

NOVEL PHOTOUREIDOMETHYLATION TO 1,1-DIPHENYLETHYLENE WITH
TETRAMETHYLUREA INVOLVING ELECTRON TRANSFER

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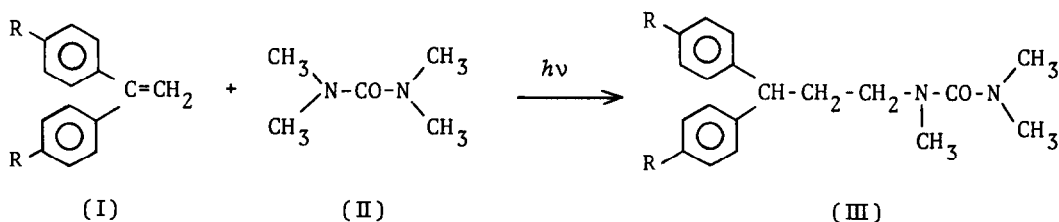
(Received in Japan 1 March 1978; received in UK for publication 21 April 1978)

Little is known about the photochemical reaction of ureas.¹ Recently, we have reported the reaction of tetramethylurea with photoexcited species such as carbonyl compounds excited in $n-\pi^*$ triplet² and aromatic nitriles in $\pi-\pi^*$ singlet.³

As a part of our studies of the photochemical reactions of the compounds containing *N,N*-dimethylcarbonyl group,²⁻⁴ we now wish to report the novel ureidomethylation to 1,1-diphenylethylene (I) having electron withdrawing substituents with tetramethylurea (II), in which electron transfer from II to I excited in $\pi-\pi^*$ triplet is involved.

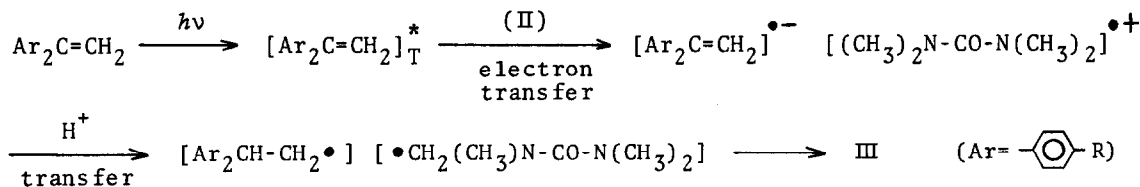
Irradiation of a solution of Ia or Ib with II in acetonitrile gave the ureidomethylated product (IIIa or IIIb) in 95% or 92% yields,⁵ respectively. However, in the case of the reaction of Ic with II in the same solvent, ureidomethylated product (IIIc) was obtained in 29% yield, along with propionamide derivative (IVc, 5.5%), small amounts of 1,1,4,4-tetraphenylbutane, 1,1'-ethylenebis[1,3,3-trimethyl]urea, and tetramethyloxamide.

The reaction of Ic with II to afford IIIc was sensitized with xanthone and with phenanthrene and quenched with piperylene effectively. Furthermore, the



- (a) R=CN
- (b) R=CO₂CH₃
- (c) R=H
- (d) R=CH₃
- (e) R=OCH₃

(a) 95%; (b) 92%

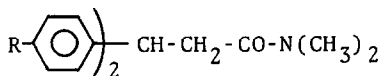


Scheme

ureidomethylation was markedly suppressed when the reaction of Ic with II was carried out in non-polar solvents (yield of IIIc; 1% in benzene, 5% in cyclohexane).

From these results as well as the fact that anti-Markownikoff adduct is obtained, the possibility can be ruled out that hydrogen abstraction⁶ of triplet I from II is followed by coupling of the resulting radicals. Therefore, we would like to propose the reaction path involving electron transfer from II to I excited in π - π^* triplet, to give rise to 1,1-diphenylethylene radical anion and tetramethylurea radical cation in the primary step, as shown in scheme.

On the contrary, in the case of I having electron donating substituents, propionamide derivatives (IV) were formed in considerable yields. Irradiation of Id with II gave III d and IV d in 27% and 12% yields, respectively. The photoreaction of Ie with II led to the formation of III e and IV e in 7% and 25% yields, respectively. In these cases, electron transfer is difficult to occur owing to electron donating substituents and as a result, cleavage of urea giving rise to amide radical takes place.



(IV)

(c) R=H

(d) R=CH₃(e) R=OCH₃

REFERENCES AND FOOTNOTE

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