at 67–67.5°; no other material could be isolated as a by-product. When this material reacted with sodium methoxide, very little neutral material could be isolated from the product; instead, acidification of the crude reaction product gave a liquid (61%). This liquid was unsaturated toward permanganate and bromine; it gave a positive test for the nitro group with ferrous sulfate, and a precipitate with 2,4-dinitrophenylhydrazine. On the basis of analogy, structure XI was assigned to this substance. It is thus derived from Ib by cleavage of the ring between C-2 and C-3.

EXPERIMENTAL PART[3]

5-Nitro-4-phenyl-2-hexanone (IIIa). Nitroethane (22.5 g., 0.3 mole) was added with shaking to a solution of sodium methoxide (6 g., 0.26 mole)in methanol (100 cc.), and the resulting fine slurry was added to a solution of benzalacetone (29.2 g., 0.2 mole) in dry methanol (100 cc.). The mixture was heated on the steam-bath until it was homogeneous, allowed to stand overnight at room temperature, and then acidified with acetic acid (20 cc.) and cooled. The solid (16.8 g., m.p., 38–42°) was removed; the mother liquor, when concentrated to a volume of 100 cc. and cooled, deposited a second crop (5 g., m.p., 38–42°). The total yield was 48%. The analytical sample, crystallized from methanol, melted at 49.0–49.5°.

Anal. Calc'd for $C_{12}H_{15}NO_3$: C, 65.12; H, 6.83.
Found: C, 65.8; H, 7.09.

The nitroketone was stable toward neutral permanganate and toward bromine in carbon tetrachloride. It was soluble in aqueous sodium hydroxide (30%).

5-Bromo-5-nitro-4-phenyl-2-hexanone (IVa). *A*. A solution of sodium methoxide (from sodium, 1.06 g., 0.046 gram-atom) in dry methanol (50 cc.) was added to a solution of IIIa (9.3 g., 0.042 mole) in dry chloroform (20 cc.) and dry methanol (50 cc.). This solution of the *aci*-nitro compound was added, with stirring and cooling (below −20°) to a solution of bromine (7.4 g., 0.046 mole) in chloroform (40 cc.). The mixture was stirred for 30 minutes and then poured into water (500 cc.). The organic layer was removed and washed successively with aqueous sodium bisulfite, aqueous sodium bicarbonate, and water. The solvent was removed, the residue was taken up in ethanol (40 cc.), and the solution was set aside in a refrigerator for several hours. The solid (7.3 g., m.p. 81–84°) was removed; a second crop (0.5 g., m.p. 78–81°) was obtained by concentration of the mother liquor. The total yield was 62%. The analytical sample, recrystallized from methanol, was white and melted at 86.5–87.0°.

Anal. Calc'd for $C_{12}H_{14}BrNO_3$: C, 48.01; H, 4.70.
Found: C, 48.3; H, 5.03.

The bromo compound was stable toward neutral permanganate, and gave a strong yellow-orange color with a solution of sodium iodide in acetone. When IIIa was brominated in neutral solution, no pure product could be obtained, nor could any cyclopropane be obtained by action of potassium acetate upon the crude product.

The *semicarbazone* was recrystallized from aqueous ethanol, m.p. 150–151° (dec.). It decomposed easily when heated, and was difficult to purify.

Anal. Calc'd for $C_{13}H_{17}BrN_4O_3$: C, 43.71; H, 4.80.
Found: C, 44.6; H, 5.01.

B. Bromine (40 g., 0.25 mole) was added dropwise to the cooled (−20°) alkaline reaction product (from nitroethane, 18.8 g., 0.25 mole) described under IIIa above, and the mixture was kept cold for an hour. The solid, isolated as described under *A* above (2 crops) weighed 60.8 g. (72%) and melted at 83–85°.

3-Phenyl-2-methyl-2-nitro-1-acetylcyclopropane (Ia). A solution of potassium acetate (30 g., 0.3 mole) and the bromo compound IVa (30 g., 0.1 mole) in dry ethanol (250 cc.) was refluxed for 12 hours. Potassium bromide (9.6 g., theory 11.9 g.) was removed and the solvent was removed from the filtrate under reduced pressure. Water (1 l.) was added to the residue and the mixture was extracted with ether (750 cc.). The extract was washed with aqueous sodium bicarbonate, water, and dried (magnesium sulfate). Ether was removed and the residue (26 g.) was evaporatively distilled under a high vacuum. The distillate (b.p., 120–145°/2-3 μ) was dissolved in methanol (30 cc.) and the solution was set aside in a refrigerator at −15° for several days. The solid (1.6 g., m.p. 58–60°) was removed. Solvent was removed from the filtrate and the residue was distilled; the distillate (11.3 g., b.p., 120–150°/0.6–2 μ) could not be induced to crystallize. Redistillation gave a light yellow liquid (7.36 g., 34%)

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[3] Microanalyses by W. Cummings, B. K. Davis, L. Errede, R. E. Kelly, H. Turner, and E. Wheeler.

boiling at 106–118°/1.3 μ. A center cut, b.p., 103–116°/0.8–4 μ., n_D^{24} 1.5323, was taken for analysis.

