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[1] 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 2537Å for 75 hr. [time required to ensure disappearance of (**2**)] an equimolar mixture of diphenyldiazomethane and cyclohexyl isocyanide in cyclohexane. Absorption[2] 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_4, the amide (**4**) was obtained as a colourless solid, m.p.

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† 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.[3] Apparently, ketenimine formation proceeds by an electrophilic attack by isocyano-carbon upon the electron-rich carbon of either (**2**) (preferred) or diphenylcarbene.

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.[4]

$$\underset{(\mathbf{1})}{C_6H_{11}NC} + \underset{(\mathbf{2})}{Ph_2CN_2} \xrightarrow[-N_2]{h\nu} \underset{(\mathbf{3})}{C_6H_{11}N{=}C{=}CPh_2}$$

$$(\mathbf{3}) \xrightarrow{H_3O^+} \underset{(\mathbf{4})}{C_6H_{11}NH{\cdot}CO{\cdot}CHPh_2}$$

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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. ($CHCl_3$) 4·98 μm ($>C{=}C{=}N^-$). Elemental analyses were satisfactory.

[1] J. H. Boyer and J. de Jong, *J. Amer. Chem. Soc.*, 1969, **91**, 5929.

[2] C. L. Stevens and J. C. French, *J. Amer. Chem. Soc.*, 1954, **76**, 4398, reports absorption at 4·98 μm for *N*-methyldiphenylketenimine.

[3] 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.

[4] 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.