[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Mechanism of the Thermal Decomposition of Alkyl Nitrites in the Liquid Phase: the Pyrolysis of Optically Active 2-Octyl Nitrite

BY NATHAN KORNBLUM AND EUGENE P. OLIVETO[1,2]

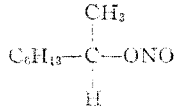
The thermal decomposition of methyl, ethyl, *n*-propyl, isopropyl and *n*-butyl nitrites in the vapor phase at 170–240° has been investigated by Steacie and his co-workers.[3] They concluded that the major over-all reaction is the same in each case, *viz.*

$$2RCH_2ONO \longrightarrow RCHO + RCH_2OH + 2NO \qquad (1)$$

The vapor phase reaction has also been studied by F. O. Rice and Rodowskas,[4] who proposed the mechanism[5]

$$\begin{array}{c} RCH_2ONO \longrightarrow RCH_2O\cdot + NO \\ RCH_2O\cdot + RCH_2ONO \longrightarrow RCH_2OH + R\dot{C}HONO \\ R\dot{C}HONO \longrightarrow RCHO + NO \\ \hline 2RCH_2ONO \longrightarrow RCH_2OH + RCHO + 2NO \end{array}$$

The present investigation represents a test of Rice's hypothesis. According to the proposed mechanism pyrolysis of optically active 2-octyl nitrite

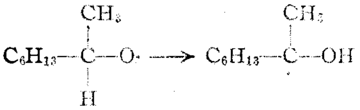


$$C_6H_{13}-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}-ONO$$

should give 2-octanol, 2-octanone and nitric oxide, and the 2-octanol should be optically active.

Upon treating *d*-2-octanol, $[\alpha]^{25}D$ +9.30°, with nitrosyl chloride in pyridine *d*-2-octyl nitrite, $[\alpha]^{25}D$ +6.44°, was obtained. This, when heated at 100° for eight days, underwent complete decomposition and the 2-octanol produced (80% yield) had $[\alpha]^{25}D$ +9.23°. Thus, in complete conformity with Rice's mechanism, no racemization had taken place.

If Rice's mechanism is accepted, then it follows that the secondary alkoxyl radical is optically stable and that a rearrangement such as



$$C_6H_{13}-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}-O\cdot \longrightarrow C_6H_{13}-\underset{\cdot}{\overset{\displaystyle CH_3}{C}}-OH$$

does not take place with facility, if at all, in the liquid phase at 100°. Clearly, more precise information concerning the optical stability of alkoxyl radicals will be of value not only because of its bearing on the mechanism of the thermal decomposition of alkyl nitrites, but also because of its own rather considerable intrinsic interest.

The present study was also concerned with the possibility that the pyrolysis of alkyl nitrites might not follow the same course in the liquid and vapor phases. Since all previous work on the thermal decomposition of alkyl nitrites had been conducted in the gas phase, at temperatures distinctly greater than 100°, it was of interest to establish whether or not the products of the liquid phase decomposition correspond to those previously obtained in the vapor phase.

In addition to *d*-2-octanol, the liquid phase thermal decomposition of *d*-2-octyl nitrite at 100° gave a number of other products. As one would anticipate from equation (1), 2-octanone was the other principal organic product. Just as with *d*-2-octanol, it was also formed in 80% yield so that these two, between them, account for four-fifths of the organic material. Nitric oxide, however, was produced in only 37% of the amount to be expected from equation (1). This led to a careful study of the other components of the reaction mixture whereupon eight additional compounds were found (Table I).

TABLE I

PRODUCTS FROM THE THERMAL DECOMPOSITION OF 1.02 MOLES OF *d*-2-OCTYL NITRITE

Product	Amount, millimoles	Nitrogen, gram-atoms
d-2-Octanol	380	
2-Octanone	380	
Nitric oxide	380	0.38
Nitrogen	280	.56
Nitrous oxide	24	.05
Acetic acid	22.6	
Heptanoic acid	12.6	
2-Octyl acetate	3	
2-Octyl heptanoate	3	
Capronitrile	20	.02
Tarry residue	(11.2 g.)	.02
Carbon dioxide[a]		
	Total	1.03

[a] This required a separate experiment since ordinarily the system was swept out with carbon dioxide.

