cation over concentrated sulfuric acid. Paper chromatography showed that the resulting sirup contained "α"-D-isosaccharinic acid and its 1,4-lactone as well as a third component with a R_α[21] value in irrigant A of 0.45. This component was separated from the other by paper chromatography. It was obtained as a clear sirup, quite soluble in methanol and water, but insoluble in ethanol. A portion of the sirup was dissolved in 25 ml. of 0.1 *N* hydrochloric acid solution and refluxed for 1 hr. Paper chromatography of this solution indicated only "α"-D-isosaccharino-1,4-lactone.

The remaining sirup was dried for 12 hr. over phosphorus pentoxide in an Abderhalden drier.

Anal. Calcd. for $C_6H_{13}O_5N$: N, 7.8. Found: N, 7.6.

A portion of the "α"-D-isosaccharinamide sirup was dissolved in 500 ml. of water and 250 ml. of Amberlite IR-120 (H^+) cation exchange resin added. This mixture was stirred for 30 min., the resin removed by filtration and washed with 500 ml. of water. Filtrate and washings were combined and concentrated under reduced pressure (45–50°) to a sirup. Paper chromatography of this sirup indicated mainly "α"-D-isosaccharino-1,4-lactone in addition to a small amount of the amide.

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[21] R_α is the rate of movement relative to "α"-D-isosaccharino-1,4-lactone.

Photolysis of Nitrite Esters in Solution. VII. Photochemistry of *dl*-Bornyl and *dl*-Isobornyl Nitrites

PETER KABASAKALIAN AND EDWARD R. TOWNLEY

Chemical Research and Development Division, Schering Corporation, Bloomfield, New Jersey

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The complete photolysis of either *dl*-bornyl or *dl*-isobornyl nitrite in trichlorotrifluoroethane yielded the following products (determined quantitatively by instrumental methods): *dl*-1,8,8-trimethyl-2-hydroxy-2-azabicyclo[3.2.1]octan-3-one (III) (*ca.* 30%), *dl*-1,6-α-campholenaldehyde (IV) (*ca.* 20%), and *dl*-1,10-α-campholenaldehyde (V) (*ca.* 12%). The photolytically activated *dl*-1-nitroso-α-campholanaldehyde (I) was shown to be the precursor for III.

Robinson, *et al.*,[1] have recently reported the formation of steroidal hydroxamic acids during the photolysis of the following C-17β-nitrite esters: 5α-androstane-3α,17β-diol 3α-acetate 17β-nitrite, testosterone 17β-nitrite, 19-nortestosterone 17β-nitrite, estradiol 3-benzoate 17β-nitrite, and estradiol 3-methyl ether 17β-nitrite. The conditions were not favorable for the Barton reaction. The photolyses of bornyl and isobornyl nitrites were undertaken to determine whether the geometric form of the former would favor hydroxamic acid formation to a greater extent than would the geometric form of the latter compound.

TABLE I

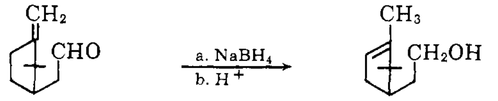
dl-BORNYL AND *dl*-ISOBORNYL NITRITE PHOTOLYSIS[a] PRODUCT COMPOSITION[b]

Products	Yields, % *dl*-Bornyl nitrite	Yields, % *dl*-Isobornyl nitrite
dl-1,8,8-Trimethyl-2-hydroxy-2-azabicyclo[3.2.1]octan-3-one	31	32
dl-1,6-α-Campholenaldehyde	19	20
dl-1,10-α-Campholenaldehyde	12	12
dl-Borneol	1	. . .
dl-Isoborneol	. . .	1
dl-Camphor	<1	<1
dl-1-Nitroso-α-campholanaldehyde	0	0

[a] Photolysis light source λ > 300 mμ. [b] Composition determined by instrumental analysis.

