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PHOTOLYSIS AND PYROLYSIS OF CAMPHOR NITRIMINE

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In the course of our study of the properties of a nitro group bonded to nitrogen we have investigated the photochemical and pyrolytic transformations of camphor nitrimine.

Camphor nitrimine (I) was prepared by the action of sodium nitrite on camphor oxime.[1] The nitrimine was found to be free of oxime by gas chromatography.

Photolysis of a methanolic solution of camphor nitrimine (5.00g in 300 ml) under nitrogen using light of 2537Å in a Rayonet, Srinivasan-Griffin photochemical reactor for 36 hours afforded a brilliant green oil (4.01g). Analysis of this oil by glpc (Dow Corning high vacuum grease on Chromosorb W) indicated the presence of at least eight components. In order of increasing elution time these were identified as compounds II-IX shown in FIG. 1 along with their relative amounts. Compounds II-VII were identified by retention time comparison with the authentic sample and mass spectra. Compounds III-VI were also collected by preparatory gas chromatography and the IR and NMR spectra were compared with authentic samples.[2,3,4,5]

The seventh peak was shown to be VIII by the following spectral data: MS, $M^+ = 181$, mol. wt. calc for $C_{11}H_{19}NO$: 181; IR: 2245 cm^{-1} for CN, 1390 and 1365 cm^{-1} for $C(CH_3)_2$, 1130 and 1070 cm^{-1} for the ether linkages; NMR: 9.32τ (3H, singlet) and 9.07τ (3H, singlet) for $C(CH_3)_2$, 8.93τ (3H, singlet) for $-CH_3$, 8.39τ - 8.05τ(5H, multiplets) for ring protons, 7.71τ (2H, distorted doublet) for $-CH_2CN$ and 6.83τ (3H, singlet) for $-OCH_3$. Confirmation of structure VIII was obtained by comparison of retention time (high vacuum grease and Carbowax on Chromosorb W

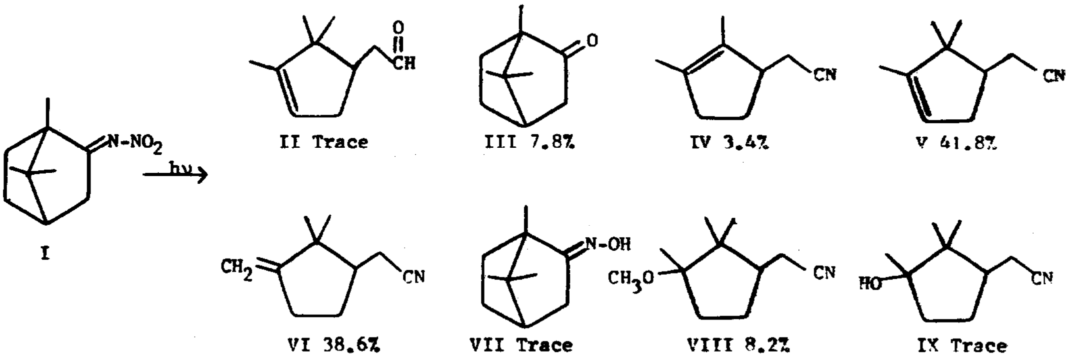


FIG. 1

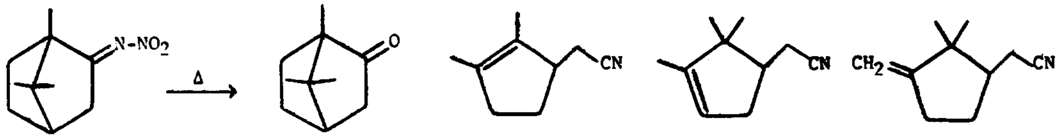
columns) and mass spectra (on line from glpc) with material made by methoxymercuration of V.[6]