Nitric oxide has recently been found to react with 2-octanone at 100°, in the dark, with the production of acetic acid, heptanoic acid and capronitrile, the nitric oxide being reduced to

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[1] E. I. du Pont de Nemours and Co. Fellow, 1946–1947.

[2] Present address: Schering Corporation, Bloomfield, New Jersey.

[3] Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, pp. 141–143.

[4] F. O. Rice and Rodowskas, THIS JOURNAL, **57**, 350 (1935).

[5] Rice and Rodowskas (ref. 4) studied the ethyl nitrite decomposition at 425°. They concluded that at pressures greater than about one third of an atmosphere, reaction (1) preponderates. However, at pressures of approximately 1 mm. they found that methyl radicals are formed in abundance and suggested that the predominant reaction is

$$\begin{array}{c} CH_3CH_2ONO \longrightarrow CH_3CH_2-O\cdot + NO \\ CH_3CH_2-O\cdot \longrightarrow HCHO + CH_3\cdot \\ CH_3\cdot + CH_3CH_2ONO \longrightarrow CH_4 + CH_3\dot{C}H-ONO \\ CH_3\dot{C}HONO \longrightarrow CH_3CHO + NO \\ \hline 2CH_3CH_2ONO \longrightarrow HCHO + CH_4 + CH_3CHO + 2NO \end{array}$$

nitrogen and nitrous oxide.[6] It appears probable, therefore, that the various minor products obtained upon heating 2-octyl nitrite at 100° arise from a set of secondary reactions, namely, cleavage of 2-octanone by nitric oxide and esterification of 2-octanol by the acids formed. The large amount of elementary nitrogen produced is especially noteworthy.

Experimental[7,8]

***d*-2-Octanol.**—Racemic 2-octanol was resolved according to Ingersoll.[9] The *d*-2-octanol obtained had n^{20}_{D} 1.4262; lit. value,[10] n^{20}_{D} 1.4264, $[\alpha]^{25}_{\mathrm{D}} + 9.30°$ ($c = 5$, ethanol); lit. value,[9] $[\alpha]^{17}_{\mathrm{D}} + 9.8°$.

***d*-2-Octyl Nitrite.**—*d*-2-Octyl nitrite was prepared in 80% yield by the action of nitrosyl chloride on *d*-2-octanol; n^{20}_{D} 1.4080; $[\alpha]^{25}_{\mathrm{D}} + 6.44$ ($c = 5$, ethanol); lit. value,[11] n^{20}_{D} 1.4082.

Thermal Decomposition of *d*-2-Octyl Nitrite.—One hundred and sixty-two grams (1.02 moles) of *d*-2-octyl nitrite was decomposed by heating at 100 ± 2° for eight days in a three-neck flask fitted with a condenser, thermometer and a gas inlet tube. Prior to the reaction the system was swept out overnight with a stream of carbon dioxide which had previously passed through 96% sulfuric acid, Drierite and cotton. During the reaction a slow stream of carbon dioxide was maintained. The exit gases, upon leaving the condenser, were passed through two ice-traps, two wash bottles containing mixed acid (9 parts 96% sulfuric acid: 1 part 65% nitric acid) and finally collected over 50% aqueous potassium hydroxide. To eliminate photochemical effects, the reaction flask and condenser were painted black, and the reaction was carried out in a dark-room.[12] At the end of eight days there was no nitrite left, as evidenced by a negative Griess-Ilosvay test.[13] The liquid in the reaction flask now weighed 124 g. and was dark-brown in color. There was less than 0.1 ml. of liquid in the ice-traps. The organic liquid (124 g.) was extracted with three 50-ml. portions of water, giving a water extract (fractions A_1, A_2, A_3) and an organic residue (fraction B).

Acetic Acid.—Fraction A_1 required 14.9 meq. of sodium hydroxide for neutralization; fraction A_2 required 7.0 meq., and fraction A_3 0.7 meq.

Fraction A_1 (which did not decolorize alkaline permanganate) was concentrated under reduced pressure at room temperature to *ca.* 25 ml. (fraction A_4). When the first 50-ml. portion of the distillate was rectified through an 18″ concentric tube column rated at 65 plates, no liquid boiling lower than 100° was obtained. (The column easily and cleanly separated a prepared solution of 3% acetonitrile in water into its components.) Thus, little or no acetonitrile was present.