Results

Table I lists the *dl*-bornyl and *dl*-isobornyl nitrite photolysis product composition as determined by quantitative analytical methods when the photolytic radiation consisted of wave lengths greater than 300 mμ from a mercury arc light source. The hydroxamic acid, *dl*-1,8,8-trimethyl-2-hydroxy-2-azabicyclo[3.2.1]octan-3-one, product was characterized by its infrared absorption spectra,[2] color reactions,[3] and comparison with the work of Robinson, *et al.*[1] The *dl*-1,6-α-campholenaldehyde product, containing an *endo* double bond possessing a characteristic infrared absorption band at 12.55 μ[4] was identified by comparison with authentic *dl*-1,6-α-campholenaldehyde prepared by the photolysis of *dl*-camphor.[5] The *dl*-1,10-α-campholenaldehyde product, containing an *exo* double bond possessing a characteristic infrared absorption band at 11.37 μ,[4] was characterized by reaction 1: (a) sodium borohydride



(1)

reduction to *dl*-1,10-α-campholenyl alcohol; and (b) acid isomerization to the stable *dl*-1,6-α-cam-

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(1) C. H. Robinson, O. Gnoj, A. Mitchell, R. Wayne, E. Townley, P. Kabasakalian, E. P. Oliveto, and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 1771 (1961).

(2) D. Hadzi and D. Prevorsek, *Spectrochim. Acta*, **10**, 38 (1957).

(3) U. T. Hill, *Ind. Eng. Chem., Anal. Ed.*, **18**, 317 (1946); U. T. Hill, *ibid.*, **19**, 932 (1947).

(4) M. Kagawa, *Pharm. Bull.* (Tokyo), **4**, 423 (1956).

(5) R. Scrinivasan, *J. Am. Chem. Soc.*, **81**, 2604 (1959).

pholenyl alcohol.[4] *dl*-1,6-α-Campholenyl alcohol and its *p*-nitrobenzoate derivative were compared with authentic material obtained by carrying out the identical reaction sequence on *dl*-1,6-α-campholenaldehyde obtained from the *dl*-camphor photolysis.

Table II lists the *dl*-isobornyl nitrite photolysis product composition using black light radiation ($300\ m\mu < \lambda < 400\ m\mu$) before and after exposure to sunlight to destroy the *dl*-1-nitroso-α-campholanaldehyde product.

TABLE II
dl-ISOBORNYL NITRITE BLACK LIGHT PHOTOLYSIS[a] PRODUCT COMPOSITION[b]

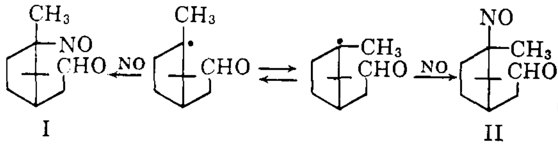
Products	Exposure to sunlight, % Before	After
dl-1,8,8-Trimethyl-2-hydroxy-2-azabicyclo[3.2.1]octan-3-one	15	23
dl-1,6-α-Campholenaldehyde	16	18
dl-1,10-α-Campholenaldehyde	10	11
dl-1-Nitroso-α-campholanaldehyde	25	0
dl-Isoborneol	1	1
dl-Camphor	<1	<1

[a] Photolysis light source: $300\ m\mu < \lambda < 400\ m\mu$. [b] Composition determined by instrumental analysis.

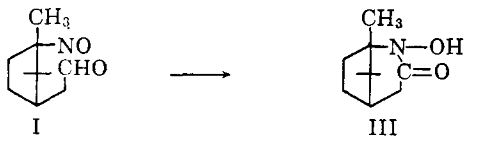
Discussion

The principal product (*ca.* 30%) identified in both photolysis mixtures was a cyclic hydroxamic acid, *dl*-1,8,8-trimethyl-2-hydroxy-2-azabicyclo-[3.2.1]octan-3-one. This result is similar to those reported by Robinson, *et al.*,[1] who proposed the formation of the cyclic hydroxamic acid *via* a tertiary nitroso intermediate.

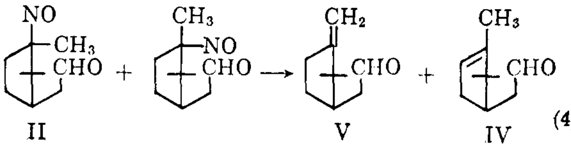
Probably two tertiary nitroso monomers are formed since there is evidence[1] that the cleaved radical racemizes before coupling with nitric oxide as shown in reaction 2. Only one isomer, I, is conformationally favored to yield the hydroxamic acid (maximum theoretical yield 50%). The proposed tertiary nitroso compounds can undergo further reactions to produce either hydroxamic acid, reaction 3 or α-campholenaldehydes, reaction 4. An attempt to produce the tertiary nitroso intermediate by photolyzing *dl*-isobornyl nitrite with black light (the visible portion of the photolysis light source filtered out) and with the exclusion of external visible light was successful.



