

### *The Isolation of Terephthaldinitrile N-Oxide*

By Yoshio IWAKURA, Masayasu AKIYAMA and Kuniharu NAGAKUBO

(Received February 24, 1964)

We wish to report the isolation and characterization of terephthaldinitrile *N*-oxide (I) as a stable compound. Although the chemistry of nitrile *N*-oxides has extensively been studied by several groups of workers in recent years,<sup>1-3)</sup> few nitrile *N*-oxides<sup>4-6)</sup> have been isolated in a pure state because of the ease of their dimerization to furoxans.<sup>3,6,7)</sup>

Terephthaldihydroxamic chloride (II), the starting material in this work, has been used by several previous investigators, but no dinitrile *N*-oxide has been isolated.<sup>7-9)</sup>

To a solution of 0.233 g. of II<sup>8)</sup> (m. p. 185°C) in 20 ml. of methanol, an equivalent amount of triethylamine in 20 ml. of methanol was added at room temperature. I was soon precipitated out of the mixture as colorless needles. It was filtered and washed thoroughly with methanol (a 70% yield). When the sample was heated gradually, it showed a definite m. p. at 241~243°C (decomp.). On the other hand, when it was put in a bath heated at 150°C, it decomposed instantly.

Found: C, 59.79; H, 2.66; N, 17.77. Calcd.

1) a) R. Huisgen, *Proc. Chem. Soc.*, **1961**, 357; b) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); c) R. Huisgen, *ibid.*, **75**, 742 (1963).

2) a) N. Barbulescu and P. Grünanger, *Gazz. chim. ital.*, **92**, 138 (1962); b) N. Barbulescu and A. Quilico, *Gazz. chim. ital.*, **91**, 326 (1961), and many previous papers.

3) C. Grundmann, *Angew. Chem.*, **75**, 450 (1963).

4) H. Wieland, *Ber.*, **40**, 1667 (1907).

5) S. Califano, R. Scarpati and G. Speroni, *Atti accad. nazl. Lincei Rend., Classe sci. fis. mat. e nat.*, **23**, 263 (1958); *Chem. Abstr.*, **52**, 12557 (1958).

6) S. Califano, R. Moccia, R. Scarpati and G. Speroni, *J. Chem. Phys.*, **26**, 1777 (1957).

7) R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, **25**, 546 (1960).

8) M. S. Chang and A. J. Matuszko, *ibid.*, **28**, 2260 (1963).

9) A. Ricca, *Gazz. chim. ital.*, **91**, 83 (1961).

for  $C_8H_4N_2O_2$ : C, 60.00; H, 2.52; N, 17.50.

Infrared spectra were obtained on Nujol mulls and a KBr disc: 841(m), 1025(w), 1100(s), 1284(w), 1350(s), 1405(w) and 2330(s)  $cm^{-1}$ . Absorptions at 1350 and 2330  $cm^{-1}$  have been reported to be characteristic of aryl nitrile *N*-oxides.<sup>7)</sup> No bands corresponding to furans<sup>10)</sup> were detected. I is soluble or slightly soluble in dioxane, acetonitrile, chloroform, ethylene dichloride, *o*-dichlorobenzene and *m*-cresol, but insoluble in benzene, diethyl ether, ligroin and carbon tetrachloride.

By the addition reaction of 50 mg. of I with methyl methacrylate at room temperature, 40 mg. of 1,4-bis(5'-methyl-5'-methoxycarbonyl-3'- $\Delta^{2'}$ -isoxazolinyl)benzene<sup>11)</sup> was separated as a crystalline compound from the reaction mixture; m. p. 172~173°C (from methanol).

10) N. E. Boyer, G. M. Czerniak, H. S. Gutowsky and H. R. Snyder, *J. Am. Chem. Soc.*, **77**, 4238 (1955).

11) A. Quilico, G. S. D'Alcontres and P. Grünanger, *Gazz. chim. ital.*, **80**, 479 (1950); *Chem. Abstr.*, **45**, 3836 (1951). In this report, methyl 3-phenyl-5-methyl-2-isoxazoline-5-carboxylate is described.

Found: C, 60.16; H, 5.48; N, 8.03. Calcd. for  $C_{18}H_{20}N_2O_6$ : C, 59.99; H, 5.59; N, 7.77.

$\nu_{C=O}$ , 1728(s)  $cm^{-1}$  (Nujol).

By treating I with allyl alcohol in tetrahydrofuran, 1,4-bis(5'-hydroxymethyl-3'- $\Delta^{2'}$ -isoxazolinyl)benzene<sup>12)</sup> was obtained; m. p. 214~216°C(decomp.) (from ethanol).

Found<sup>13)</sup>: C, 61.16; H, 5.98; N, 10.33. Calcd. for  $C_{14}H_{16}N_2O_4$ : C, 60.86; H, 5.84; N, 10.14.

Infrared absorptions: 3150~3400  $cm^{-1}$  region and 1046, 1055  $cm^{-1}$  doublet (primary alcohol).

Further studies are in progress on addition reactions of I with various mono- and difunctional unsaturated compounds.

*Research Laboratory of Resources Utilization  
Tokyo Institute of Technology  
Meguro-ku, Tokyo*

12) G. S. D'Alcontres and P. Grünanger, *Gazz. chim. ital.*, **80**, 741 (1950); *Chem. Abstr.*, **46**, 971 (1952). Here 3-phenyl-5-hydroxymethyl-2-isoxazoline is described.

13) The authors are indebted for the microanalyses to the staff of the Analytical section of the Department of Organic Chemistry, Tokyo Institute of Technology.