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

THE REACTION OF NITROPARAFFINS AND ALICYCLIC KETONES. II[1]

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The need for moderate amounts of 1-nitromethyl-1-cyclohexene and related compounds for another problem has led to a study of the reaction of the nitroparaffins with the methylcyclohexanones, some substituted cyclohexenones, and some other dicarbonyl compounds.

The reaction of nitromethane and cyclohexanone has been reported to yield three types of products. When sodium ethoxide is used as the condensing agent, 1-nitromethyl-1-cyclohexanol is the main product (1, 2); in the presence of piperidine or diethylamine as the catalyst, some 1-nitromethyl-1-cyclohexanol is formed, but 1-nitromethyl-1-cyclohexene and 1,1-bis(nitromethyl)cyclohexane are the principal products (3, 4).

Lambert and Lowe (4) also report the formation of a small amount of a solid, $C_{14}H_{20}N_2O_3$, from the reaction of nitromethane and cyclohexanone in the presence of diethylamine, and state that the structure of this compound is unknown. In the present investigation, this same solid was isolated when the reaction was catalyzed by piperidine, and similar solids were isolated from the reaction of 3-methyl- and 4-methyl-cyclohexanone and nitromethane. A study of these solids is under way at the present time.

Of the three methylcyclohexanones, 2-methylcyclohexanone gave the smallest yield of the corresponding nitromethylcyclohexene and 4-methylcyclohexanone gave the best yield.

When methylamine was used as the catalyst for the reaction of nitromethane with cyclohexanone, the yield of 1-nitromethyl-1-cyclohexene was 48% as compared to 26% with piperidine as the condensing agent and no solid by-product was formed.

Nitromethane reacted by 1,4-addition with 3-methyl-2-cyclohexen-1-one, 3-methyl-5-*n*-propyl-2-cyclohexen-1-one, and isophorone in the presence of piperidine. The formation of ketone derivatives established the structure of the adducts. There was no reaction when sodium ethoxide was used as the catalyst.

When 1,2-cyclohexanedione and 1,4-cyclohexanedione were used in place of the cyclohexanones, only intractable tars were obtained if either sodium ethoxide or piperidine was used as the condensing agent. In the presence of solid potassium carbonate, one carbonyl group of each diketone reacted with nitromethane to form 2-hydroxy-2-nitromethyl-1-cyclohexanone and 4-hydroxy-4-nitromethyl-1-cyclohexanone respectively, even though a large excess of nitromethane was used. The formation of 2,4-dinitrophenylhydrazones confirmed the identity of these compounds.

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[1] Abstracted from the Ph. D. dissertation of Floyd B. Erickson (1949) and the Master's dissertation of James M. Shackelford (1951).

Yakubovich (5) has reported the addition of one molecule of nitromethane to one carbonyl group of phenanthrenequinone in the presence of solid potassium carbonate or solid potassium hydroxide.

In the present investigation, it was found that one carbonyl group of acenaphthenequinone reacted by 1,2-addition with nitromethane, nitroethane, and 1-nitropropane in the presence of solid potassium hydroxide. There was no reaction when potassium carbonate was substituted for potassium hydroxide, and with piperidine as the catalyst the product was a tar. Phenanthrenequinone reacted only with nitromethane.

No identifiable product was obtained from aceanthrenequinone, anthraquinone, or the naphthoquinones.

EXPERIMENTAL[2]

Materials. The *alkylcyclohexenones* were prepared by the procedure of Horning, Denekas, and Field (6). *1,2-Cyclohexanedione* was obtained from cyclohexanone as described by Vander Harr, Voter, and Banks (7) and *1,4-cyclohexanedione* was prepared by the method of Vincent, Thompson, and Smith (8). *Acenaphthenequinone* was prepared by the procedure in Organic Syntheses (9).

1-Nitromethyl-4-methyl-1-cyclohexene. The preparation of this compound is typical and is described in detail. A solution of 116 ml. (0.87 mole) of 4-methylcyclohexanone, 51 ml. (0.95 mole) of nitromethane, and 6 ml. of piperidine was heated under gentle reflux for 24 hours. After the solution had cooled, the solid which had separated was removed and the water formed during the reaction was separated. The filtrate was fractionated through a short column packed with glass helices to yield 47 g. of unchanged starting material; 39 g. (29%) of the olefin, b.p. 100–104° (10 mm.); and a high-boiling residue. A center cut of the olefin distilling at 96–98° (9 mm.), n_D^{20} 1.4821 was taken for analyses.

