Photoextrusion of Isocyanides from Monoimines of Tetramethylcyclobutane-1,3-dione

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Summary Photolysis of the monoanil (**2a**), the *N*-cyclohexylimine (**2b**) and the *N*-n-propylimine (**2c**) of tetramethylcyclobutane-1,3-dione (**1**) in furan gave the corresponding isocyanides (**4a,b,c**) and tetramethylcyclopropanone, isolated as its adduct (**5**) with furan when using (**2a,b**).

Photoextrusion of an isocyanide (**4**) from a monoimine (**2**) of tetramethylcyclobutane-1,3-dione (**1**) is a new reaction of interest in the photochemistry of small and medium ring alicyclic ketones.[1] One previous report claimed the anil (**2a**) to be inert to irradiation in furan[2] and another described both decarbonylation and ring expansion into an imine of 2-methoxy-4-oxo-3,3,5,5-tetramethyltetrahydrofuran upon irradiating both (**2a**) and the *N*-cyclohexylimine (**2b**) in methanol.[3] The imines (**2a,b**) were prepared as previously reported from the diketone (**1**).[2,3] The *N*-n-propylimine (**2c**),† b.p. 84—86° (5 mm), was

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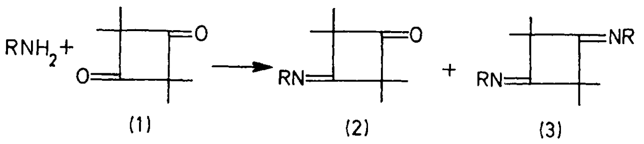
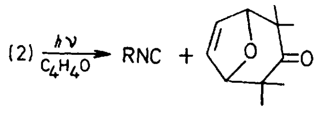
† Satisfactory elemental analyses were obtained.

prepared in 50% yield by refluxing (**1**) in benzene with a molar equivalent of n-propylamine in the presence of *p*-toluenesulphonic acid.





$$\mathrm{RNC} \xrightarrow{\mathrm{H_3\overset{+}{O}}} \mathrm{RNHCHO}$$

(a); R = Ph , (b); R = cyclohexyl , (c); R = Pr^n

A solution of 2·2g (10 mmol) of the anil (**2a**) in 500 ml of degassed furan was irradiated at 254 nm[‡] for 40 h and the solution gradually darkened and became opaque. Gas chromatographic analysis of the crude product mixture showed phenyl isocyanide (**4a**).[§] Standard chromatographic procedure isolated 80 mg (5·2%)[¶] of the adduct (**5**) from furan and tetramethylcyclopropanone, and 121 mg (25%) of formanilide. In a separate experiment authentic isocyanide (**4a**) was hydrated by water provided by alumina into formanilide.

From similar treatment, the *N*-cyclohexylimine (**2b**) gave cyclohexyl isocyanide (**4b**) (32%), i.r. absorption (isocyano-group) at 2146 cm^{-1} (hydration into *N*-cyclohexylformamide by alumina not detected) and a trace of the adduct (**5**); the n-propylimine (**2c**) afforded *N*-n-propyl isocyanide (**4c**), identified in the product mixture by i.r. absorption at 2145 cm^{-1} (isocyano-group) and isolated as *N*-n-propylformamide (25%) after hydration by silica gel during chromatography, (a similar hydration of other alkyl and aryl isocyanides by silica has been established). When furan was replaced by cyclohexane, the imines (**2**) were recovered nearly quantitatively after comparable irradiation. If it can be assumed that dissociation into an isocyanide and tetramethylcyclopropanone occurred in cyclohexane then recombination gave back starting material whereas in furan a competitive addition gave the adduct (**5**). The photochemistry of combinations of cyclopropanones and isocyanides is under investigation.

We thank N.S.F. for a grant.

(*Received*, 14*th January* 1974; *Com.* 034.)

[‡] R. P. R. Rayonet Unit with 16 low pressure lamps.

[§] Except for (**2c**) all compounds were previously known and were identified by direct comparison with authentic material.

[¶] All yields are based on recovered imine (**2**).

[1] D. R. Morton and N. J. Turro, *J. Amer. Chem. Soc.*, 1973, **95**, 3947; J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, 1970, **21**, 499.
[2] R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Chem. Comm.*, 1964, 144.
[3] H. U. Hostettler, *Helv. Chim. Acta*, 1966, **49**, 2417.