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# PHOTOCHEMICAL REACTION OF 3-ARYL-2-ISOXAZOLINES WITH METHYLATED BENZENES[1]

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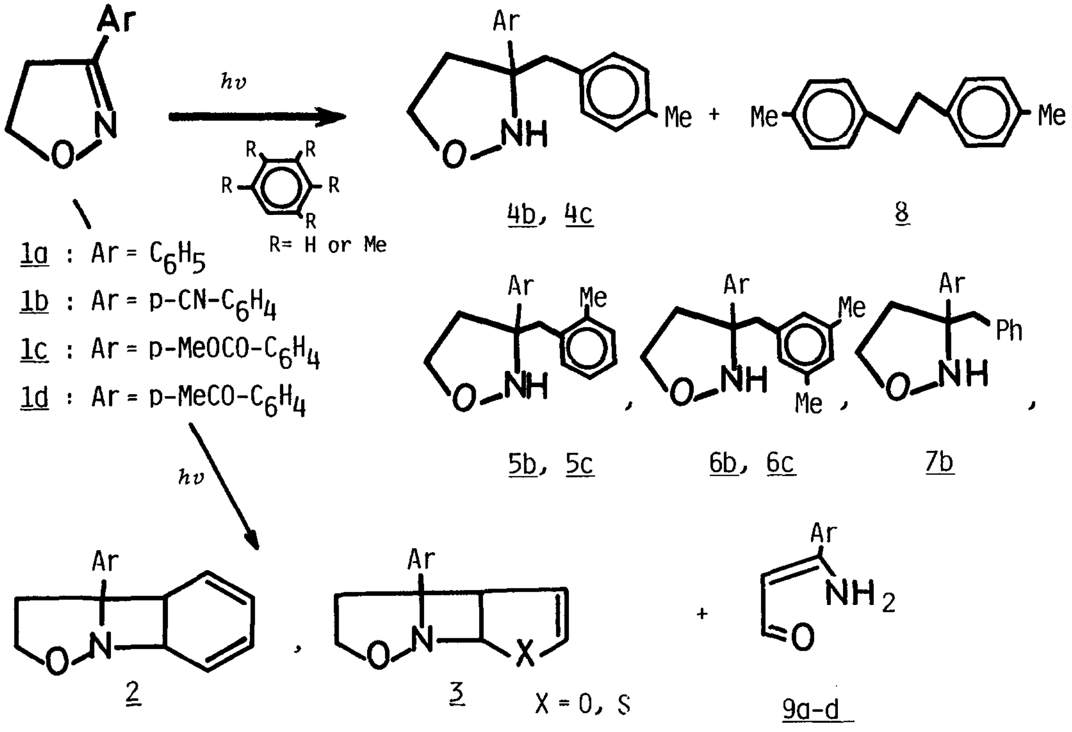
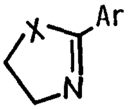
Summary: Irradiation of 3-aryl-2-isoxazolines (1b and 1c) results in a hydrogen abstraction reaction from toluene, xylene or mesitylene by the carbon-nitrogen double bond to give isoxazolidine derivatives.

It is well known that the excited state of imines have little tendency to undergo hydrogen atom abstraction.[2] In this paper, we wish to describe the first example of intermolecular hydrogen abstraction reaction of 2-isoxazoline derivatives which involves the carbon-nitrogen double bond. In previous reports, we described the formations of novel [2+2] photoadducts (2 and 3) by carring out the irradiation of isoxazolines in the presence of benzene or heteroaromatic compounds.[3,4] Thus, we found that 3-aryl-2-isoxazolines possessing cyano and methoxycarbonyl groups in the phenyl ring readily undergo photocycloaddition with benzene, furan or thiophene. As a result of the electronic requirements of the photoreaction, we expected a higher efficiency of product formation when electron rich compounds such as toluene (or anisole) were used. Instead, an unusual hydrogen abstraction reaction by the carbon-nitrogen double bond occurred to give isoxazolidine derivatives rather than [2+2] cycloadduct when methyl substituted benzenes were used as substrates. The formation of isoxazolidines can be suggested to arise from the excited complexes of 2-isoxazolines (1b-c). In connection with this study, the photoreactions of 2-aryl-1-pyrrolines and 2-aryl-2-oxazolines were also investigated.

