[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

CYCLOPROPANES. XIII.[1] 1-ACETYL-2-NITRO-3-PHENYLCYCLOPROPANE AND ITS REACTION WITH SODIUM METHOXIDE

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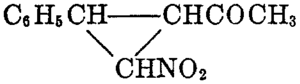
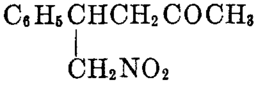
The secondary nitrocyclopropyl ketone, 1-acetyl-2-nitro-3-phenylcyclopropane (I), has been synthesized and its behavior toward alkali has been examined. The γ-nitroketone II, obtained in 38% yield by addition of nitromethane to benzalacetone, was brominated in alkaline solution. No monobromo compound could be isolated; instead, the product was a mixture of II and the dibromo compound III. When two moles of bromine were used the dibromo compound III, an unstable solid, was formed in 54% yield. Action of sodium iodide upon III likewise produced only a mixture of II and III, and no monobromo compound. Bromination of II in neutral solution led to a complex mixture from which no pure material could be isolated. Action of potassium acetate upon III did not give a bromonitrocyclopropane; instead, one of the bromine atoms was reductively removed, and the product was the cyclopropane I.

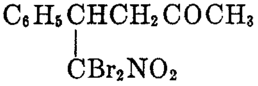


I



$C_6H_5\underset{\displaystyle CH_2NO_2}{CH}CH_2COCH_3$

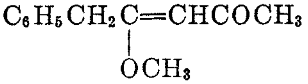
II



$C_6H_5\underset{\displaystyle CBr_2NO_2}{CH}CH_2COCH_3$

III

Action of sodium methoxide upon I produced the methyl enol ether IV of a 1,3-diketone. The double bond in IV was not definitely located, but structure IV is in analogy with known examples of this reaction. The enol ether IV was hydrolyzed to the 1,3-diketone phenylacetylacetone (V), identified as the copper enolate and by hydrolysis to phenylacetic acid, which was identified as the *p*-phenylphenacyl ester.



$C_6H_5CH_2\underset{\displaystyle OCH_3}{C}{=}CHCOCH_3$

IV

$C_6H_5CH_2COCH_2COCH_3$

V

EXPERIMENTAL PART

5,5-Dibromo-5-nitro-4-phenyl-1-pentanone (III). The nitroketone II (1) (59 g., 0.29 mole) was dissolved in methanolic sodium methoxide (from sodium, 14 g., 0.58 gram-atom, and methanol, 200 cc.), and to this solution there was added, with stirring and cooling (−20°), a solution of bromine (93 g., 0.58 mole) in chloroform (50 cc.). The solid was removed, washed successively with water and methanol (50 cc.), and dried. It weighed 115 g. (54%) and melted at 133–135° (dec.). The analytical sample was crystallized from ethanol; it melted at 133–135° (dec.).

Anal. Calc'd for $C_{11}H_{11}Br_2NO_3$: C, 36.18; H, 3.04.

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[1] Paper XII, Smith and Showell, *J. Org. Chem.*, **17**, preceding paper (1951).

Found: C, 36.86; H, 3.26.

The substance decomposed easily and was difficult to crystallize. A 2,4-dinitrophenylhydrazone was prepared; this formed orange needles melting at 159–160° (dec.).

Anal. Calc'd for $C_{17}H_{15}Br_2N_5O_6$: C, 37.43; H, 2.75.

Found: C, 38.14; H, 2.81.

When the bromination of II was carried out as above, but with one equivalent each of alkali and bromine, the white solid product softened at about 50° and melted indefinitely at 96–99° (dec.). The analytical values showed that this was a mixture of II with a brominated product (or products); two kinds of crystals could be detected visually. When the mixture was suspended in ethanol, a part dissolved rapidly. At this point, the solution was decanted from the undissolved large prisms. The prisms melted at 133–135°; the decanted solution, on cooling, deposited more of these prisms. The solution was decanted again, and set aside, when it deposited white needles of II. No monobromo compound could be found. Addition of bromine (8 g.) to a chloroform (60 cc.) solution of II (10.3 g.) in the presence of ultraviolet light and a little benzoyl peroxide led to a mixture from which no pure material could be obtained by crystallization, and which decomposed when attempts were made to distill it.

