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Reaction of Tetramethylurea with Photoexcited Carbonyl Compounds

Yuji Tsujimoto, Akihiro Nakahara, Yoshiyuki Nishimura,
Takuji Miyamoto, and Yoshinobu Odaira

Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita-shi, Osaka 565

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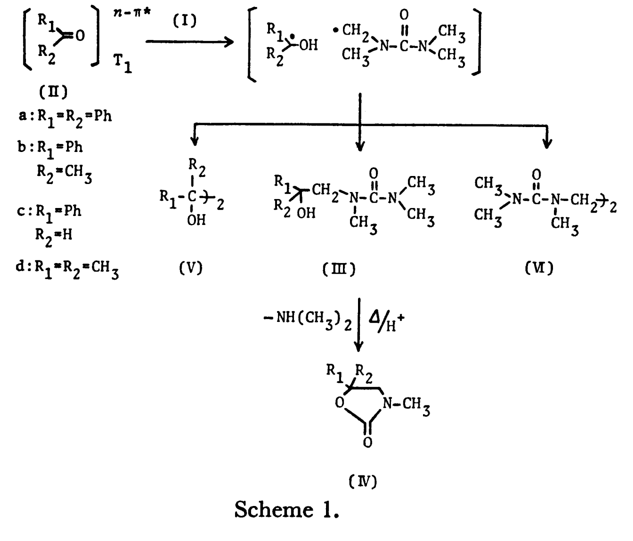
Synopsis. The photoreaction of tetramethylurea (I) with some carbonyl compounds (II) afforded in good yields the respective urea derivatives (III), which were converted into 2-oxazolidinones (IV).

Many studies have been carried out on the photochemistry of amides, and some interesting photoreactions such as photocyclization of α,β-unsaturated amides,[1] photooxidation of *N*-alkylamides,[2] and photoamidation to unsaturated systems[3] have been found. It has been reported that a new photobenzoylation of the olefin takes place preferentially in the photoreaction of *N*,*N*-dimethylbenzamide with 1,1-diphenylethylene.[4] On the other hand, little is known of the photoreactions of ureas except for the photolysis of tetramethylurea in vapor phase.[5] The present study was undertaken to see whether photochemical hydrogen abstraction from tetramethylurea (I) by *n*-*π** photoexcited carbonyl compounds (II) can occur. We wish to report that hydrogen abstraction occurs very easily to give the urea derivatives (III) in good yields, and that 2-oxazolidinones (IV) can be prepared from the obtained ureas (III). In the present study, benzophenone (II-a), acetophenone (II-b), benzaldehyde (II-c), and acetone (II-d) were used as carbonyl compounds.

Irradiation of I and II-a in acetonitrile through a Pyrex filter for 10 h afforded the urea (III-a) and 2-oxazolidinone (IV-a) in 46 and 4% yields, respectively, together with the pinacol (V-a) and the dimeric urea (VI). The photoreaction of I with II-b under the same conditions as above gave rise to the urea (III-b) and 2-oxazolidinone (IV-b) in 30 and 11% yields, respectively, along with the pinacol (V-b) and VI. Similarly, the photoreaction with II-c gave the urea (III-c) and 2-oxazolidinone (IV-c) in 26 and 11% yields, the urea (III-d) being obtained in 24% yield with II-d.



Scheme 1.

From the results, it was proved that photochemical hydrogen abstraction from I occurred very efficiently.

Concerning the formation of IV obtained as byproducts, it was clarified by the following experiments that IV-a—d were derived from III-a—d. When III-a was heated in benzene for 10 h, IV-a was obtained almost quantitatively. In the above reaction, the presence of acid enhanced the rate of cyclization. Consequently, in the case of ureas (III-b—d), each cyclization was carried out with acid. The reaction is illustrated in Scheme 1.

The hydrogen abstraction from I by *n*-*π** triplet of II results in the formation of a carbinol radical and a ureidomethyl radical, which are precursors of three sets of the coupling products III, V, and VI. III can undergo cyclization to 2-oxazolidinones (IV), accompanied by the elimination of dimethylamine by heat or with acid.

Experimental

Material. Commercial tetramethylurea (I) and carbonyl compounds (II) were purified by the usual methods before use. Dimeric urea (VI) was prepared by the reported method.[6]

General Procedure for Photoreaction. Carbonyl compounds (II) and three molar excess of tetramethylurea (I) were dissolved in acetonitrile. After the solution was bubbled with nitrogen for 10 min, it was irradiated with a 500 W high-pressure mercury lamp through a Pyrex filter for 10 h at room temperature. After evaporation of the solvent, unreacted I was recovered *in vacuo*, and the residue was chromatographed on silica gel, except in the case of acetone (II-d). Dimeric urea (VI) was eluted with ether-benzene (4: 6), and confirmed by comparison with an authentic sample.

Photoreaction of I with Benzophenone (II-a). A solution of I [7.0 g, 0.06 mol] and II-a [3.6 g, 0.02 mol] in acetonitrile (40 ml) was irradiated. The following products were isolated. Elution with benzene–petroleum ether gave benzopinacol (V-a) [527 mg, 30%], and the first elution with ether–benzene (2: 8) gave 2-oxazolidinone (IV-a) [206 mg, 4%], mp 137—140 °C; Mass *m*/*e* 253 (M$^+$); IR (KBr) 1750, 740, 700 cm^{-1}; NMR (CCl$_4$) δ, 2.8 (s, 3H), 4.0 (s, 2H), 7.0—7.5 (m, 10H). Found: C, 75.67; H, 5.79; N, 5.47%. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53%. Next elution with ether–benzene (2: 8) gave urea (III-a) [2.65 g, 46%] mp 147—148.5 °C; Mass *m*/*e* 298 (M$^+$); IR (Nujol) 3400, 1630, 750, 700 cm^{-1}; NMR (CCl$_4$), 2.5 (s, 3H), 2.64 (s, 6H), 4.0 (s, 2H), 5.5 (s, 1H), 7.0—7.6 (m, 10H). Found: C, 72.28; H, 7.48; N, 9.23%. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.45; H, 7.43; N, 9.39%.

