

## ***N*-Cyclohexyldiphenylketenimine from Cyclohexyl Isocyanide and Diphenyldiazomethane**

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*Summary* Cyclohexyl isocyanide (**1**) reacts with diphenyldiazomethane (**2**) to produce *N*-cyclohexyldiphenylketenimine (**3**) in a new photo-reaction which may be attributed to an increased electrophilicity at the isocyano-carbon.

THE discovery of an intramolecular insertion of isocyano-carbon into a benzene ring<sup>1</sup> initiated a search for other reactions of this group in an excited state functioning as an electrophilic carbene.

Compound (**3**) is produced (50%) by irradiating† at 2537 Å for 75 hr. [time required to ensure disappearance of (**2**)] an equimolar mixture of diphenyldiazomethane and

cyclohexyl isocyanide in cyclohexane. Absorption<sup>2</sup> at 4.98 μm confirmed the presence of (**3**) in the reaction mixture. After the solvent had been removed, chromatographic separation of the residue from a column of silica gel gave unreacted cyclohexyl isocyanide (5%) on elution with benzene-hexane (1:4), followed by an unidentified deep purple oil eluted by benzene-hexane (2:3) and by benzene. Next, the azine (23%) of benzophenone was eluted by benzene and then *N*-cyclohexyldiphenylacetamide (**4**) (50%) by ether-benzene (1:9). In a separate experiment, hydrolysis of (**3**) on silica gel to produce (**4**) in quantitative yield was established. After being recrystallized from CCl<sub>4</sub>, the amide (**4**) was obtained as a colourless solid, m.p.

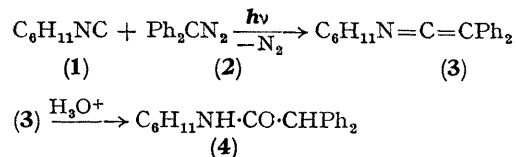
† Irradiation was carried out in a Rayonet RPR 100 photochemical chamber reactor (Southern New England Ultraviolet Co.) equipped with 16 low-pressure mercury 2537 Å lamps.

and mixed m.p. 151.5—152°. Its i.r. and n.m.r. spectra were identical with those obtained from an authentic sample.‡

After standing for a week without irradiation, a mixture of (1) and (2) in cyclohexane does not produce (3) in a detectable amount; however, the concentration of (2) diminishes.<sup>3</sup> Apparently, ketenimine formation proceeds by an electrophilic attack by isocyano-carbon upon the electron-rich carbon of either (2) (preferred) or diphenyl-carbene.

A comparable yield of (3), isolated as the amide (4), was obtained when a mixture of (2) in a six-fold molar excess of (1) was irradiated at 2537Å for 48 hr. The unidentified

purple oil was also formed. In another experiment, irradiation of (1) in cyclohexene brought about no detectable interaction between the two which were recovered.<sup>4</sup>



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‡ An authentic sample was prepared from cyclohexylamine and diphenylacetyl chloride. The amide (4) was transformed into an imidyl chloride by treatment with phosphorus pentachloride. Elimination of hydrogen chloride from the latter by triethylamine gave the ketenimine (1), a colourless solid, m.p. 49.5—50°, i.r. (CHCl<sub>3</sub>) 4.98 μm (>C=C=N<sup>-</sup>). Elemental analyses were satisfactory.

<sup>1</sup> J. H. Boyer and J. de Jong, *J. Amer. Chem. Soc.*, 1969, **91**, 5929.

<sup>2</sup> C. L. Stevens and J. C. French, *J. Amer. Chem. Soc.*, 1954, **76**, 4398, reports absorption at 4.98 μm for *N*-methyldiphenylketenimine.

<sup>3</sup> The azine of benzophenone slowly forms from diphenyldiazomethane on storage neat or in solution. W. E. Parham and W. R. Hasek, *J. Amer. Chem. Soc.*, 1954, **76**, 935.

<sup>4</sup> T. R. Oakes, H. G. David, and F. J. Nagel, *J. Amer. Chem. Soc.*, 1969, **91**, 4761; and E. Winterfeldt, *Angew. Chem. Internat. Edn.*, 1967, **6**, 434, describe 2:1 adducts obtained in dark reactions between certain acetylenes and isocyanides. A Halleux, *ibid.*, 1964, **3**, 752, describes a 1:1:1 adduct obtained in a dark reaction between an isocyanide, dichlorocarbene and ethanol. Attempts to detect a 1:1 adduct between an isocyanide and an acetylene or between an isocyanide and dichlorocarbene were unsuccessful. The reactions may be examples of one-step three-centre mechanisms in analogy to the dark addition of immonium ions and anions to isonitriles. I. Ugi, *ibid.*, 1962, **1**, 8.