When a solution of 3-(p-cyanophenyl)-2-isoxazoline (1b)[3] in p-xylene was irradiated with RUL-3000Å lamps (43W) using a quartz vessel for 27 hr at room temperature, two coupling products, whose structure was assigned as 3-(p-cyanophenyl)-3-(p-methylbenzyl)isoxazolidine (4b)[5] and dimethyl dibenzyl (8), were isolated in 58 and 14 % (based on 1b) yield. These products were also accompanied by 3-amino-3-(p-cyanophenyl)-2-propanal (9b[3], 22 %) as well as some recovered starting material (5 %).[7] When o-xylene or mesitylene was used as solvent, the corresponding hydrogen abstraction and recombination products, (5b)[8] and (6b)[9], could be isolated in 48 and 18 % yield, respectively. The photoreaction of 1b with toluene was quite complicated and isoxazolidine (7b)[10] could be detected in only 2-5 % yield. The p-methoxycarbonylphenyl derivative (1c)[4] gave isoxazolidines, (4c, 5c, and 6c)[11], whereas the unsubstituted 3-phenyl-2-isoxazoline (1a) did not undergo a similar photoreaction. The formation of isoxazolidines (4-7) represents one of the few example of an intermolecular hydrogen abstraction by a carbon-nitrogen double bond. Same isoxazolines were quantitatively recovered on photolysis in anisole. This is probably the result of an internal filter effect by the solvent (i.e., all of the incident light was absorbed by anisole).



The hydrogen abstraction reactions of 1b-c are considered to proceed by the singlet excited state forming an exciplex with aromatic hydrocarbons for several reasons: 1) The dibenzyl derivatives isolated originate from the benzyl radical which was formed by the hydrogen abstraction of compounds 1b-c. 2) Both p-cyanophenyl and p-methoxycarbonylphenyl derivatives (1b and 1c) produce the same type of photoproducts while the other isoxazolines do not undergo a similar photoreaction. The Ar-C=N-O chromophores of these two substrates were previously found to function as electron acceptors in the [2+2] photocycloaddition reactions with benzene, furan and thiophene.[3,4] 3) The aromatic hydrocarbons suppress formation of N-O scission products[3] such as 9, which originate from singlet excited states. Aromatic hydrocarbons also quench the fluorescence of the 2-isoxazolines. 4) 3-p-Acetylphenyl-2-isoxazoline (1d) dose not undergo the hydrogen abstraction reaction in spite of the fact that it contains an analogous electron withdrawing group. This probably reflects the facile intersystem crossing of this system to the triplet state. This would tend to suggest that the triplet state of isoxazolines are not responsible for the hydrogen abstraction reaction. 5) When tolunitriles are used, no related isoxazolidine could be detected. No hydrogen abstraction reaction could be observed when isopropanol was used as the solvent. These results suggest that an excited complex between the singlet excited state of electron deficient carbon-nitrogen double bond and the methylated benzene plays an important role for the formation of the isoxazolidine derivatives.[12]



10a: X=$CH_2$,Ar= $C_6H_5$
10b: X=$CH_2$,Ar=p-CN-$C_6H_4$
11a: X= O, Ar= $C_6H_5$
11b: X= O, Ar=p-CN-$C_6H_4$

In order to determine whether a similar photochemical reaction would occur with pyrrolines (10a and 10b)[13]or oxazolines (11a and 11b)[14], the photoreactions were carried out in xylene. However, only polymeric material was formed thereby indicating that the C=N-O chromophore is neccessary for the hydrogen abstraction and recombination reaction to proceed.