Photoreaction of I with Acetophenone (II-b). A solution of I [26.1 g, 0.23 mol] and II-b [8.9 g, 0.07 mol] in acetonitrile (150 ml) was irradiated. The work-up as above gave the following products: Pinacol (V-b) [3.94 g, 44%], mp 123—125 °C [lit,[7] 122 °C (racemic), 117—118 °C (meso)], urea (III-b) [5.30 g, 30%], mp 155—158 °C; Mass *m*/*e* 236 (M$^+$);

IR (Nujol) 3400, 1590, 760, 700 cm^{-1}, 2-oxazolidinone (IV-b) [1.61 g, 11%], Mass *m/e* 191 (M$^+$); IR (neat) 1740, 760, 690 cm^{-1}; NMR (CCl$_4$) δ, 1.65 (s, 3H), 2.8 (s, 3H), 3.5 (s, 2H), 7.0—7.5 (m, 5H).

Photoreaction of I with Benzaldehyde (II-c). A solution of I [20.9 g, 0.18 mol] and II-c [6.4 g, 0.06 mol] in acetonitrile (60 ml) was irradiated. The work-up as above gave the following products: Pinacol (V-c) [1.29 g, 11%], mp 137—138 °C [lit,[8] 137.5—138 °C], urea (III-c) [3.40 g, 26%], mp 88—90 °C; IR (KBr) 1600 cm^{-1}; Mass *m/e* 222 (M$^+$); NMR (CDCl$_3$) δ, 2.8 (s, 6H), 2.9 (s, 3H), 3.1, 3.6 (ABX *octet*, $J_{ab}=15$ Hz, $J_{ax}=9$ Hz, $J_{bx}=3$ Hz, 2H), 4.9 (ABX *q*, 1H), 5.4 (s, 1H), 7.0—7.5 (m, 5H). Found: C, 64.75; H, 8.29; N, 12.48%. Calcd for $C_{12}H_{18}N_2O_2$: C, 64.84; H, 8.16; N, 12.60%. 2-Oxazolidinone (IV-c) [1.17 g, 11%], IR (neat) 1750 cm^{-1}.

Photoreaction of I with Acetone (II-d). A solution of I [23.9 g, 0.21 mol] and II-d [4.0 g, 0.069 mol] in acetonitrile (60 ml) was irradiated. After evaporation of the solvent, unreacted I was recovered *in vacuo*. The remaining residue was distilled under reduced pressure (0.5—0.8 Torr). Besides VI, the urea (III-d) was obtained, [2.78 g, 24%], bp 86 °C (0.55 Torr); IR (neat) 1600 cm^{-1}; Mass *m/e* 174 (M$^+$); NMR (neat) δ, 1.25 (s, 6H), 2.8 (s, 6H), 3.0 (s, 3H), 3.3 (s, 2H), 4.7 (s, 1H).

Cyclization of III to 2-Oxazolidinones (IV). 3-Methyl-5,5-diphenyl-2-oxazolidinone (IV-a): A solution of III-a [344 mg, 1.15 mmol] in benzene (15 ml) was refluxed for 10 h. Evaporation of the solvent gave crude product (IV-a) [300 mg, 100%]. Recrystallization from benzene afforded a sample identical with the authentic sample. 3,5-Dimethyl-5-phenyl-2-oxazolidinone (IV-b): A solution of III-b [140 mg, 0.59 mmol] in chloroform (5 ml) containing a trace of sulfuric acid was stirred for 4 h at room temperature. After the mixture had been washed with water, the organic layer was dried over calcium chloride. Evaporation of the solvent gave crude product (IV-b) [96 mg, 85%]. 3-Methyl-5-phenyl-2-oxazolidinone (IV-c): A solution of III-c [98 mg, 0.44 mmol] in benzene (3 ml) with a trace of sulfuric acid was stirred for 1 h. The same work-up as above gave crude product (IV-c) [29 mg, 37%]. 3,5,5-Trimethyl-2-oxazolidinone (IV-d): A solution of III-d [90 mg, 0.51 mmol] in chloroform (5 ml) containing a trace of sulfuric acid was stirred for 4 h at room temperature. The same work-up as above gave crude product (IV-d) [54 mg, 80%]. Separation by GLC (10% FEAP) gave an analytical sample, Mass *m/e* 129 (M$^+$); IR (neat) 1740 cm^{-1}; NMR (CCl$_4$) δ, 1.4 (s, 6H), 2.75 (s, 3H), 3.15 (s, 2H).

References

1) O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.*, **89**, 4243 (1967); **90**, 2333 (1968).

2) W. H. Sharkey and W. E. Mochel, *J. Am. Chem. Soc.*, **81**, 3000 (1959).

3) D. Elad and J. Rokah, *J. Org. Chem.*, **29**, 1855 (1964).

4) Y. Katsuhara, R. Tsujii, K. Hara, Y. Shigemitsu, and Y. Odaira, *Tetrahedron Lett.*, **1974**, 453.

5) J. R. Majer, S-A. M. A. Naman, and J. C. Robb, *J. Chem. Soc., B*, **1970**, 93.

6) W. R. Boon, *J. Chem. Soc.*, **1947**, 307.

7) "Beilstein Handbuch der Organischen Chemie," Band 6, EII (1944), p. 979.

8) R. Kuhn and O. Rebel, *Chem. Ber.*, **60**, 1565 (1927).