

To a suspension of 5.7 g. (0.15 mole) of lithium aluminum hydride in 100 ml. of absolute ether there was added, over a period of 30 min., the dried ether extract from above. The mixture was stirred at room temperature for 1 hr. and then refluxed for 1 hr. more. The excess lithium aluminum hydride was destroyed with moist ether followed by water and the solid material was filtered off. The organic layer was washed twice with a saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Hydrogen chloride gas was passed into this ether solution and the mixture was then allowed to evaporate. After washing the resulting residue with hexane, 6.57 g. (34%<sup>12</sup>) of white, crystalline neomenthylamine hydrochloride was obtained. Recrystallization from hexane gave a sample, m.p. 192.5–195.0°,  $[\alpha]^{25}_D +18.2^\circ$  in chloroform ( $c = 2.17$ ) (lit.,<sup>13</sup> m.p. 189°  $[\alpha] +21.5^\circ$ ).

On acetylation of the neomenthylamine hydrochloride with acetic anhydride in the presence of sodium hydroxide solution there was obtained (+)-*N*-acetylneomenthylamine, m.p. 172–173.5° (softening at 169°),  $[\alpha]^{17}_D +52.9^\circ$  in chloroform ( $c = 1.20$ ) (lit.,<sup>13</sup> m.p. 169–170°,  $[\alpha]_D +53.0^\circ$ ).

By treating neomenthylamine hydrochloride with benzoyl chloride in a mixture of pyridine and benzene, there was obtained (+)-*N*-benzoylneomenthylamine, m.p. 124.5–125° (softening at 122°),  $[\alpha]^{25}_D +23.6^\circ$  (chloroform,  $c = 2.79$ ) (lit.,<sup>13</sup> m.p. 121.5°,  $[\alpha]_D +22.7^\circ$ ).

**Acknowledgment.**—This research was supported in part by a grant from the National Science Foundation.

(12) The optimum conditions for the best yield of neomenthylazide and therefore the amine have not been established.

(13) J. L. Simonsen, "The Terpenes," Vol. I, 2nd ed., Cambridge University Press, Cambridge, England, 1953, p. 245.

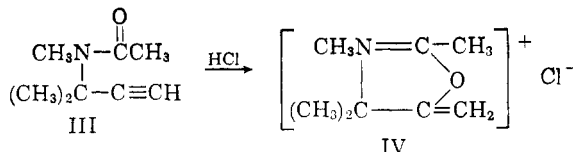
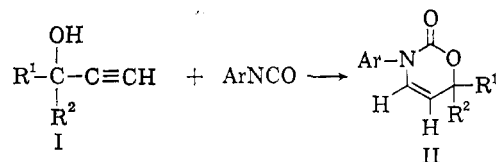
## Reactions of Acetylenes. I. *t*-Ethyne Alcohol with Isocyanates

NELSON R. EASTON, DONALD R. CASSADY,  
AND ROBERT D. DILLARD

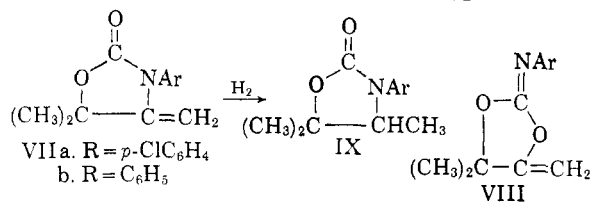
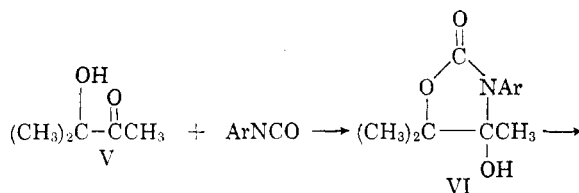
*Lilly Research Laboratories, Indianapolis 6, Indiana*

