Synthesis and Properties of *NN'*-Dimethylcarbodi-imide Pure Monomer

By G. RAPI* and G. SBRANA

(*Istituto di Chimica Organica dell'Università di Firenze, via G. Capponi 9, Firenze, Italy*)

THE chemistry of the carbodi-imides, R–N=C=N–R^1, an interesting class of organic compounds, was recently reviewed by Kurzer and his co-workers.[1]

The first member of the series of *NN'*-disubstituted carbodi-imides, namely MeN=C=NMe (I) has never been obtained until now, although indirect evidence for its formation in the reaction of *NN'*-dimethylthiourea (II) with yellow mercuric oxide was found by Lecher and his co-workers.[2] The failure to prepare (I) was ascribed by these and other authors[3] to the fact that (I) polymerizes very fast and therefore cannot be isolated.

Whilst studying the vibrational spectra of these compounds, we succeeded, to our surprise, in the preparation of pure *NN'*-dimethylcarbodi-imide, and found that, when properly purified, it can be stored in a freezer for a long time without any significant polymerization.

The desulphurization of freshly prepared *NN'*-dimethylthiourea with yellow mercuric oxide, used by Lecher and his co-workers without success, was actually found to be the most convenient method for the preparation of (I). A modification was found to be critical for the success of the operation; the synthesis was made at low temperature (−10°) in a proper solvent, with good yields, the rate of polymerization being strongly reduced.

It was also found that the choice of the solvent was important, not only to ensure a good rate of reaction but also for the applicability of an efficient method of purification. Several solvents, including ether, n-heptane, carbon tetrachloride, carbon disulphide, and methylene chloride, were used but only the last one gave a good yield and allowed the purification of the desired product.

Compound (II) [m.p. 62—63° (from $CHCl_3$)[4]] was prepared from methyl isothiocyanate and methylamine in alcohol.[5] The preparation of *NN'*-dimethylcarbodi-imide proceeds under the following conditions: 0·2 mole of (II) and 10 g. of anhydrous Na_2SO_4 were added to CH_2Cl_2 (130 ml.) cooled at −10° and vigorously stirred under dry nitrogen, HgO (0·2 mole) previously heated for 2 hr. at 55—60° was then added gradually. The reaction was followed by the i.r. spectra, the criterion being the decrease in intensity of the NH deformation band of (II), at 1560 $cm.^{-1}$ and the increasing of the N=C=N stretching band of (I) at 2147 $cm.^{-1}$. After 4 hr. the reaction was complete. The mixture was cooled at −50° and centrifuged (5000 rev./min.). The supernatant was distilled (1 mm. Hg) with a flow of dry nitrogen, the distillation flask in an ice bath and the collecting flask being maintained at −80°. Under these conditions, the compound (I) is collected in the solvent. At this stage of purification, the *NN'*-dimethylcarbodi-imide is quite stable and the solution can be maintained unchanged for several hours at room temperature. The solution of (I) was then concentrated (50% w/w) by distillation of the solvent at 40—41°/760 mm. Hg. Finally, (I) was separated as pure monomer by a gas chromatograph Autoprep 705 (column 20 ft. × $\frac{3}{8}$ in. packed with SE-30 30%, at 60°). The compound was collected in traps kept at liquid nitrogen temperature.

Compound (I) is a colourless liquid, b.p. 76—77°/761 mm. (capillary method), immiscible in water, completely miscible with the usual organic solvents. The molecular weight was found to be in good agreement for the monomer structure (found 71·12 by the cryoscopic method in benzene;

calc. 70·09; Found C, 50·92; H, 8·96; N, 40·20. Calc. for $C_3H_6N_2$: C, 51·41; H, 8·63; N, 39·97%.

The pure monomer is a stable compound. Two i.r. spectra of a pure liquid sample run within 30 min. (beam temperature 50°) did not show any difference in their pattern. Compound (I) was maintained unaltered at $-10°$ for a week.

The u.v. spectrum in n-heptane has a shoulder at about 210 mμ log ε 3·0. The i.r. spectrum shows intense peaks at 2930, 2882, 2140, 1460, 1400, 1130, 977, 815, and 615 $cm.^{-1}$.

We are indebted to Drs. L. Mazza and N. Gelsomini for analysis and gas chromatographic purification. This research was supported by the Italian National Research Council.

(*Received, November* 13*th*, 1967; *Com.* 1226.)

---

[1] F. Kurzer and K. Douraghi-Zadeh, *Chem. Rev.*, 1967, **67**, 107; see also H. G. Khorana, *Chem. Rev.*, 1953, **53**, 145; H. G. Khorana, "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest," John Wiley, New York, 1961.

[2] H. Lecher, F. Graf, C. Henck, H. Köberle, F. Güadinger, and F. Heydweiller, *Annalen*, 1925, **445**, 35.

[3] P. A. S. Smith, "The Chemistry of Open-chain Organic Nitrogen Compounds," W. A. Benjamin, New York, vol. 1, p. 251–259.

[4] K. W. F. Kohlraush and J. Wagner, *Z. phys. Chem.*, 1939, **45**, *B*, 229.

[5] R. Andreasch, *Monatsh.*, 1881, **2**, 276.