A portion of fraction A_4 was converted to the S-benzyl thiuronium salt in 50% yield; m.p. 138–139°. This did not depress the m.p. of authentic S-benzyl thiuronium acetate[6]; m.p. 139–140°. *Anal.* Calcd. for $C_{10}H_{14}N_2O_2S$: N, 12.4. Found: N, 12.2. Another portion of fraction A_4 was converted to the *p*-phenylphenacyl ester in 65% yield. This melted at 107–108° and did not depress the m.p. of authentic *p*-phenylphenacyl ester of acetic acid; m. p. 108–109°. *Anal.* Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.6. Found: C, 75.8; H, 5.4.

Heptanoic Acid.—Fraction B was extracted with three 35-ml. portions of 30% sodium carbonate solution, giving an aqueous alkaline extract (fraction C) and an organic residue (fraction D). Fraction C was acidified with 85% phosphoric acid and steam distilled. The distillate, which required 12.6 meq. of sodium hydroxide for neutralization, was then concentrated under reduced pressure at room temperature to a volume of *ca.* 15 ml. A portion was converted to the S-benzyl thiuronium salt in 70% yield; m.p. 147–148°; it did not depress the m.p. of an authentic sample[6] of S-benzyl thiuronium heptanoate, m.p. 148–149°. *Anal.* Calcd. for $C_{15}H_{24}N_2O_2S$: N, 9.4. Found: N, 9.6.

A *p*-phenylphenacyl ester was also prepared in 80% yield, m.p. 60–61°; this did not depress the m.p. of an authentic sample of the *p*-phenylphenacyl ester of heptanoic acid, m.p. 61–62°. *Anal.* Calcd. for $C_{21}H_{24}O_3$: C, 77.8; H, 7.5. Found: C, 77.7; H, 7.5.

Fraction D.—Extraction of fraction D with 0.1 *N* alkali did not remove any more acids. About 500 ml. of water was added and the mixture was distilled under reduced pressure at 30–35°. The non-distillable residue was extracted with petroleum ether, dried over Drierite, and the solvent was removed by ordinary distillation; there was left 11.2 g. of a black, viscous liquid. *Anal.* Found: C, 71.0; H, 12.0; N, 2.9.

The organic distillate (fraction D_1) was mechanically separated from the water layer and treated with Drierite. The dry, yellow liquid weighed 106 g., had n^{20}_{D} 1.4193, and analyzed 45% 2-octanone[14] and 44% 2-octanol.[15]

One hundred grams of the yellow liquid (n^{20}_{D} 1.4193) was rectified under reduced pressure. Twenty-two fractions were obtained and these, with the exception of fraction 3 (3.1 g.), were further studied.

Identification of Capronitrile.—Fractions 1 and 2, b.p. 63–68° at 27 mm. pressure, n^{20}_{D} 1.4100 to 1.4113, were combined (total 3.1 g.). Only these two fractions contained nitrogen. An unsuccessful attempt was made to isolate the nitrogen-containing component by rectification through a 65-plate column. A 0.5-ml. portion of the distillate, now about 20% richer in the nitrogen-containing component, was hydrolyzed to the amide.[16] The amide (50 mg.) had m.p. 98–99° (lit. m.p. 101°)[17] and did not depress the m.p. of authentic caproamide, m.p. 99–100°. *Anal.* Calcd. for $C_6H_{13}NO$: C, 62.6; H, 11.3; N, 12.1. Found: C, 62.4, 62.5; H, 11.3, 11.5; N, 12.1.

Another 0.5-ml. portion of the distillate was converted to the anilide[18] (150 mg.), m.p. 94–95° (lit. m.p. 96°),[17] which did not depress the m.p. of authentic caproanilide, m.p. 94–95°. *Anal.* Calcd. for $C_{12}H_{17}NO$: N, 7.4. Found: N, 7.5, 7.6.

Isolation of 2-Octanone.—Fractions 4–10; b.p. 69–70° (27 mm.); n^{20}_{D} 1.4148 to 1.4150; were combined (total, 39.6 g.) and an 8.4-g. sample was rectified through the 65 plate column. There was obtained 7.5 g. of analytically pure 2-octanone, b.p. 75–76° (20 mm.), n^{20}_{D} 1.4159; lit. value[19] n^{20}_{D} 1.41518. *Anal.* Calcd. for $C_8H_{16}O$: C, 74.9; H, 12.6. Found: C, 74.9; H, 12.5.