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The recent publication<sup>1</sup> claiming the formation of 1,3-oxazine-2-ones (II) from the reaction of *t*-ethynyl alcohols (I) with an aryl isocyanate did not appear logical in view of previous findings from these laboratories.<sup>2</sup> This earlier work showed that *N*-acyl derivatives of *t*-ethynylamines (III) gave five-membered rings (IV) on cyclization with mineral acid. An examination of the n.m.r. spectrum of compound II ( $R^1 = R^2 = \text{CH}_3$ ,  $\text{Ar} = p\text{-ClC}_6\text{H}_4$ ) showed a series of four peaks centered at 5.93  $\tau$ . The coupling constants were small (about 3 c.p.s.), and the system was much closer to that expected for non-equivalent 1,1-hydrogens rather than either *cis* or *trans* 1,2-hydrogens. The availability of the keto alcohol



made possible an unequivocal alternative synthesis which proved the ring size. Treatment of V with *p*-chlorophenyl isocyanate and subsequent dehydration of the resulting carbinol (VI) gave a compound identical to that prepared from 3-methyl-1-butyn-3-ol ( $R^1 = R^2 = \text{CH}_3$ ) and *p*-chlorophenyl isocyanate. Since this procedure has been used for the synthesis of oxazoles,<sup>3</sup> the identity of the



two materials established that the correct structure is VIIa and not II. The synthesis of oxazoles by the above procedure<sup>3</sup> would also appear to eliminate the possibility of an oxygen ring closure and thus rule out the other possible structure VIII.

Further proof of the exocyclic double bond, and therefore a five-membered ring, was obtained by hydrogenation of VII to give IX ( $\text{Ar} = \text{C}_6\text{H}_5$ ). The n.m.r. spectrum of IX showed the doublet for the C-methyl split by the proton centered at 8.87  $\tau$  and a quartet centered at 5.91  $\tau$  for the hydrogen at the 4-position. Of interest also is the fact that the two methyl groups at the five position were chemically non-equivalent and showed their peaks at 8.52  $\tau$  and 8.62  $\tau$ .

In the reaction of ethynyl alcohols with phenyl isocyanate, the open chain urethane was isolated; this could be readily converted to the oxazolindione by treatment with sodium ethoxide in ethanol.

### Experimental

All melting points are uncorrected and were obtained in an open capillary tube.

**3-*p*-Chlorophenyl-4-methylene-5-ethyl-5-methyloxazolindione-2-one.**—This was prepared from *p*-chlorophenyl iso-

(1) S. L. Shapiro, V. Bandurco, and L. Freedman, *J. Org. Chem.*, **26**, 3710 (1961).

(2) N. E. Easton, R. Dillard, M. Livezey, D. E. Morrison, and G. F. Hennion, Am. Chem. Soc. Meeting, New York, 1960, Abstracts 44-O.

cyanate and 3-methyl-1-pentyne-3-ol according to ref. 1. Heating larger quantities of these reactants gave an uncontrollable exothermic reaction.

**3-*p*-Chlorophenyl-4-methylene-5,5-dimethyloxazolidine-2-one (from 3-Methyl-1-butyne-3-ol).**—A mixture of 15 g. (0.1 mole) of *p*-chlorophenyl isocyanate, 10 g. (0.12 mole) of 3-methyl-1-butyne-3-ol, and 0.1 g. of sodium acetate was warmed on a steam bath. After warming for about 0.5 hr., a vigorous reaction occurred. After heating an additional 4 hr. on the steam bath, chloroform was added; the mixture was filtered, and the chloroform was distilled at reduced pressure. After recrystallization from methanol, a 65% yield of product, m.p. 98–99°, was obtained.

*Anal.* Calcd. for  $C_{12}H_{12}ClNO_2$ : C, 60.63; H, 5.10; N, 5.89. Found: C, 60.65; H, 5.12; N, 5.84.

**3-Phenyl-4-methylene-5,5-dimethyloxazolidine-2-one (from 3-Methyl-1-butyne-3-ol).**—A mixture of 30 g. (0.36 mole) of 3-methyl-1-butyne-3-ol, 30 g. (0.28 mole) of phenyl isocyanate, and 1 g. of sodium acetate was heated on a steam bath for 4 hr. Ether was added to the cooled mixture, and the insoluble salt was removed by filtration. The solvent was removed by vacuum distillation. After recrystallization from a mixture of ether–petroleum ether (b.p. 30–60°) the 1,1-dimethylpropargyl-*N*-phenylcarbamate melted at 94–95°.

*Anal.* Calcd. for  $C_{12}H_{13}NO_2$ : C, 70.91; H, 6.45. Found: C, 70.95; H, 6.50.

The infrared curve showed a band at 3.03  $\mu$  for the acetylenic hydrogen.

