589. *The Reaction of* 1-*Nitromethylcycloheptene with Selenium Dioxide.*

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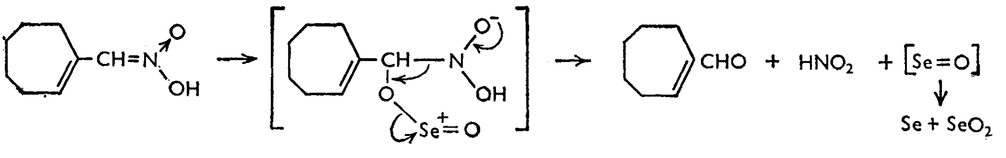
1-Nitromethylcycloheptene and selenium dioxide give 1-formylcycloheptene and cyclohept-1-enecarboxylic acid.

THE only record of the action of selenium dioxide on nitroalkanes is the statement, without experimental details, by Rabjohn and Harjes,[1] that nitromethane in dioxan gives formic acid. We have studied the reaction of 1-nitromethylcycloheptene [2] which might have been expected to introduce a hydroxyl group in the α-position to the double bond. The reaction was carried out in organic solvents in presence of a small quantity of water or in acetic anhydride. However, the reaction in ethanol gave 1-formylcycloheptene (33%) and cyclohept-1-enecarboxylic acid (14·3%); in dioxan the same products were formed (40·5% and 6·4% respectively; total conversion in both cases *ca.* 47%); in acetic anhydride, 16% of the aldehyde was obtained. The acid was probably formed *via* the aldehyde since similar oxidations by selenium dioxide are known; [3] we also effected the oxidation by silver oxide.

The aldehyde and acid have both been prepared before,[4] by less convenient methods. The structures are confirmed by the infrared spectra: The aldehyde has bands at 2710 (CHO[5]), 1678 (αβ-unsaturated C=O), and 1639 sh (C=C [5]) cm.$^{-1}$. The acid gives an ester with bands at 1703 (αβ-unsaturated CO_2R [6]), 1641 (C=O), 1250 and 1199 (C–O stretching of $C{:}C{\cdot}CO_2R$ [6,7]) cm.$^{-1}$. Both aldehyde and ester give C–H stretching bands at 2922 (asymm.) and 2848—2850 (symm.) and 1444—1447 cm.$^{-1}$ (scissors vibration of CH_2, slightly shifted, probably because of the large ring [8]).

In all the oxidations, nitrous fumes are evolved. The reaction may occur as illustrated.



The reaction may have practical interest as the acid has cholagogic properties.[9]

[1] Rabjohn and Harjes, " Organic Reactions," Wiley & Sons, New York, 1949, Vol. V, p. 331.

[2] Eckstein, Sacha, and Urbański, *Bull. Acad. polon. Sci., Cl. III*, 1957, **5**, 213.

[3] Rabjohn, " Organic Reactions," Wiley & Sons, New York, 1949, Vol. V.

[4] Wallach, *Annalen*, 1906, **345**, 152; Braude and Evans, *J.*, 1955, 3334; Spiegel, *Annalen*, 1882, **211**, 119; Willstätter, *Ber.*, 1898, **31**, 2506; Braren and Bachner, *Ber.*, 1900, **33**, 685.

[5] Pinchas, *Analyt. Chem.*, 1957, **29**, 334.

[6] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

[7] Brugel, " Einführung in die Ultrarotspektroskopie," Steinkopff, Darmstadt, 1954.

[8] Jones and Sandorfy, " Chemical Applications of Spectroscopy," Interscience Publ. Inc., New York, 1956, p. 361.

[9] G.P. 1,005,062; *Chem. Zentr.*, 1958, 11,317.

EXPERIMENTAL

Reaction in Dioxan.—Selenium dioxide (0·2 mole, 22·2 g.) in dioxan (175 ml.) and water (7 ml.) was added during 1 hr. to a stirred solution of 1-nitromethylcycloheptene (0·2 mole, 31 g.) in dioxan (60 ml.) on a boiling water bath, and the whole was stirred there for 2—3 hr. Then, after filtration, the dioxan was removed at 60° under reduced pressure and the residue distilled in steam. The first part of the distillate (*ca.* 350 ml.) contained the aldehyde as an oil; later parts (*ca.* 500 ml.) contained crystals of the acid.

The distillate containing the aldehyde was saturated with salt and extracted with ether (4 × 35 ml.), and the extracts were dried (Na_2SO_4) and evaporated. Distillation gave the aldehyde, b. p. 70—95° (10 g., 40·5%), which after redistillation had b. p. 86—92°/10 mm., n_D^{20} 1·4792. Analysis did not show nitrogen in this product but presence of unchanged nitro-compound was disclosed by an infrared band at 1563 cm.$^{-1}$. This product gave a 2,4-dinitrophenylhydrazone, m. p. 210—212° (from acetone) (Braude and Evans [4] give m. p. 210—211°) (Found: N, 18·3. Calc. for $C_{14}H_{16}O_4N_4$: N, 18·4%), and a semicarbazone, m. p. 204—205° (lit.,[4] m. p. 203—204° and 210—211°) (Found: N, 23·1. Calc. for $C_9H_{15}ON_3$: N, 23·2%).