Anal. Calc'd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44.
Found: C, 61.71; H, 8.61.

The solid (5.8 g., 4.5%) was recrystallized from ethylene glycol monoethyl ether to yield colorless crystals which darkened at 240° and melted with decomposition at 257–258°.

Anal. Calc'd for $C_{16}H_{24}N_2O_3$: C, 65.72; H, 8.24.
Found: C, 65.62; H, 8.41.

1-Nitromethyl-3- or 5-methyl-1-cyclohexene. The yield of olefin from 116 ml. of 3-methylcyclohexanone was 30%, b.p. 98–104° (12 mm.). The analytical sample distilled at 94–97° (12 ml.), n_D^{20} 1.4835.

Anal. Calc'd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44.
Found: C, 61.94; H, 8.38.

The solid (1.14 g. 0.9%) darkened at 247° and melted with decomposition at 260–261°.

Anal. Calc'd for $C_{16}H_{24}N_2O_3$: C, 65.72; H, 8.24.
Found: C, 65.59; H, 8.46.

1-Nitromethyl-2- or 6-methyl-1-cyclohexene. The yield of olefin from 116 ml. of 2-methylcyclohexanone was 8.3%, b.p. 90–95° (10 mm.). The analytical sample distilled at 92–93° (9 mm.), n_D^{20} 1.4894.

Anal. Calc'd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44.
Found: C, 61.99; H, 8.66.

1-Nitromethyl-1-cyclohexene. The best yield of this olefin was obtained as follows: A mixture of 38 g. (0.4 mole) of cyclohexanone and 24.8 g. (0.8 mole) of nitromethane was cooled to 5° in an ice-bath. To this cold solution was added 3.1 g. (0.1 mole) of anhydrous

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[2] The melting points are uncorrected. The carbon and hydrogen analyses were done by R. A. Carpenter, J. S. Finney, and P. D. Strickler.

liquid methylamine. The mixture was kept at 8–10° for 17 days, protected by a potassium hydroxide drying tube. The solution was acidified with 10% hydrochloric acid and extracted with ether. The ether solution was washed well with water and dried over Drierite. The solvent was removed on a steam-bath and the residue was fractionated to yield 27 g. (48%) of olefin, b.p. 95–96° (12 mm.), n_D^{25} 1.4850.

Condensation of 3-methyl-2-cyclohexen-1-one and nitromethane. A solution of the ketone (95.7 g., 0.87 mole), 51 ml. (0.87 mole) of nitromethane, and 6 ml. (0.06 mole) of piperidine was refluxed gently for 24 hours. The solution was fractionated to yield unchanged starting material; 56 g. (37.5 %) of 3-methyl-3-nitromethyl-1-cyclohexanone, b.p. 120–125° (1 mm.); and a high-boiling residue. The analytical sample distilled at 123–124° (1 mm.), n_D^{20} 1.4891.

Anal. Calc'd for $C_8H_{13}NO_3$: C, 56.12; H, 7.65.
Found: C, 55.86; H, 7.78.

The *semicarbazone* of this adduct melted at 169.5–170.5°.

Anal. Calc'd for $C_9H_{16}N_4O_3$: C, 47.36; H, 7.06.
Found: C, 47.21; H, 7.33.

Condensation of isophorone and nitromethane. 3-Nitromethyl-3,5,5-trimethyl-1-cyclohexanone was obtained in 9.2% yield, b.p. 118–124° (1 mm.). The analytical sample distilled at 130–132° (2 mm.), n_D^{20} 1.4911.

Anal. Calc'd for $C_{10}H_{17}NO_3$: C, 60.28: H, 8.60.
Found: C, 60.33; H, 8.44.

The *oxime* of this adduct melted at 114–115°.

Anal. Calc'd for $C_{10}H_{18}N_2O_3$: C, 56.05; H, 8.46.
Found: C, 55.97; H, 8.20.

Condensation of 3-methyl-5-n-propyl-2-cyclohexen-1-one and nitromethane. The yield of 3-methyl-3-nitromethyl-5-*n*-propyl-1-cyclohexanone was 25%, b.p. 130–135° (1 mm.). The analytical sample distilled at 134–135° (1 mm.), n_D^{20} 1.4794.

Anal. Calc'd for $C_{11}H_{19}NO_3$: C, 61.95; H, 8.98.
Found: C, 61.92; H, 9.06.