Isolation of 2-Octyl Acetate.—Fractions 11–16, b.p. 70° (27 mm.) to 68° (15 mm.); n^{20}_{D} 1.4150 to 1.4235; gave a positive hydroxamic acid test for esters[20] and were

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[6] Oliveto, Ph.D. Thesis, Purdue University, June, 1948.

[7] Analyses by Miss L. Roth and Mr. H. Galbraith of this department.

[8] All melting points uncorrected.

[9] Ingersoll, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 400.

[10] Kornblum, Lichtin, Patton and Iffland, THIS JOURNAL, **69**, 307 (1947).

[11] Kornblum and Oliveto, *ibid.*, **69**, **465** (1947).

[12] The photochemical decomposition of alkyl nitrites is well established; *cf.* ref. 2 p. 143; Coe and Doumani, THIS JOURNAL, **70**, 1516 (1948); Horswell and Silverman, *Ind. Eng. Chem., Anal. Ed.*, **13**, 555 (1941).

[13] Bose, *Analyst*, **56**, 504 (1931).

[14] The procedure of Iddles [*Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939)] was adapted to 2-octanone (*cf.* ref. 6). The accuracy is 3–5%. The 2,4-dinitrophenylhydrazone produced had m. p. 66–67° (lit. m. p[6]. 66–67°) and did not depress the m. p. of authentic 2-octanone-2,4-dinitrophenylhydrazone. *Anal.* Calcd. for $C_{14}H_{21}N_4O_4$: N, 18.2. Found: N, 18.4.

[15] Determined by the acetic anhydride method (Shriner, "Quantitative Analysis of Organic Compounds," Edward Bros., Ann Arbor, Mich., 1940, p. 39). An accuracy of 5% was obtained.

[16] McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 146.

[17] McElvain, *ibid.*, p. 186.

[18] McElvain, *ibid.*, p. 184.

[19] Ceuterick, *Bull. soc. chim. Belg.*, **45**, 545 (1936).

[20] Davidson, *J. Chem. Ed.*, **17**, 81 (1940).

combined (total = 3.9 g.). Upon rectification through the 65-plate column there was obtained 0.6 g. of a colorless liquid, b.p. 81° (18 mm.), n^{20}D 1.4180. *Anal.* Calcd. for $C_{10}H_{20}O_2$: C, 69.8; H, 11.7; sapon. equiv., 172. Found: C, 69.9; H, 11.9; sapon. equiv., 166. An S-benzylthiuronium salt was prepared from the neutral solution; m.p. 138–139° (40% yield). It did not depress the m.p. of an authentic sample of S-benzyl thiuronium acetate, m.p. 139–140°.

Isolation of *d*-2-Octanol.—Fractions 17–22, b.p. 68° (15 mm.), were combined (total = 40.1 g.); n^{26}D 1.4249, lit. value,[10] n^{20}D 1.4264; $[\alpha]^{25}$D + 9.23° (c = 5, ethanol). A 5-g. portion, esterified with phthalic anhydride in the presence of pyridine,[10] gave a 95% yield of *d*-2-octyl hydrogen phthalate, m.p. 71–73°. This, after one recrystallization from petroleum ether (b.p. 60–70°), melted at 73–74° (lit. m.p.[9] 75°) and did not depress the m.p. of authentic *d*-2-octyl hydrogen phthalate, m.p. 74–75°. The purified ester had $[\alpha]^{25}$D + 47.5° (c = 5, ethanol). (The *d*-2-octyl hydrogen phthalate obtained during the resolution of 2-octanol had $[\alpha]^{25}$D + 47.7°). *Anal.* Calcd. for $C_{16}H_{22}O_4$: C, 69.0; H, 8.0. Found: C, 69.1; H, 8.2. The ester was hydrolyzed[9] to *d*-2-octanol; n^{20}D 1.4262 (lit.[10] 1.4264), $[\alpha]^{25}$D + 9.27° (c = 5, ethanol). The *d*-2-octanol used to prepare the *d*-2-octyl nitrite had $[\alpha]^{25}$D + 9.30°.

