[CONTRIBUTION FROM THE ROHM & HAAS COMPANY]

tert-Carbinamines. V. The Addition of Isothiocyanic Acid to Camphene

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The addition of isothiocyanic acid to camphene gave 2-isothiocyanatoisocamphane.

Isothiocyanates are obtained by the addition of nascent isothiocyanic acid to certain olefins.[1] When 73 per cent aqueous sulfuric acid was slowly added to a suspension of sodium thiocyanate in molten camphene, a crystalline isothiocyanate (I) of the expected composition and with the characteristic infrared absorption was obtained. By analogy with the usual behavior of camphene in acid-catalyzed addition reactions,[2] I was assumed to be the hitherto unreported isobornyl isothiocyanate.

Confirmation of the supposed structure by alternative syntheses was sought. The addition of hydrogen cyanide to camphene, following Ritter's directions,[3] gave a formamide (II) which was converted to an amine (III) by basic hydrolysis. The isothiocyanate I was obtained from this amine by a standard procedure.

Isobornylamine (IV) was prepared by catalytic hydrogenation of camphoroxime[4,5] and was converted to isobornyl isothiocyanate (V), which differed from I in mixture melting point and infrared absorption.

Other differences between derivatives of the amine (III) and isobornylamine were also noted. The formamide (II) bore no resemblance to isobornylformamide[6] in melting point, solubility characteristics, or infrared spectrum. The N-benzoyl[3,7] and N-phenylcarbamyl[7] derivatives of the two amines were also different.

The skeletal identity indicated by the conversion of III into the isothiocyanate I was confirmed by lithium aluminum hydride reduction of both I and II to the same N-methyl derivative (VI) of III, characterized as the N-phenylcarbamyl derivative. The boiling point of VI was not the same as the value reported for N-methylisobornylamine.[8]

Stein and co-workers[9] have recently obtained II, III, and VI and have shown that they are 2-aminoisocamphane (III)[5] and derivatives. Further support for the *tert*-carbinamine structure of III was gained by the failure in attempted aminolysis of methyl formate with III. The resistance of the most active esters to aminolysis by *tert*-carbinamines is known.[10]

From the combined evidence of the present work and the above-cited communication,[9] it is concluded that I must be 2-isothiocyanatoisocamphane. Its formation furnishes a second new example of addition to camphene resulting in a nonrearranged product.

EXPERIMENTAL[11]

2-Isothiocyanatoisocamphane (I). Sodium thiocyanate (41 g., 0.5 mole) suspended in molten camphene (68 g., 0.5 mole) was stirred at 55 to 60° while 73% sulfuric acid (42 g.) was slowly added during two hours. The mixture was stirred at 55° for five hours, cooled, and diluted with benzene (200 ml.) and water (100 ml.). The benzene layer was removed and washed with aqueous sodium carbonate solution and water. Distillation gave 56 g. (57%) of an oil, b.p. 107–108°/2 mm. which solidified. Recrystallization from ethanol gave 42 g. of a white solid, m.p. 80–82°; after several similar recrystallizations, m.p. 84–86°. In 5% carbon tetrachloride solution, the isothiocyanate band was centered about 2090 cm.$^{-1}$, with a second weak peak at 1980 cm.$^{-1}$. In 1% solution, the main band was split[12] into two almost equal peaks at 2105 and 2140 cm.$^{-1}$.

Anal. Calc'd for $C_{11}H_{17}NS$: N, 7.2; S, 16.4. Found: N, 7.0; S, 16.1.

2-Formamidoisocamphane[9] (II) was prepared according to Ritter's directions,[3] except that hydrogen cyanide (27 g., 1 mole) was added as a liquid to a solution of camphene (136 g., 1 mole) in concentrated sulfuric acid (102 g.) and acetic acid (500 ml.) at 30–34°. After standing overnight, the dark mixture was slowly poured into 2 l. of water. The oil which separated did not solidify. After washing with water, it was dissolved in ethanol, reprecipitated with water, and chilled until solid. The product was sucked free of oils and washed with pentane to give a tan solid which was decolorized with Nuchar in hot ethanol. Cooling gave two

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[1] L. S. Luskin, G. E. Gantert, and W E Craig, *J. Am. Chem. Soc.*, **78**, 4965 (1956).

[2] R. H. Eastman and C. R. Noller, in H. Gilman, *Organic Chemistry*, John Wiley & Sons, Inc., New York, N. Y., Vol. IV, p. 654.

[3] J. J. Ritter and P. P. Minieri, *J. Am. Chem. Soc.*, **70**, 4045 (1948); J. J. Ritter, U. S. Patent 2,573,673.

[4] K. Alder and G. Stein, *Ann.*, **525**, 237 (1936).

[5] W. Hückel and F. Nerdel, *Ann.*, **528**, 57 (1937).

[6] M. O. Forster, *J. Chem. Soc.*, **73**, 386 (1898).

[7] K. Stephan and T. Hammerich, *J. prak. Chem.*, (2), **129**, 285 (1931).

[8] R. Wegler and W. Frank, *Ber.*, 69, 2071 (1936).

[9] G. A. Stein, M. Sletzinger, H. Arnold, D. Reinhold, W. Gaines, and K. Pfister, *J. Am. Chem. Soc.*, **78**, 1514 (1956). Our work was essentially complete before the appearance of this communication.

[10] E. M. Arnett, J. G. Miller, and A. R. Day, *J. Am. Chem. Soc.*, **72**, 5635 (1950).

[11] We wish to thank T. P. Callan, Jr. and J. W. Nash who supervised the analyses and Helen Miklas for infrared measurements.