The above aldehyde (28·3 g.) in alcohol (225 ml.) at 13° was treated dropwise with sodium metabisulphite (30·4 g.) in water (225 ml.) (temperature rise to 21°) and stirred at 13° for 5 hr. The precipitate was filtered off and washed with ether. 11·5 g. of it were decomposed with sodium carbonate (7·5 g.) in water (75 ml.). The aldehyde, recovered with ether, had b. p. 80—81°/15 mm., n_D^{20} 1·4922) (3·5 g.), and gave only a very weak infrared nitro-band.

With semicarbazide hydrochloride (22·3 g.) and crystalline sodium acetate (33·5 g.) in water (210 ml.) the crude aldehyde gave, in 4 hr., 75% of semicarbazone, m. p. 198—201°. This was steam-distilled with oxalic acid (25·2 g.) in water (100 ml.). Recovery of the aldehyde from the distillate as above gave 85·5% of material, b. p. 91—92°/24 mm., n_D^{20} 1·4998, which gave no nitro-band in the infrared spectrum.

The acid was recovered from the original steam-distillate by saturation with salt and extraction with ether (3 × 50 ml.), then removed from the ether by aqueous sodium carbonate and precipitated therefrom by acidification. The crude acid (1·8 g., 6·4%; m. p. 48—50°) recrystallised from 1 : 2 aqueous alcohol (1 g. per 15 ml.) and then had m. p. 51—52° (lit.,[4] m. p. 49—51° to 53—54°).

With thionyl chloride cyclohept-1-enecarboxylic acid gave its acid chloride (95·5%), b. p. 120°/30 mm., d_4^{20} 1·1264, n_D^{20} 1·5120, and thence by concentrated aqueous ammonia the amide, m. p. 125—126° (lit.,[10] m. p. 126°) (Found: N, 10·3. Calc. for $C_8H_{13}ON$: N, 10·1%).

Removing water during 24 hr. azeotropically from a boiling mixture of the acid (4·9 g.), ethyl alcohol (7 ml.), benzene (21 ml.), and concentrated sulphuric acid (0·49 g.), evaporation under reduced pressure, and distillation gave the ester, b. p. 118°/27 mm., d_4^{20} 0·9910 (Braren and Bachner [4] give b. p. 106—116°/14 mm.). The same ester was obtained from the acid chloride and ethyl alcohol.

The aldehyde had infrared bands at 3348vw, 3048sh, 2922vs, 2848s, 2710m, 1678vs, 1639vs, 1522vw, 1444s, 1400m, 1380m, 1359w, 1316m, 1272m, 1231s, 1184s, 1141m, 1131w, 1097m, 1075m, 1003w, 967m, 953m, 894m, 859s, 797m, and 731m cm.$^{-1}$.

The ester had infrared bands at 2973sh, 2922vs, 2850s, 1703vs, 1641s, 1547vw, 1447s, 1364m, 1328vw, 1278s, 1250vs, 1213m, 1199vs, 1172sh, 1147s, 1112m, 1094m, 1067s, 1028s, 997w, 969w, 950vw, 903vw, 853m, 784m, and 746s cm.$^{-1}$.

Reaction in Alcohol.—Selenium dioxide (22·2 g.) in anhydrous (35 ml.) and 95% alcohol (110 ml.) was added in 1 hr. to a stirred solution of 1-nitromethylcycloheptene in boiling anhydrous alcohol (60 ml.), and the whole stirred for 7 hr., then cooled, filtered, and evaporated under reduced pressure. Steam-distillation, etc., as before, gave the aldehyde [8·1 g., 32·7%; identified by its derivatives (mixed m. p.s)] and the acid (4·0 g., 14·3%).

Reaction in Acetic Anhydride.—Selenium dioxide (8·3 g.) was added in portions of *ca.* 2 g. to 1-nitromethylcycloheptene in acetic anhydride at 50°, and the whole stirred at 90° for 11 hr. Next morning the solid was filtered off and extracted with ether. The ether extract yielded 2 g. (16%) of aldehyde which was identified as above.

Oxidation of the Aldehyde to the Acid.—1-Formylcycloheptene (37·3 g.) was boiled with a solution of freshly prepared silver oxide in aqueous ammonia for 3 hr. After filtration the

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[10] Bachner and Jacobi, *Ber.*, 1898, **31**, 2004; Bachner, *Ber.*, 1899, **32**, 705.

solution was acidified with 50% sulphuric acid and distilled in steam. Recovery of cyclohept-1-enecarboxylic acid from the distillate by means of ether and crystallisation from aqueous alcohol gave an acid (0·85 g., 20%), m. p. and mixed m. p. 51—52°.

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