(2)

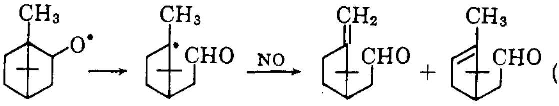


(3)



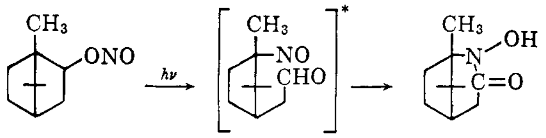
(4)

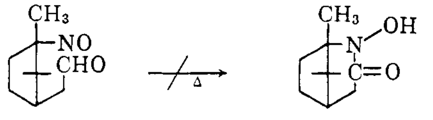
An unknown mixture of isomeric tertiary nitroso compounds, (I and II) *dl*-1-nitroso-α-campholanaldehyde, was produced (*ca.* 25%) with a corresponding decrease (*ca.* 23%) in the other identified products. The hydroxamic acid (III) yield was halved (reduced from 32 to 15%) while the *dl*-1,6-α-campholenaldehyde (IV) and *dl*-1,10-α-campholenaldehyde (V) were only slightly reduced (from 20 and 12% to 16 and 10%, respectively). The *decrease ratio* of hydroxamic acid to total α-campholenaldehydes was *ca.* 3:1. The tertiary nitroso monomer was found to be thermally stable in the reaction medium in the absence of visible light. Although it took almost three weeks at 60° to destroy completely all the tertiary nitroso monomer, there was no increase found in the hydroxamic acid (which was stable under these conditions) content. However, sunlight readily (two hours) caused the disappearance of the blue tertiary nitroso. On exposure to sunlight [or a neon lamp (λ 585–660 $m\mu$) for two days] the hydroxamic acid content increased corresponding to a 30% yield while the α-campholenaldehydes increase corresponded to only a 10% yield. The *increase ratio* of hydroxamic acid to total α-campholenaldehydes was *ca.* 3:1 identical to the *decrease ratio* when black light was used during the photolysis, thus indicating that the predominant source for the α-campholenaldehydes was not reaction 4 but probably reaction 5 a disproportionation reaction with nitric oxide. This reaction is kinetically controlled since an appreciable fraction (*ca.* 0.4) of the thermodynamically unstable *dl*-1,10-α-campholenaldehyde was produced. There was no evidence for the production of the saturated analog.



(5)

The thermal stability of the tertiary nitroso monomer and the fact that the hydroxamic acid is only produced under photolytic conditions indicates that only the activated (high energy) tertiary nitroso compound, I, with the proper conformation is capable of hydroxamic acid production. Black light photolysis, reaction 6, produced the activated compound I which underwent hydroxamic acid formation while the tertiary nitroso, reaction 7, which probably had been deactivated by collision processes survived the photolysis. However, the latter on activation by visible light, reaction 8, was able to produce hydroxamic acid.


(6)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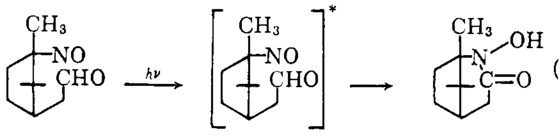
(8)

Experimental

***dl*-Bornyl Nitrite.**—This was prepared according to the general method of Hunter and Marriott[6]: m.p. 33–36°; λ_{max}^{MeOH} 358 mμ (ε 69); λ_{max}^{Nujol} 6.08 μ and 6.11 μ.

Anal. Calcd. for $C_{10}H_{17}NO_2$: N, 7.64. Found: N, 7.79.

***dl*-Isobornyl Nitrite.**—Prepared as above: m.p. 31–33°; λ_{max}^{MeOH} 359 mμ (ε 69); λ_{max}^{Nujol} 6.08 μ and 6.11 μ. The infrared absorption spectra in the fingerprint region (8–14 μ) was different from that of *dl*-bornyl nitrite.

Anal. Calcd. for $C_{10}H_{17}NO_2$: N, 7.64. Found: N, 7.51.

