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On Preparation and Properties of 1-Cycloöctenylnitromethane

by

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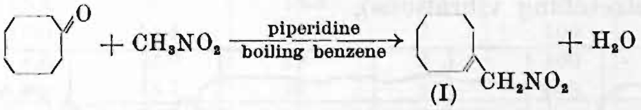
Presented by T. URBAŃSKI on July 23, 1958

When carrying out further experiments on the condensation of cyclic ketones with nitroparaffins in presence of basic catalysts, we found that cycloöctanone (azelaone) also reacted with nitromethane in benzenic solution in conditions similar to those described for the reaction of cycloheptanone and nitromethane [1]. Water was also formed during the reaction of cycloöctanone, but the amount of water was not proportional to the nitroölefine formed, and this was most likely due to the formation of by-products having the structure of enamine. This will be a subject of a special investigation.

The reaction of formation of nitroölefine was slow, the yield was ca. 9.3% calculated on the ketone used. The reaction can be represented by the equation:



(I)

It was possible to raise the yield of (I) up to 13.5% by recyclising foreruns which contain regenerated cycloöctanone.

1-Nitromethylcycloöctene (I) gives an uncertain reaction characterizing primary nitroparaffins. It possesses a scent similar to that of turpentine.

The ultraviolet absorption spectrum of solutions in ethyl alcohol has been determined in a spectrophotometer Unicam SP-500, with quartz optics.

The absorption curve (Fig. 1) shows two shoulders. The shape of the curve is not typical for electronic spectrum of nitroaliphatic compounds.

On the contrary, the infra-red absorption spectrum (Fig. 2) confirmed the suggested structure (I). The capillary film of the liquid substance was examined in a Hilger H-800 spectrophotometer with a 60° prism of sodium chloride, and automatic registration.

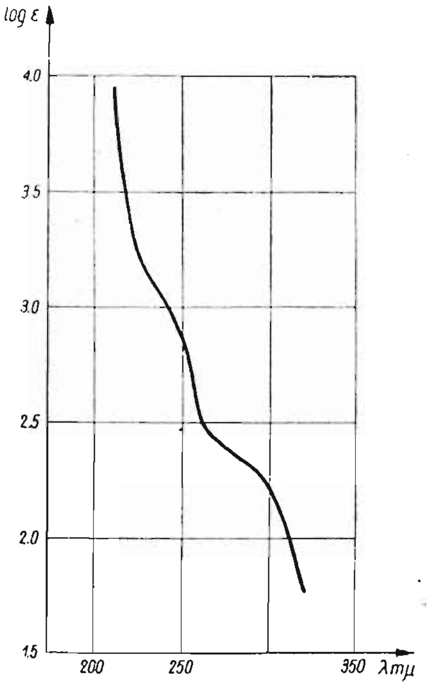


Fig. 1

The characteristic bands have the following frequencies, in cm^{-1}: 2928 (vs), 2863 (s), 1669 (w), 1547 (vs), 1466 (s), 1447 (s), 1397 (s), 1372 (vs), 1306, 1280 (vw), 1266 (vw), 1197, 1151 (vw), 1066 (vw), 1019 (w), 950 (w), 898 (w), 878 (w), 828 (sh), 797 (w), 762 (vw).

(Abbreviations: vs — very strong, s — strong, w — weak, vw — very weak, sh — shoulder).

The band characterizing stretching vibrations C—H is split in two:

a very strong band near to 2938 cm^{-1} which should probably be ascribed to asymmetric vibrations, and a band of medium strength and frequency 2863 cm^{-1} characterizing most likely symmetric vibrations of methylenic group in cycloöctane [2].

The nitroölefinic structure (I) is confirmed by the existence of the band near to 1669 cm^{-1}, typical for the bond C = C in cycloölefines. The nitro group is characterized by two typical bands of 1547 cm^{-1} (asymmetric stretching vibrations) and 1372 cm^{-1} (symmetric stretching vibrations).

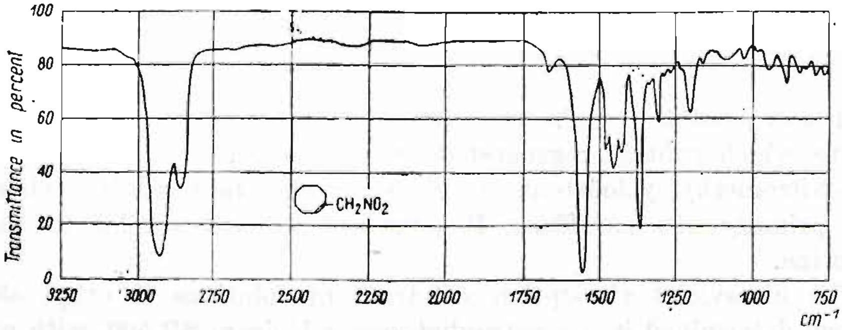


Fig. 2

Experimental

Cycloöctanone (azelaone) was prepared by the improved method already described elsewhere [3].

The product had b. p. 110° under 56 mm. Hg, m. p. 23°, n_D^{20} 1.4695.

Reaction of azelaone with nitromethane. 12.6 g (0.1 mol.) of azelaone, 18.3 g (0.3 mol.) of nitromethane were dissolved in 50 ml. of benzene. After adding 1.5 ml. of piperidine as a catalyst, the solution was refluxed for several hours. The water formed during the reaction was collected in the azeotropic still-head. After 18 hours 0.8 ml. o water were collected. Further boiling does not produce any increase of the quantity of water.

The anhydrous solution was distilled under reduced pressure: 10-15 mm. Hg to collect foreruns and 2 mm. Hg to fractionate the product.

Foreruns contain benzene, nitromethane and piperidine. The fraction *A* (b. p. 65-70° under 2 mm. Hg) was mainly composed of azelaone. The fraction *B* (b. p. 100;106° under 2 mm. Hg) was collected for further purification.

The fraction *A* was completed with fresh azelaone to 20.6 g. and after mixing with 29 g. of nitromethane, 2 ml. of piperidine and 100 ml. of benzene, a new reaction was carried out.

The reaction was repeated a few times. The quantity of reagents and the yields are tabulated (Table I).

TABLE I

Reaction No	Substances used					Product	
	Azelaone		Nitromethane g.	Piperidine ml.	Benzene ml.	fraction *A* g.	fraction *B* g.
	fresh g.	regenerated g.					
1	12.6	—	18.3	1.5	20	8.6	2.8
2	12.0	8.6	29	2	100	12.0	5.0
3	8.6	12.0	29	2	100	13.7	5.0
4	6.9	13.7	29	2	100	13.0	6.0
Total	40.1						18.8

The combined fractions *B* redistilled under reduced pressure and 4.9 g. of pure, colourless product, boiling at 95-98 under 4 mm. Hg were obtained.

Analysis:

$C_9H_{15}O_2N$ requires 8.2% N
found 8.5% N
$n_D^{20} = 1.4959$
$d^{20} = 1.0554$
M_R calculated 46.90
experimental 46.76

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