The solid, crystallized three times from ethanol, melted at 59.5–60.0°.

Anal. Calc'd for $C_{12}H_{13}NO_3$: C, 65.76; H, 5.98.
Found (solid): C, 66.0; H, 6.07.
Found (liquid): C, 66.1; H, 6.58.

Both the solid and liquid gave the following tests: positive with ferrous sulfate for nitro group; negative toward neutral permanganate and toward bromine in carbon tetrachloride; strongly positive iodoform reaction; precipitate with 2,4-dinitrophenylhydrazine reagent. However, the 2,4-dinitrophenylhydrazone was a low-melting solid which could not be recrystallized.

The *semicarbazone* (of solid isomer) was recrystallized from aqueous ethanol; it was difficult to purify. It melted at 194–195° (dec.), but the melting point was greatly affected by the rate of heating.

Anal. Calc'd for $C_{13}H_{16}N_4O_3$: C, 56.51; H, 5.84.
Found: C, 56.3; H, 7.10.

Attempts were made to oxidize the methyl ketone (liquid) to an acid according to the procedure of King (3). Although a pyridinium iodide was formed, it gave no acid when it was refluxed with aqueous sodium hydroxide.

3-Phenyl-2-methyl-2-nitrocyclopropyl m-nitrostyryl ketone. A solution of potassium hydroxide (0.25 g.) in ethanol (5 cc.) was added dropwise to a solution of the solid methyl ketone Ia (0.5 g.) and *m*-nitrobenzaldehyde (0.35 g.) in ethanol (5 cc.). The light yellow solid (0.5 g., 62%) was removed and crystallized several times from ethanol, when it melted at 159.5–161.0°.

Anal. Calc'd for $C_{19}H_{16}N_2O_5$: C, 64.77; H, 4.58.
Found: C, 64.34; H, 5.06.

The unsubstituted benzal derivative was an oil.

Action of sodium methoxide upon Ia. *Liquid mixture of stereoisomers.* The liquid Ia (10.7 g., 0.05 mole, b.p., 103–116°/0.8–4 μ, n_D^{24} 1.5323) was added with stirring to methanolic sodium methoxide (from sodium, 4.6 g., 0.2 gram-atom, and dry methanol, 60 cc.). The temperature rose gradually from 30 to 48°, the solution became yellow, and sodium nitrite separated. The solution was stirred for one hour at room temperature, the sodium nitrite was removed, and the filtrate was poured into water (400 cc.) and extracted with ether. Ether layer = A, aqueous layer = B. The ether layer A was washed with aqueous potassium carbonate and water, and the solvent was removed. The residual oil (3.6 g.) when distilled gave, 5-methoxy-4-phenyl-4-hexene-2-one (V) (2.3 g., 22%) boiling at 80–95°/2–3 mm.; n_D^{20} 1.5175, n_D^{25} 1.5161 (see below). The aqueous layer B was acidified, extracted with ether (500 cc.), and discarded. The ether layer, initially green, gradually became orange. It was dried (magnesium sulfate) and the solvent was removed. The residual orange oil (6.0 g.) was distilled; the distillate (1.4 g.) was a yellow liquid boiling at 120–123°/0.5–0.6 mm.; n_D^{26} 1.5432. The majority of the material remained in the distillation flask as a viscous intractable gum. The distillate gave a positive test for the nitro group with ferrous sulfate, decolorized permanganate, and gave a precipitate with 2,4-dinitrophenylhydrazine. In spite of all attempts to keep it or to purify it, the substance slowly deepened in color and decomposed into a thick oil. It was most probably IX, 3-benzal-4-nitro-2-pentanone.