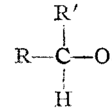
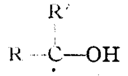
Isolation of 2-Octyl Heptanoate.—A yellow 4-g. residue remained from the rectification of 100 g. of yellow liquid (n^{20}D 1.4193). This had n^{20}D 1.4285 and gave a test for esters.[20] It was rectified through the 65-plate column. There was obtained 0.7 g. of a colorless liquid; b.p. 112° at 10 mm., n^{20}D 1.4320. *Anal.* Calcd. for $C_{15}H_{30}O_2$: C, 74.3; H, 12.4; sapon. equiv., 242. Found: C, 74.4; H, 12.2; sapon. equiv., 240. An S-benzylthiuronium salt was prepared from the neutral solution; m.p. 147–148° (65% yield). It did not depress the m.p. of authentic S-benzylthiuronium heptanoate, m.p. 148–149°.

Nitric Oxide.—The two wash-bottles containing 96% sulfuric acid + 65% nitric acid had absorbed 11.4 g. of nitric oxide (titration with standard permanganate).[21]

Nitrous Oxide and Nitrogen.[22]—The gases collected over potassium hydroxide totaled 6750 ml. (S.T.P.). Upon analysis in a conventional Orsat apparatus, 8% of the gas was found to be nitrous oxide (determined by slow combustion with hydrogen) and the remaining 92% was inert (nitrogen). Carbon dioxide, carbon monoxide, olefins, saturated hydrocarbons, oxygen, nitric oxide and nitrogen dioxide were all absent.

Demonstration of the Formation of Carbon Dioxide in the Thermal Decomposition of *dl*-2-Octyl Nitrite.—Ten grams of *dl*-2-octyl nitrite was decomposed at 100 ± 2° over a period of eight days in a slow stream of dry oxygen-free nitrogen. The exit gases were passed through 96% sulfuric acid, glass wool and finally through two U-tubes containing Ascarite; the Ascarite tubes gained 177 mg. (4.0 meq. of carbon dioxide). The Ascarite which reacted did not give a test for cyanide.[23] The liquid remaining in the flask weighed 7.3 g., and contained 0.9 meq. of acetic acid and 0.7 meq. of heptanoic acid.

Summary

The thermal decomposition of *d*-2-octyl nitrite in the liquid phase at 100° gives ***optically pure*** *d*-2-octanol in excellent yield. In addition to confirming F. O. Rice's mechanism for the pyrolysis of alkyl nitrites, this indicates that alkoxyl radicals of the type  $R-\overset{\overset{R'}{|}}{\underset{\underset{H}{|}}{C}}-O\cdot$ do not rearrange to  $R-\overset{\overset{R'}{|}}{\underset{\cdot}{C}}-OH$ in the liquid phase at 100°.

The other major organic product is 2-octanone. Small amounts of acetic acid, heptanoic acid, 2-octyl acetate, 2-octyl heptanoate and capronitrile are also produced. These probably arise from the cleavage of 2-octanone by nitric oxide followed by esterification of 2-octanol by the acids formed.

The gaseous products of the reaction are nitrogen, nitric oxide, nitrous oxide and carbon dioxide.

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[21] Milligan, *J. Phys. Chem.*, **28**, 544 (1924).

[22] We are indebted to Professor P. J. Elving of this department for his kind assistance in connection with the gas analyses.

[23] Lander and Walden, *Analyst*, **36**, 266 (1911).

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

The Optical Crystallographic Properties of Some Sulfonamides and their Derivatives

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The optical crystallographic properties of organic compounds are useful for purposes of identification. This is particularly true of compounds containing aromatic or heterocyclic ring systems where examples of strong dispersion of several types and strong double refraction are frequently observed. Thus the optical crystallographic properties of the sulfonamides and their derivatives should prove useful in their characterization.

Optical crystallographic studies of some of the therapeutically important sulfonamides have received the attention of several investigators. Except for sulfanilamide these data are more or less incomplete. The optical properties of sulfanilamide and of a series of Schiff bases have been determined by White.[2] Grove and Keenan[3] reported the optical properties of two forms of sulfathiazole. Prien and Frondel[4] reported the application of the optical properties of sulfanilamide, sulfathiazole and sulfapyridine, and their

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[1] (a) From a portion of the dissertation submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy at the University of Colorado, August, 1944. (b) Present address: University of New Mexico, Albuquerque, New Mexico.

[2] White, unpublished thesis, University of Colorado, 1940.

[3] Grove and Keenan, THIS JOURNAL, **63**, 97 (1941).

[4] Prien and Frondel, *J. Urol.*, **46**, 784 (1941).