In summary, this work is noteworthy that two 2-isoxazolines (1b and 1c) undergo a most unusual photochemical hydrogen abstraction reaction with methyl benzenes which involves the carbon-nitrogen double bond. Further studies dealing with the photobehavior of compounds 1b-c are in progress.

## References and Notes

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2. A. Padwa, Chem. Rev., 77, 37 (1977) and references therein.
3. T. Kumagai, K. Shimizu, Y. Kawamura, and T. Mukai, Terahedron, 37, 3365 (1981).
4. T. Kumagai, Y. Kawamura, and T. Mukai, Chem. Lett., to be submitted.
5. Product 4b[6]: pale yellow needles, mp 115.5-116.5°C; IR (KBr) 3420, 2910, 2225, 1609, 1062, 843 cm$^{-1}$; NMR(CDCl$_3$) δ 2.31(3H, s), 2.50(2H, t, J= 7.0 Hz), 3.03(1H, d, J= 13.9 Hz), 3.10(1H, d, J= 13.9 Hz), 3.7-4.0(2H, m), 4.80 (NH), 6.79(2H, d, H= 7.9 Hz), 7.04(1H, d, J= 7.9 Hz), 7.50(2H, d, J= 8.6 Hz) 7.62(2H, d., J= 8.6 Hz); UV(EtOH) λmax= 224 (ε 16,800), 232 (17,600), 265 (1,200), 274 (sh, 1,100) and 280 nm (sh, 750).
6. All new compounds gave satisfactory elemental analyses and Mass spectra.
7. The formations of 4-(p-cyanophenyl)-3-oxazoline and p-dicyanobenzene were observed in 0.5-2 % yields.
8. Product 5b[6]: colorless amorphous crystal, mp 86-87°C; IR (KBr) 3425, 2970, 2230, 1610, 1084 cm$^{-1}$; NMR(CDCl$_3$) δ 2.08(3H, s), 2.3-2.7(2H, m), 2.95(1H, d, J= 14.7 Hz), 3.20(1H, d, J= 14.7 Hz), 3.6-4.1(2H, m), 5.27(NH), 6.9-7.2 (4H, m), 7.4-7.6(4H, m); UV(EtOH) λmax= 231 (ε 16,580), 266 (sh, 2,020), 272 (2,170) and 279 nm (1,930).
   Product 6b[6]: pale yellow oil ; IR (CCl$_4$) 3410, 2230, 1041, 924 cm$^{-1}$; NMR (CDCl$_3$) δ 2.25(6H, s), 2.50(2H, t, J= 7.3 Hz), 2.98(1H, d, J= 13.8 Hz), 3.08(1H, d, J= 13.8 Hz), 3.7-4.0(2H, m), 5.39(NH), 6.58(2H, s). 6.91(1H, s), 7.5-7.7(4H, m).
9. Dibenzyl derivatives were obtained in 10-40 % yield (based on 1b) on photolyses of 1b in methyl substituted benzenes.
10. Product 7b was not purified; NMR(CDCl$_3$) δ 2.50(2H, t, J= 7.3 Hz), 3.01(1H, d, J= 13.9 Hz), 3.16(1H, d, J= 13.9 Hz), 3.7-4.1(2H, m), 5.4(NH), 6.8-7.3 (5H, m), 7.4-7.8(4H, m).
11. Product 4c[6]: mp 99-101°C, 46 % yield; 5c[6]: 85-86°C, 41 % yield; 6c[6]: mp 136-137°C, 38 % yield; These isoxazolidines were also accompanied by dibenzyl derivatives in 10-50 % yield (based on the starting isoxazoline).
12. Triplet sensitization and chemical sensitization were ruled out since added acetophenone had no influence on the photoreaction.
13. Compound 10b[6]: mp 99-99.5°C; UV(cyclohexane) λmax= 257.5 (ε 20,400) and 296 nm (sh, 1,000).
14. Compound 11b[6]: mp 115.5-116°C; UV(cyclohexane) λmax= 259.5 (ε 12,400) and 292 nm (sh, 2,990).

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