Solid isomer of Ia. The solid cyclopropane (0.33 g., m.p. 58–60°) in methanol (2 cc.) was added dropwise to a solution of sodium (0.5 g.) in methanol (10 cc.). After ten minutes, the solution was poured into water (100 cc.) and extracted with ether (50 cc.). The aqueous layer was acidified; no organic material separated. The ether layer was dried (magnesium sulfate), the solvent was removed, and the residue (0.3 g., 98%, n_D^{30} 1.5130) was identical with V obtained from the liquid Ia.

5-Methoxy-4-phenyl-4-hexene-2-one (V) immediately decolorized bromine in carbon tetrachloride, as well as permanganate in acetone. The iodoform test was positive, and the substance gave a pale yellow precipitate with 2,4-dinitrophenylhydrazine. The substance was difficult to purify, and the analytical values for carbon were always somewhat low.

Anal. Calc'd for $C_{13}H_{16}O_2$: C, 76.42; H, 7.89; OCH_3 (one), 15.2.
Found: C, 75.5; H, 8.08; OCH_3, 11.6.

The "semicarbazone" (VI), prepared in the usual way and crystallized from ethanol, melted at 188–189°. This was not a simple semicarbazone, for its formation from V was accompanied by loss of the elements of methanol as well as those of water.

Anal. Calc'd for $C_{14}H_{19}N_3O_2$: C, 64.36; H, 7.33; N, 16.03.
Calc'd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.60; N, 18.41.
Found: C, 68.4; H, 6.81; N, 18.4.

The ultraviolet spectrum[4] of V was determined in 2,2,4-trimethylpentane; *c*, 1.64×10^{-4} moles/l.

The enol ether V (3.2 g., 16%, b.p. 94–103°/0.25 mm.) was also obtained from the bromonitroketone IVa (30 g., 0.1 mole) when the latter was added to a solution of sodium methoxide in methanol. The solution was refluxed for one hour, poured into water, and extracted with ether. The products from several experiments (yields 13–19%) were combined and distilled through a Piros-Glover column. The bulk of the material boiled at 104.4°/3 mm., and had n_D^{28} 1.5177.

Ozonolysis of V. The enol ether V (6 g., 0.03 mole), dissolved in ethyl bromide (70 cc.), was subjected to the action of a stream of ozonized oxygen (3.4 % O_3) at −70° for 48 minutes (one mole of O_3). The solution was concentrated to 20 cc. and was added dropwise to a mixture of water (25 cc.), zinc dust (4 g.), and traces of silver nitrate and hydroquinone. The mixture was refluxed for 20 minutes, cooled, extracted with ether (50 cc.), and the extract was dried (magnesium sulfate). Ether and ethyl bromide were removed by distillation (no methyl acetate could be found in the distillate); the residue, when distilled, gave a yellow liquid (0.4 g.) boiling at 70–90°/0.2 mm. This liquid gave a violet color with ferric chloride and was identified as benzoylacetone by conversion to the copper compound, m.p. and mixture m.p. 193–196°; literature value, 195–196° (4).

2,5-Dimethyl-3-phenylfuran (VII). The enol ether V (8.3 g., 0.4 mole) was refluxed for one hour in methanol (30 cc.) containing hydrochloric acid. The mixture was poured into water (75 cc.), extracted with ether (100 cc.), and the extract was washed with aqueous sodium bicarbonate, water, and dried (magnesium sulfate). The solvent was removed and the residue was distilled through a Piros-Glover column. The distillate (4.34 g., 61%) a colorless liquid, boiled at 102.2°/2 mm.; n_D^{28} 1.5608.

Anal. Calc'd for $C_{12}H_{12}O$: C, 83.69; H, 7.03.
Found: C, 83.3; H, 7.23.

The substance gave a negative test with 2,4-dinitrophenylhydrazine, and with ferric chloride. The ultraviolet spectrum of VII was determined in 2,2,4-trimethylpentane; *c*, 6.48×10^{-4} moles/l.[4]

Furan VII *from the nitroketone* IIIa. The nitroketone (5 g., 0.022 mole) was added to a solution of sodium (1 g.) in methanol (15 cc.). The orange solution was acidified with hydrochloric acid (6 cc.), refluxed for two hours and poured into water (100 cc.). The product, removed by ether extraction and purified as described above, weighed 0.3 g. (8%), boiled at 90–91°/1 mm.; n_D^{30} 1.5572. It gave the same adduct, m.p. 105–107°, as that obtained from VII derived from V.

3,6-Dimethyl-4-phenyl-3,6-endooxy-1,2,3,6-tetrahydrophthalic anhydride (VIII). A solution of the furan VII (2 g., 0.012 mole) and maleic anhydride (1.2 g., 0.012 mole) in ether (10 cc.) was set aside at −15° overnight. The solid (1.6 g., m.p. 107–108°) was removed and crystallized from ether, when it melted at 107.5–108.5° (dec.). The mother liquor yielded a second crop (0.26 g., m.p. 104–105°); the total yield was 58%.