An alcoholic solution of the 1,1-dimethylpropargyl-*N*-phenylcarbamate from the above reaction was added slowly to a solution of 2 g. of sodium in ethanol. After the ensuing exothermic reaction had subsided, water was added to the solution, and the resulting mixture was extracted with ether. After drying over magnesium sulfate, the ether solution was concentrated at reduced pressure. Recrystallization of the resulting solid from ethanol gave a product that melted at 94–95°. An over-all yield of 38 g. (68%) was obtained.

*Anal.* Calcd. for  $C_{12}H_{13}NO_2$ : C, 70.91; H, 6.45; N, 6.89. Found: C, 70.63; H, 6.76; N, 6.94.

**3-Aryl-4-methylene-5,5-dimethyloxazolidine-2-one (from 3-Hydroxy-3-methyl-2-butanone).**—One-tenth mole of aryl isocyanate was added slowly to 10 g. (0.10 mole) of 3-hydroxy-3-methyl-2-butanone with swirling. The mixture became warm and was heated on the steam bath for 4 hr. The infrared spectrum of the crude product showed this material to be, at least in part, the substituted 4-hydroxyoxazolidinone (VI). The material was then refluxed in toluene containing 0.5 g. of *p*-toluenesulfonic acid, and the water was separated with a Dean-Stark trap. After cooling, the mixture was poured into water; the organic layer was separated, dried over magnesium sulfate, and the solvent was distilled under reduced pressure. The residue was crystallized from methanol. These products were obtained in 80–90% yield and were identical in all respects to those prepared from the acetylenic alcohols.

**3-Phenyl-4,5,5-trimethyloxazolidine-2-one.**—3-Phenyl-4-methylene-5,5-dimethyloxazolidine-2-one (15 g.) was hydrogenated at 50 p.s.i. in the presence of 5 g. of 5% palladium-on-carbon, using 250 ml. of ethanol as the solvent and warmed by a heat lamp. The product (13 g., 86% yield) was crystallized from methanol and melted at 98–99°.

*Anal.* Calcd. for  $C_{12}H_{15}NO_2$ : C, 70.22; H, 7.37; N, 6.82. Found: C, 70.54; H, 7.57; N, 7.09.

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### An *N*-Methylpyrrolidone–Diacetylene Complex. Its Use in the Isolation of Diacetylene

NORMAN SHACHAT

*Research Laboratories, Rohm & Haas Company, Philadelphia, Pennsylvania*

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During an investigation of certain reactions of diacetylene (1,3-butadiyne) in which *N*-methylpyrrolidone was employed as the solvent, it was observed that the hydrocarbon and the solvent formed a colorless crystalline 1:1 molecular complex which precipitated from the solution. The complex appeared to be quite stable while kept under a solution of diacetylene in *N*-methylpyrrolidone; however, a pure sample of the solid could not be isolated by filtration, presumably owing to the high vapor pressure of diacetylene in the complex and the low vapor pressure of *N*-methylpyrrolidone. The best samples, obtained by filtration under slight positive nitrogen pressure, still contained some excess *N*-methylpyrrolidone. Analyses of these samples for acetylenic hydrogen by the method of Barnes and Molinini<sup>1</sup> showed a molar ratio of *N*-methylpyrrolidone: diacetylene of  $1.2 \pm 0.1:1$ . Efforts to prepare a similar solid complex with other solvents, namely *N*-vinylpyrrolidone, *N*-ethylpyrrolidone, pyrrolidone, butyrolactone, and *N,N*-dimethylformamide, were unsuccessful.

The *N*-methylpyrrolidone–diacetylene complex provides a convenient tool for the isolation and purification of diacetylene.

A sample of the complex which contained some excess *N*-methylpyrrolidone began to crystallize at 26°, and, as the first few crystals appeared in the mixture, the temperature rose sharply to 27.5°. At 15.5°, the material was almost completely solid. Pure diacetylene melts at –36°, pure *N*-methylpyrrolidone at –24°. When the complex was treated with ether, benzene, ethanol, or water, diacetylene gas was evolved and a homogeneous solution resulted. An infrared spectrum of a satu-

(3) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Co., New York, N. Y., 1947, p. 390.

(1) L. Barnes, Jr., and L. J. Molinini, *Anal. Chem.*, **27**, 1025 (1955).