[12] D. Williams, *J. Chem. Phys.*, **8**, 513 (1940) found similar splitting with phenyl isothiocyanate in carbon tetrachloride solution.

crops which were washed with pentane; the white solid, weighed 42.5 g. (27%), m.p. 166–172°; after recrystallization from acetonitrile, m.p. 172–175°.

Anal. Calc'd for $C_{11}H_{19}NO$: C, 72.9; H, 10.6; N, 7.7. Found: C, 72.8; H, 10.5; N, 7.8.

2-Aminoisocamphane (III).[5,9] A solution of II (46 g., 0.5 mole), ethanol (125 ml.), and 10% aqueous sodium hydroxide (124 g.) was heated under reflux for 48 hours. The semisolid which remained after evaporation of alcohol was decanted and solidified by addition to ice-water; the white solid, after drying, weighed 33.7 g. (88%), m.p. 168–169°. Infrared analysis showed slight contamination with starting material.

Anal. Calc'd for $C_{10}H_{19}N$: N, 9.15. Found: N, 8.85.

The *N-benzoyl* derivative[13] was decolorized with Nuchar in ethanol and precipitated with water, m.p. 118–120°. A mixture of *d*- and *l*-benzamidoisocamphane was reported to have m.p. 125°.[5]

Anal. Calc'd for $C_{17}H_{23}NO$: C, 79.3; H, 9.0; N, 5.4. Found: C, 79.1; H, 9.0; N, 5.4.

The *N-phenylcarbamyl* derivative was prepared in ether and recrystallized twice from methanol, m.p. 238–240°.

Anal. Calc'd for $C_{17}H_{24}N_2O$: N, 10.3. Found: N, 10.2.

The compound was converted to the *isothiocyanate* (I) by a conventional procedure,[14] m.p. and mixture m.p. with the material obtained above, 84–86°.

Anal. Calc'd for $C_{11}H_{17}NS$: N, 7.2. Found: N, 7.1.

Isobornylamine (IV) was obtained by the catalytic hydrogenation of *dl*-camphoroxime in acetic acid with platinum oxide.[4] The crude product was converted to its N-phenylcarbamyl derivative[7] as above, m.p. 252–255° (dec.): mixture m.p. with the N-phenylcarbamyl derivative of III, 214–216°.

Anal. Calc'd for $C_{17}H_{24}N_2O$: N, 10.3. Found: N, 10.1.

Isobornylformamide. A mixture of IV (7.7 g., 0.05 mole), formic acid (50 g.), and toluene was heated under reflux for 6 hours.[6] Evaporation of the acid layer gave an oil which was solidified in water. After two recrystallizations from aqueous alcohol, there was obtained 2.2 g., m.p. 69–71°.

Anal. Calc'd for $C_{11}H_{19}NO$: N, 7.7. Found: N, 7.7.

Formamidoisocamphane (II) was obtained similarly in low yield from III; after recrystallization from acetonitrile, m.p. 165–168°.

Anal. Calc'd for $C_{11}H_{19}NO$: N, 7.7. Found: N, 7.5.

An attempt to prepare II by heating III with excess methyl formate under reflux for 7 days gave only starting materials.

Isobornyl isothiocyanate (V). A solution of IV (2.0 g., 0.013 mole) in chloroform (25 ml.) was added to a stirred solution of thiophosgene (1.5 g., 0.013 mole) in chloroform, followed by 25 ml. of *N* sodium hydroxide solution at room temperature.[15] After two hours of stirring, the mixture was separated and the aqueous layer was extracted with chloroform. The combined extracts were evaporated to remove solvent and the residue was sublimed (72–74°/0.2 mm.) to give a white solid (1.8 g., 72%); after two recrystallizations from 95% ethanol, m.p. 85–86°, mixture m.p. with I, 75–76°. Infrared absorption in carbon tetrachloride solution showed isothiocyanate peaks at 2100 and 2130 cm.$^{-1}$; the spectrum in other regions differed markedly from that of I.

Anal. Calc'd for $C_{11}H_{17}NS$: N, 7.2; S, 16.4. Found: N, 7.1; S, 16.5.

N-Methylaminoisocamphane (VI).[9,16] A solution of I (26 g., 0.13 mole) in anhydrous ether (50 ml.) was added slowly to a suspension of lithium aluminum hydride (11.25 g.) in ether (125 ml.) which was heated under reflux. After stirring overnight, the mixture was treated with 150 ml. of isopropyl alcohol, followed by 60 ml. of 50% aqueous isopropyl alcohol, and filtered. The solid was washed with isoisopropyl alcohol and ether. The filtrate was distilled, giving 15 g. (70%) of colorless oil, b.p. 97–98°/15 mm. A portion (6.7 g.) was dissolved in 0.5 *N* hydrochloric acid (75 ml.) and extracted with benzene to remove unreduced isothiocyanate. The amine was liberated by the addition of excess sodium hydroxide and extracted with benzene. Distillation gave 5.5 g. of the pure amine, b.p. 78°/7 mm., n_D^{25} 1.4870.

Anal. Calc'd for $C_{11}H_{21}N$: N, 8.4; Neut. equiv., 167. Found: N, 8.4; Neut. equiv., 168.

Similar reduction of II gave VI in 80% yield, requiring no purification, b.p. 97–98°/15 mm., n_D^{25} 1.4869, d_{25}^{25} 0.9341. The infrared spectra of both preparations were identical.

Anal. Found: N, 8.2; Neut. equiv., 168.

Both preparations gave the same *N-phenylcarbamyl* derivative, m.p. and mixture m.p. 149–150°.

Anal. Calc'd for $C_{18}H_{26}N_2O$: N, 9.8. Found: N, 9.7.

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[16] W. G. Young, R. A. Clement, and Chin-Hua Shih, *J. Am. Chem. Soc.*, **77**, 3061 (1955).