A solution of sodium iodide (1.65 g.) in acetone (20 cc.) was added to a solution of the dibromoketone III (4.03 g.) in acetone (40 cc.). A red color appeared at once; the solvent was removed and the residue was poured into water (50 cc.) and extracted with ether (100 cc.). The ether extract was washed with aqueous sodium bisulfite, dried (magnesium sulfate), and the solvent was removed. The residue was dissolved in ethanol and the solution was cooled. The white solid (1 g.) was unchanged III, m.p. and mixture m.p. 133–135°. No other pure material could be isolated.

3-Phenyl-2-nitro-1-acetylcyclopropane (I). A solution of potassium acetate (59 g., 0.6 mole) and the dibromoketone III (57 g., 0.16 mole) in ethanol (500 cc.) was refluxed for ten hours. The solvent was removed and the residue was poured into water (1.5 l.) and extracted with ether (750 cc.). The extract was washed with aqueous sodium bicarbonate and water, dried (magnesium sulfate), decolorized (Norit), and the solvent was removed. The residue, which could not be induced to crystallize (methanol, −15°) was distilled from a "sausage" flask under a high vacuum. The distillate, a light orange oil (14 g., 31%, n_D^{25} 1.5364), was then fractionated under a pressure of about 1 μ. Several fractions, boiling from 66° to 134°, were collected. The pure liquid cyclopropane I boiled at 130–134°, and weighed 4 g.

Anal. Calc'd for $C_{11}H_{11}NO_3$: C, 64.37; H, 5.40.

Found: C, 64.5; H, 5.88.

The cyclopropane was inert toward permanganate, and gave no color with sodium iodide in acetone. It reacted slowly with bromine in carbon tetrachloride with evolution of hydrogen bromide. The iodoform test was positive. No solid benzal derivatives could be obtained. The 2,4-dinitrophenylhydrazone, crystallized from aqueous dioxane, melted at 207.5–208.5°.

Anal. Calc'd for $C_{17}H_{15}N_5O_6$: C, 52.98; H, 3.92.

Found: C, 53.2; H, 4.17.

A solution of the cyclopropane I (1 g.) in methanol (5 cc.) was added dropwise to methanolic sodium methoxide (from sodium, 1 g., and methanol, 25 cc.), and the orange-red solution was allowed to stand at room temperature for one hour. Sodium nitrite separated; this was removed and the filtrate was poured into water (100 cc.) and extracted with ether (100 cc.). The extract was washed with water, the solvent was removed, and the residue was refluxed for 30 minutes with methanol (10 cc.) containing hydrochloric acid (0.1 cc.). The solution was diluted with water (75 cc.) and extracted with ether. The extract was washed with aqueous sodium bicarbonate and water, dried (magnesium sulfate), and the solvent was removed. The residual oil (0.63 g., 83%) gave a strong red color with ferric chloride. This oil (0.35 g.) was dissolved in methanol (2 cc.) and the solution was poured into saturated aqueous copper acetate (2 cc.). The light blue solid (0.45 g., m.p., 215–220°) was removed and crystallized from benzene, m.p. 235–236°. The literature value is 223° (2).

Anal. Calc'd for $C_{22}H_{22}CuO_4$: C, 63.84; H, 5.36.
Found: C, 64.8; 64.7; H, 5.54; 5.80.

The liquid diketone (0.15 g.) was warmed for three hours with aqueous sodium hydroxide (3 cc., 10%). The cooled solution was extracted with ether, the aqueous layer was acidified with sulfuric acid (6 *N*) and again extracted with ether (50 cc.). The second ether extract was washed with water, the solvent was removed, and the residue was converted into the *p*-phenacyl ester. This, after crystallization from aqueous ethanol, melted at 61–63°. The *p*-phenacyl ester of phenylacetic acid melts at 63° (3).

SUMMARY

The γ-nitroketone II, resulting from addition of nitromethane to benzalacetone, could not be converted into a monobromo derivative by bromination in alkaline solution. Instead, a dibromo compound III was obtained. When the dibromo compound was cyclized by action of potassium acetate, one of the bromine atoms was reductively eliminated and the bromine-free cyclopropane I was formed.

Action of methanolic alkali upon the cyclopropane gave the methyl enol ether IV of a 1,3-diketone V.

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REFERENCES

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(2) MORGAN AND PORTER, *J. Chem. Soc.*, **125**, 1269 (1924).
(3) DRAKE AND SWEENEY, *J. Am. Chem. Soc.*, **54**, 2060 (1932).