The *semicarbazone* of this adduct melted at 130–132°.

Anal. Calc'd for $C_{12}H_{22}N_4O_3$: C, 53.31: H, 8.25.
Found: C, 53.14; H, 8.40.

1,2-Cyclohexanedione and nitromethane. The diketone (8 g.), 15 ml. of nitromethane, and 2 g. of anhydrous potassium carbonate were refluxed for ten minutes, then cooled and the solid was separated. Recrystallization of the reaction product from absolute alcohol chilled with Dry Ice gave a white compound, m.p. 92.5–93°; yield, 4 g. (35%).

Anal. Calc'd for $C_7H_{11}NO_4$: C, 48.55; H, 6.39.
Found: C, 48.44; H, 6.18.

The *2,4-dinitrophenylhydrazone* of this adduct melted at 173–174°.

Anal. Calc'd for $C_{13}H_{15}N_5O_7$: C, 44.19; H, 4.28.
Found: C, 44.47; H, 4.47.

1,4-Cyclohexanedione and nitromethane. The same amounts of reagents as specified above yielded 1 g. (9%) of adduct, m.p. 124.5–125°.

Anal. Calc'd for $C_7H_{11}NO_4$: C, 48.55; H, 6.39.
Found: C, 48.09; H, 6.41.

The *2,4-dinitrophenylhydrazone* of this adduct melted at 93.5–94.5°.

Anal. Calc'd for $C_{13}H_{15}N_5O_7$: C, 44.19; H, 4.28.
Found: C, 44.40; H, 4.17.

Acenaphthenequinone and the nitroparaffins. (*a*) *Nitromethane.* The quinone (3 g.) 1 g. of solid potassium hydroxide, and 10 ml. of nitromethane in 50 ml. of absolute alcohol were stirred for ten minutes. The temperature rose to 50° and the mixture was allowed to stand for one hour. The solid which separated was collected, washed with cold methanol to remove most of the color, and then added to 50 ml. of cold 20% hydrochloric acid and stirred for one hour. The solid was again collected and dried in a desiccator, then dissolved in 20 ml. of hot dioxane and filtered. To the filtrate was added 80 ml. of hot petroleum ether

(60–68°). After three recrystallizations, the pale yellow compound melted at **127–128°**; yield, 1 g. (25%).

Anal. Calc'd for $C_{13}H_9NO_4$: C, 64.51; H, 3.69.
Found: C, 64.30; H, 3.53.

(*b*) *Nitroethane.* The yield of this adduct was 1.5 g. (31%) m.p. 133–134°.

Anal. Calc'd for $C_{14}H_{11}NO_4$: C, 65.41; H, 4.28.
Found: C, 65.62; H, 4.41.

(*c*) *1-Nitropropane.* The yield of adduct from this reaction was 0.8 g. (19%), m.p. 139–140°.

Anal. Calc'd for $C_{15}H_{13}NO_4$: C, 66.45; H, 4.80.
Found: C, 66.32; H, 4.91.

SUMMARY

The three methylcyclohexanones reacted with nitromethane in the presence of piperidine to form the corresponding methyl-1-nitromethyl-1-cyclohexene.

Three alkyl-2-cyclohexen-1-ones reacted with nitromethane in the presence of piperidine by 1,4-addition to the conjugated system.

One carbonyl group of 1,2- and 1,4-cyclohexanedione reacted with nitromethane in the presence of potassium carbonate by 1,2-addition.

One carbonyl group of acenaphthenequinone reacted by 1,2-addition with three nitroparaffins in the presence of solid potassium hydroxide.

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REFERENCES

(1) Fraser and Kon, *J. Chem. Soc.*, 604 (1934).
(2) Nightingale, Erickson, and Knight, *J. Org. Chem.*, **15**, 782 (1950).
(3) Hass and Riley, *Chem. Revs.*, **32**, 384 (1943).
(4) Lambert and Lowe, *J. Chem. Soc.*, 1517 (1947).
(5) Yakubovich, *J. prakt. chem.*, **143**, 37 (1935).
(6) Horning, Denekas, and Field, *J. Org. Chem.*, **9**, 547 (1944).
(7) Vander Harr, Voter, and Banks, *J. Org. Chem.*, **14**, 836 (1949).
(8) Vincent, Thompson, and Smith, *J. Org. Chem.*, **3**, 600 (1938).
(9) *Org. Syntheses*, **24**, 1 (1944).