Anal. Calc'd for $C_{16}H_{14}O_4$: C, 71.08; H, 5.22; Neut. equiv. (two), 135.
Found: C, 71.6; H, 5.33; Neut. equiv., 135.

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[4] The complete data may be found in the Ph.D. Thesis of John S. Showell, footnote 2.

The adduct was unsaturated toward permanganate.

3-Phenyl-2-nitro-2-methyl-1-cyclopropylmethyl carbinol (X). The liquid nitrocyclopropylketone Ia (10.8 g.) and aluminum isopropoxide (10.6 g.) were refluxed in isopropyl alcohol (100 cc., dried over lime) in an apparatus arranged for removing acetone. At the end of two hours, the distillate was free of acetone. The solvent was removed and the residue was poured into water (300 cc.) containing hydrochloric acid (20 cc.). The mixture was extracted with ether and the extract was washed with aqueous sodium bicarbonate, water, dried (magnesium sulfate), and evaporated. The dark residue (9.2 g.), gave a distillate weighing 6.91 g. (62%), boiling at 150–168°/1.3 μ; n_D^{25} 1.540. The product was redistilled and a center cut, b.p. 152–160°/10 μ, n_D^{25} 1.5361; was taken for analysis.

Anal. Calc'd for $C_{12}H_{15}NO_3$: C, 65.13; H, 6.83.

Found: C, 64.6; H, 7.05.

The *phenylcarbamate*, prepared from the carbinol (0.2 g.) and phenyl isocyanate (0.12 g.), when recrystallized from chloroform, formed white needles melting at 158–159°.

Anal. Calc'd for $C_{19}H_{20}N_2O_4$: C, 67.03; H, 5.93.

Found: C, 67.1; H, 6.29.

The carbinol X (0.45 g.) was added to a solution of sodium dichromate (0.3 g.) in sulfuric acid (0.2 cc.) and heated at 60° for 20 minutes. The mixture was poured into water (30 cc.) and extracted with ether (50 cc.). The extract was washed with aqueous sodium bicarbonate and water, dried (magnesium sulfate), and the solvent was removed. The residual oil (0.36 g., 75%) was the nitrocyclopropyl ketone Ia; it was identified by conversion to the semicarbazone, m.p. and mixture m.p. 197–199°.

A solution of the carbinol X (1 g., 0.0045 mole) in dry methanol (25 cc.) was added, dropwise and with stirring, to a solution of sodium methoxide (from sodium, 0.46 g., 0.02 gram-atom) in methanol (20 cc.). There was no visible evidence of any reaction. The solution was stirred for one hour at room temperature, poured into water (200 cc.), and extracted with ether (100 cc.). The extract was dried (magnesium sulfate) and the solvent was removed under reduced pressure. The residual oil (0.55 g., 55%) had the same refractive index as the starting material. The low recovery (55%) was caused by losses in manipulation; there was no evidence of any other product.

1-Cyclopropyl-3-phenyl-4-bromo-4-nitro-1-pentanone (IVb). Sodium methoxide (from sodium, 11.5 g., 0.5 gram-atom) in methanol (200 cc.) was added to a solution of nitroethane (37.5 g., 0.5 mole) and styryl cyclopropyl ketone (5) (86 g., 0.5 mole) in methanol (300 cc.). The solution was refluxed for 17 hours, then cooled (Dry Ice) and to it was added, dropwise and with stirring, liquid bromine (80 g., 0.5 mole). The solid was removed; a second crop was obtained by concentration of the mother liquor to half its original volume. The combined crude solids weighed 110 g., and melted at 55–60°. After crystallization from methanol (300 cc.), the substance weighed 64 g. (56%) and melted at 70–72°. The analytical sample was crystallized four times from methanol, when it melted at 75–76°.

Anal. Calc'd for $C_{14}H_{16}BrNO_3$: C, 51.55; H, 4.94; N, 4.31.

Found: C, 51.5; H, 4.99; N, 4.43.

The bromonitroketone gave a red color with sodium iodide in acetone, and a positive test for the carbonyl group with 2,4-dinitrophenylhydrazine. It was inert toward permanganate, and reacted only slowly with bromine in carbon tetrachloride, but with evolution of hydrogen bromide.

