

METAL-CATALYZED ORGANIC PHOTOREACTIONS  
PHOTOREACTION OF AROMATIC NITRILES IN METHANOL IN THE PRESENCE OF  
TITANIUM(IV) CHLORIDE

Tadashi SATO\* and Shigeo YOSHIIIE

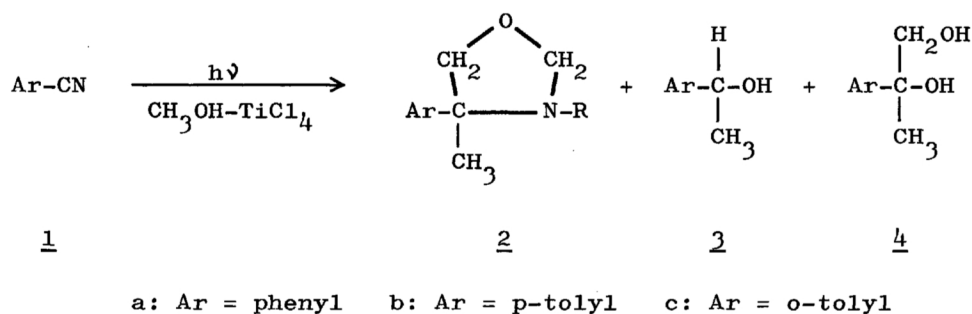
Department of Applied Chemistry, Waseda University,  
Nishiookubo 4, Shinjuku-ku, Tokyo 160

Aromatic nitriles, upon irradiation in methanol in the presence of  $\text{TiCl}_4$ , afforded substituted oxazolidines, probably through electron transfer from methanol to nitriles mediated by titanium.

It has been known that the photochemical reaction of aromatic and unsaturated nitriles proceeds mostly on carbon-carbon double bond (even in aromatic system) to the exclusion of products from reaction at the cyano group. To our best knowledge, single exception has been reported by Cantrell, who observed a 2 + 2 cycloaddition at nitrile function upon irradiation of benzonitrile with certain electron-rich olefins.<sup>1)</sup>

We now observed that aromatic nitriles reacted with methanol at nitrile function to form substituted oxazolidines under the irradiation in methanol in the presence of  $\text{TiCl}_4$ .

When a solution of benzonitrile 1a (1 ml) and  $\text{TiCl}_4$  (1 ml) in methanol (100 ml) was irradiated in a Pyrex or quartz tube with a high-pressure mercury lamp (Ushio UM-452, 450 W) for 24-40 h under the normal atmospheric conditions, 3,4-dimethyl-4-phenyloxazolidine (2a, R =  $\text{CH}_3$ ) was isolated in 20% yield. By-products (3a and 4a) were also isolated in trace amounts. When p- and o-tolunitrile were reacted under the same conditions, oxazolidines (2b and 2c, R = H) were also isolated in 11% and 15% yields, respectively. Unlike the case of benzonitrile, N-methylation did not take place in tolunitrile system. A trace amount of by-product 3b was also identified. In every case, some



amounts of polymeric substances and the starting materials were also isolated.

The dark reaction, in the presence of  $\text{TiCl}_4$ , resulted in the recovery of the starting materials. When the photolysis was carried out in the absence of  $\text{TiCl}_4$ , or in the presence of  $\text{HCl}$  alone, main portion of the starting material was recovered, accompanied by some amounts of polymeric substances.

The product identification was accomplished by elemental analyses and the following spectroscopic data.

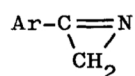
2a: MS,  $m/e$  177 (M), 162 (base peak), 146, 132, and 91. IR (neat),  $2780\text{ cm}^{-1}$  (N-CH<sub>3</sub>). NMR ( $\text{CCl}_4$ ),  $\delta$  1.35 (3H, s), 2.05 (3H, s), 3.52 and 3.65 (2H, ABq,  $J = 8\text{ Hz}$ ), 4.07 and 4.27 (2H, dist. ABq,  $J = 2\text{ Hz}$ ), and 6.7-7.2 (5H, m).

2b: IR (neat),  $3380\text{ cm}^{-1}$  (N-H). NMR ( $\text{CCl}_4$ ),  $\delta$  1.35 (3H, s), 2.21 (3H, s), 3.43 and 3.52 (2H, ABq,  $J = 7\text{ Hz}$ ), 4.03 and 4.23 (2H, ABq,  $J = 6\text{ Hz}$ ), and 6.60-7.00 (4H, q).

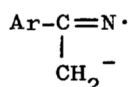
2c: MS,  $m/e$  162 (M - CH<sub>3</sub>), 147, 146 (base peak), 133, 132, 105, and 91. IR (neat),  $3320\text{ cm}^{-1}$  (N-H). NMR ( $\text{CCl}_4$ ),  $\delta$  1.40 (3H, s), 2.27 (3H, s), 3.44 and 3.74 (2H, ABq,  $J = 7\text{ Hz}$ ), 4.06 and 4.30 (2H, ABq,  $J = 6\text{ Hz}$ ), 6.65-6.85 (3H, m), and 7.17-7.35 (1H, m).

By-product 3a was identified by comparison with the authentic sample. By-product 4a was also obtained in small amount by the irradiation of acetophenone in methanol in the presence of  $\text{TiCl}_4$ .

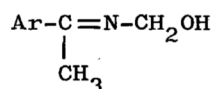
Previously we reported a  $\text{TiCl}_4$ -catalyzed photoreaction of  $\alpha,\beta$ -unsaturated ketones, in which an electron transfer from methanol to ketone mediated by the titanium was proposed.<sup>2)</sup> Although the mechanism of the present reaction has not been known, a similar electron transfer from methanol to nitrile could be speculated as an attractive working hypothesis: the radical anion of the nitrile undergoes a coupling with hydroxymethyl radical (from methanol) to produce an azirine 5, which, on further photo-assisted acceptance of the electron from methanol, cleaves at C-N bond to form a radical anion 6. Protonation and coupling with hydroxymethyl radical could afford a C-methyl intermediate 7, from which final products could be derived through a repetition of the electron transfer and coupling with methanol.



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#### REFERENCES

- 1) T. S. Cantrell, J. Amer. Chem. Soc., 94, 5929 (1972).
- 2) T. Sato, G. Izumi, and T. Imamura, Tetrahedron Letters, 1975, 2191; J. C. S. Perkin I, 1976, in press.

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