The last peak was identified as IX in part by the following spectral data: MS:M^+= 167 (weak), mol.wt. calc for $C_{10}H_{17}NO$: 167. Strong peaks were observed at M^+-17, M^+-18, and M^+-33 representing loss of OH, H_2O, and H_2O and CH_3 respectively. IR: 3500 cm^{-1} (broad) for OH, 2245 cm^{-1} for CN, 1390 and 1365 cm^{-1} for $C(CH_3)_2$ and 1120 cm^{-1} for C-O; NMR: 9.29τ (3H, singlet) and 9.01τ (3H, singlet) for $C(CH_3)_2$, 8.80τ (3H, singlet) for CH_3-C-O, 8.37τ - 8.07τ (5H, 3 distorted peaks of relative areas 2:1:2) for the ring protons, 7.66τ (2H, distorted doublet) for $-CH_2CN$.

The amount of IX present as evidenced by glpc peak area was found to depend on the amount of water in the methanol. When photolysis was carried out in 7:3 MeOH:H_2O by vol., the amount of IX increased to major proportions (36.1%). This behavior with water is consistent with the structure proposed for IX.

Further structural proof of IX was obtained through oxymercuration of V.[7] The sample obtained matched the IR spectrum, retention time and mass spectrum (on line from gas chromatograph) of IX. Reaction of this oxymercuration sample in CH_2Cl_2 with diazomethane in the presence of $AlCl_3$ gave the ether VIII (identified by glpc) as the expected product.[8] Similarly, when methylation was carried out on the material obtained from photolysis in the presence of water, the amount of VIII increased, while the peak due to IX disappeared completely. Furthermore, reaction of V with cold 25% H_2SO_4 yielded an impure oil which contained a product giving a small peak of similar retention time to IX.

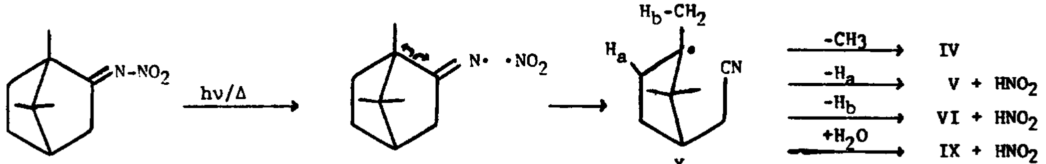
Pyrolysis of the camphor nitrimine was accomplished by heating under nitrogen to 150°C for 10 seconds. After the evolution of NO_2 had ceased, the product was vacuum distilled over as a bright green oil. This green oil gave four peaks upon gas chromatographic separation which were concluded to be the following by comparison of retention times and mass spectra with the authentic samples (high vacuum grease, Carbowax and Apiezon L on Chromosorb W columns). See FIG.2



I III 2.0% IV Trace V 51.6% VI 46.3%

FIG. 2

The products obtained lead us to propose that the initial phase of the reaction occurs through homolytic cleavage of the N-NO_2 bond and from there to the appropriate products. See FIG. 3. The abstraction of an H atom by the NO_2 radical would also produce HNO_2 which breaks

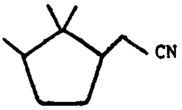


X

FIG. 3

up to form NO, NO_2 and H_2O. These products have previously been identified and measured.[4] Reaction of the radical X with water would probably lead to IX. The aldehyde II is most likely formed from camphor by secondary photolysis.[5] Studies are currently underway to determine the mechanisms of formation of III, IV, VII and VIII.

We carried out the photolysis of camphor oxime, as per the work of Sato and Obase.[2] We also recovered a large quantity of starting oxime and the products III, IV, V, VI and XI.



XI

In addition, we found the ether VIII which had not been previously reported as occurring in the photolysis of camphor oxime. Interestingly no α-campholanonitrile (XI) was observed in the photolysis of the nitrimine although we verified its occurrence in the photolysis of the oxime by comparison with material made by reaction of V with H_2 in ethanol over Adam's catalyst.[9]

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