Photochemical Rearrangement of *NN*-Dimethylphenylethynylamine into α-Phenylisobutyronitrile

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Summary Irradiation at 254 nm isomerized *NN*-dimethylphenylethynylamine[1] (**1**) in cyclohexane into α-phenylisobutyronitrile (**3**) by a new molecular rearrangement.

A solution of 1·0 g (7 mmol) of (**1**) in 250 ml of degassed anhydrous cyclohexane was irradiated in a Rayonet Reactor at 254 nm for 24 h. Monitoring by i.r. detected the appearance of a new band at 2020 cm^{-1} (C:C:N)[2] which slightly increased as irradiation was continued an additional 96 h. Irradiation was stopped after an amorphous, apparently opaque, brown deposit covered the walls of the tube. Removal of cyclohexane left 0·927 g of a brown liquid: i.r. (CCl_4) 2220 (vs doublet, $C\vdots C$ and $C\vdots N$) and 2020 cm^{-1} (s, C:C:N); n.m.r. ($CDCl_3$) δ 1·69 [s, $PhC(CN)(CH_3)_2$], 1·98 [s, $PhC(CH_3):C:NCH_3$], 2·80 [s, $PhC\vdots CN(CH_3)_2$], and 3·28 [s, $PhC(CH_3):C:NCH_3$]. Of three volatile components detected by g.c. (5% poly-*m*-phenyl ether, 6 ft × 0·25 in, 120°) two were identified by comparison with authentic material as *NN*-dimethylphenylacetamide,[3] in trace amount, and α-phenylisobutyronitrile (**3**), 7·08 mg (2·43%).[4] Unchanged (**1**) apparently polymerized during g.c. and was estimated by n.m.r. to be 0·639 g (63%) with anisole as an internal standard. The product (**3**) (Equation 1) was identical with authentic material in comparison with g.c. retention time, i.r., and n.m.r.

$$\underset{(\mathbf{1})}{PhC\vdots CNMe_2} \xrightarrow{h\nu} \underset{(\mathbf{2})}{PhC(Me):C:NMe} \xrightarrow{h\nu} \underset{(\mathbf{3})}{PhCMe_2CN} \qquad (1)$$

Preliminary experiments have revealed no photo-sensitisation when irradiation at 300 nm was carried out in the presence of acetophenone, thioxanthen-9-one, naphthalene, butane-2,3-dione, 7*H*-benz[*d,e*]anthracen-7-one, or anthracene (E_T 74, 65, 61, 55, 47, and 42 kcal mol^{-1} respectively). When irradiated in 250 ml of anhydrous benzene at 254 nm for 120 h, 0·5 g of the ynamine (**1**) was isomerized into the nitrile (**3**) to the extent of 0·13%.

We acknowledge financial support from a NASA grant.

(*Received, June* 12*th*, 1970; *Com.* 901.)

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[1] H. G. Viehe and M. Reinstein, *Angew. Chem. Internat. Edn.*, 1964, **3**, 506; Neth. Appl. 6,415,094, *Chem. Abs.*, 1966, **64**, 2006b.

[2] E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, 1968, **90**, 1223 reported i.r. absorption at 2050 cm^{-1} for PhCH:C:NPh.

[3] It is necessary to assume trace amounts of water in cyclohexane to account for hydration of the ynamine (**1**) into *NN*-dimethylphenylacetamide. H. G. Viehe, R. Fuks, and M. Reinstein, *Angew. Chem. Internat. Edn.*, 1964, **3**, 581 have observed a high sensitivity of ynamines toward moisture. Irradiation of the ynamine (**1**) in degassed spectrograde methylene chloride gave *NN*-dimethylphenylacetamide, m.p. 42—43° (Taverne, *Rec. Trav. chim.*, 1897, **16**, 37).

[4] An authentic sample was prepared according to M. Haller and E. Bauer, *Compt. rend.*, 1912, **155**, 1582.