Apparatus, Photolyses Procedure, and Analytical Methods.—These were as described in Part I,[7] Part II,[8] and Part III.[9] The sunlight exposure experiment was carried out by exposing to direct sunlight a 10-ml. aliquot of the black light photolysis solution sealed in a 50-ml. soft glass ampoule until the color of the solution changed from blue to colorless (2 hr.). The hydroxamic acid was analyzed colorimetrically using the method of Hill[3] while the α-campholenaldehydes were quantitatively determined on a Perkin-Elmer Model 154 C Vapor Fractometer unit using an Apiezon "L" column operating at 130°. The tertiary nitroso compound was determined polarographically.[9]

***dl*-1,8,8-Trimethyl-2-hydroxy-2-azabicyclo[3.2.1]octan-3-one.**—A 22.4-g. sample of *dl*-bornyl nitrite was photolyzed in 200 ml. of trichlorotrifluoroethane using a Pyrex light filter. The solution was flash evaporated to an oil (20.5 g.) and triturated with petroleum ether. The hydroxamic acid crystallized immediately; yield 4.2 g. (19%); m.p. 208–212°. An analytical sample was obtained by slurrying with petroleum ether; m.p. 214–217°; λ_{max}^{Nujol} 3.22 μ (OH), 6.12 μ (amide I), 6.62 μ (amide II), 7.11 μ (amide III).[2]

Anal. Calcd. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.44; H, 9.67; N, 7.50.

***dl*-1,6-α-Campholenyl Alcohol.**—The petroleum ether solution from above was passed through a Florisil column (54 cm. long × 2 cm. i.d., containing 100 g. of activated Florisil) to remove the remaining hydroxamic acid. The column was washed with petroleum ether until 1.0 l. of eluent had been collected. This was concentrated yielding 6.95 g. (37%) of an oil; λ_{max}^{Nujol} 3.69 μ (aldehydic C—H), 5.78 μ (C═O), 6.01 μ (C═C), 11.42 μ (R″R′C═CH₂), and 12.48 μ (R″R′C═CHR). Vapor phase chromatography (*via* the infrared absorption spectra of micro samples collected from the Vapor Fractometer) indicated the presence of two components: *dl*-1,6-α-campholenaldehyde, λ_{max}^{Nujol} 3.69 μ (aldehydic C—H), 5.78 μ (C═O), 12.55 μ (R″R′C═CHR), identical to authentic material[5] and *dl*-1,10-α-campholenaldehyde, λ_{max}^{Nujol} 3.69 μ (aldehydic C—H), 5.78 μ (C═O), 6.04 μ (C═C) and 11.37 μ (R″R′C═CH₂). A 4.3-g. sample (0.028 mole) of the α-campholenaldehyde mixture was dissolved in 250 ml. of tetrahydrofuran, to which was added dropwise with stirring 3.5 g. (0.092 mole) of sodium borohydride in 10 ml. of water. The solution was then refluxed for 45 min., cooled, acidified with 50% hydrochloric acid, concentrated to a small volume, and then added to 150 ml. of water. The resulting mixture was ether-extracted yielding 3.6 g. (0.0233 mole, 83%) of oil; λ_{max}^{Nujol} 2.98 μ (O—H), 6.04 μ (C═C), 9.5 μ (C—OH), 11.48 μ (R″R′C═CH₂), and 12.52 μ (R″R′C═CHR). A 2.0-g. sample of the α-campholenyl alcohol mixture was dissolved in 100 ml. of acetone containing 1 ml. of concentrated hydrochloric acid and allowed to stand overnight at 25°. The solution was then concentrated, poured into 100 ml. of water, neutralized, and ether-extracted, yielding 1.9 g. (29% yield from *dl*-bornyl nitrite) of oil; λ_{max}^{Nujol} 2.98 μ (O—H), 9.5 μ (C—OH), and 12.52 μ (R″R′C═CHR). Vapor phase chromatography (Apiezon "L" column at 212°) indicated a single component, *dl*-1,6-α-campholenyl alcohol, identified by comparison with authentic *dl*-1,6-α-campholenaldehyde treated in the same manner. The *p*-nitrobenzoate derivative recrystallized twice from ethanol melted at 75–78°.

Anal. Calcd. for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.50; H, 6.80; N, 4.44.

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[6] L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 285 (1936).

[7] P. Kabasakalian and E. R. Townley, *J. Am. Chem. Soc.*, Part I, **84**, 2711 (1962).

[8] P. Kabasakalian, E. R. Townley, and M. D. Yudis, *ibid.*, Part II, **84**, 2716 (1961).

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