When the above addition of nitroethane was carried out but with addition of acetic acid instead of bromine, no IIIb resulted and styryl cyclopropyl ketone was isolated in 92% recovery.

Cyclopropyl 3-phenyl-2-nitro-2-methyl-1-cyclopropyl ketone (Ib). A solution of potassium acetate (140 g., 1.4 moles, freshly fused) and the bromo compound IVb (97 g., 0.3 mole) in dry ethanol (700 cc.) was refluxed for 22 hours. The solvent was removed under reduced pressure, and the residue was poured into water (1.5 l.) and extracted with ether (1 l.). The extract was washed with aqueous sodium bicarbonate and water, dried (magnesium sulfate), and the solvent was removed. The residual oil, which could not be induced to crystallize, was distilled from a "sausage" flask. The distillate (46 g., 63%, b.p., 95–139°/20–75 μ) likewise could not be induced to crystallize. It was redistilled and separated into four fractions which were set aside in a refrigerator at −15° for several days. One of these fractions crystallized; when the other fractions were seeded with these crystals, they also deposited solid material. In this way, 23.4 g. (32%) of the cyclopropane was obtained. After crystallization from methanol, the substance formed white needles melting at 67.0–67.5°.

Anal. Calc'd for $C_{14}H_{15}NO_3$: C, 69.40; H, 6.24.

Found: C, 69.0; H, 6.50.

The cyclopropane was inert toward potassium permanganate and toward bromine in carbon tetrachloride. It gave a positive test for the nitro group with ferrous sulfate.

2,4-Dinitrophenylhydrazone. This derivative was crystallized from aqueous dioxane; a yellow solid, m.p. 202–203°.

Anal. Calc'd for $C_{20}H_{19}N_5O_6$: C, 56.47; H, 4.50.

Found: C, 56.9; H. 5.03.

Action of sodium methoxide upon Ib. A solution of the cyclopropane (15 g., 0.06 mole) in dry methanol (75 cc.) was added with stirring to methanolic sodium methoxide (from sodium, 4.8 g., 0.25 gram-atom, and methanol, 50 cc.). During the addition, the solution refluxed spontaneously. The solution was stirred for one hour at room temperature, poured into water (750 cc.), and extracted with ether (300 cc.). Ether layer = A, aqueous layer = B. A was dried (magnesium sulfate) and the solvent was removed. The very small amount (0.1 g.) of residue was refluxed for two hours with methanol (5 cc.) containing hydrochloric acid (0.1 cc.), poured into water (25 cc.), and extracted with ether (50 cc.). The ether layer was concentrated to a volume of 2 cc., maleic anhydride (0.1 g.) was added and the solution was set aside at −15° for several days. Only unchanged maleic anhydride could be recovered. Thus the neutral material obtained from Ib was not the enol ether of a 1,4-diketone, for no furan could be obtained from it. The alkaline aqueous layer B above was acidified with sulfuric acid; a dark oil separated. The mixture was extracted with ether (100 cc.), the extract was dried (magnesium sulfate), and the ether was removed. The residual oil (9.3 g.) was distilled from a "sausage" flask under high vacuum. The distillate (4.7 g., n_D^{28} 1.560), a light yellow oil, slowly decolorized permanganate in acetone and reacted with bromine in carbon tetrachloride with evolution of hydrogen bromide. It gave an orange red precipitate with 2,4-dinitrophenylhydrazine reagent, and a positive test for the nitro group with ferrous sulfate and alkali. Although not definitely identified, this material was provisionally assigned structure XI.

SUMMARY

Two tertiary nitrocyclopropyl ketones, Ia and Ib, having no hydrogen atom attached to the carbon atom holding the nitro group, have been synthesized and their behavior toward sodium methoxide has been examined. The solid stereoisomer of Ia was converted quantitatively into the enol ether V of a 1,4-diketone with cleavage of the ring between C-1 and C-2. The liquid mixture of stereoisomers of Ia was converted into the same enol ether (23%), together with an unsaturated nitro compound IX: in this case, the ring was cleaved between C-2 and C-3. The nitrocyclopropyl ketone Ib, obtained in only one form, was converted into an unsaturated nitro compound XI and gave no derivative of a 1,4-diketone. The solid ketone Ia was reduced to the nitro carbinol X; this carbinol could be oxidized to the solid ketone Ia. The nitro carbinol X was inert to the action of sodium methoxide—hence, as with the secondary nitro compounds of this series, the ketone group is necessary for any reaction of the tertiary compounds with bases.

Two examples are provided of the shifting of a Michael equilibrium bv removal of the product chemically.

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