Photochemical Reaction of NN-Dialkylmethacrylamides. An Olefin Analogue of the Type II Photoelimination of Ketones

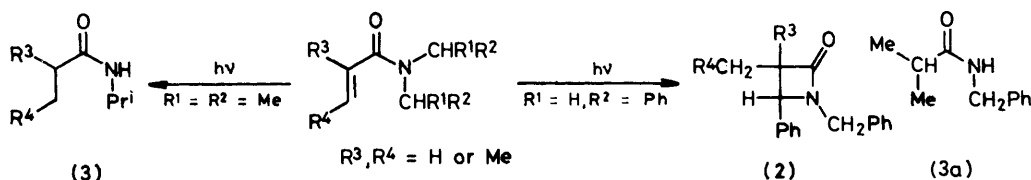By **Hiromu Aoyama,*** **Tadashi Hasegawa, Masahiko Okazaki,** and **Yoshimori Omote,** Department of Chemistry, The University of Tsukuba, Sakuramura, Ibaraki, 300–31 Japan

Both photocyclization of NN-bis(benzyl)methacrylamide (1a) to a β-lactam (2a) and photodealkylation of NN-di-isopropylmethacrylamide (1b) to N-isopropylisobutyramide (3b) were found to proceed via dimethylketen and the corresponding imine (4). The reactions provide the first example of type II reaction of aliphatic olefins. The behaviour of the 1,4-biradical intermediate involved in the reaction is discussed in relation to that of similar biradicals.

PREVIOUSLY, we have reported photocyclization of NN-bis(benzyl)-αβ-unsaturated amides to β-lactams (2) and photodealkylation of NN-di-isopropyl αβ-unsaturated amides to N-isopropyl saturated amides (3).

(3)   R¹ = R² = Me   R³,R⁴ = H or Me   (2)   (3a)

R¹ = H, R² = Ph

Both reactions were proved to proceed via intramolecular hydrogen abstraction by the β-carbon atom.[1] We postulated possible mechanisms, paths A and B,
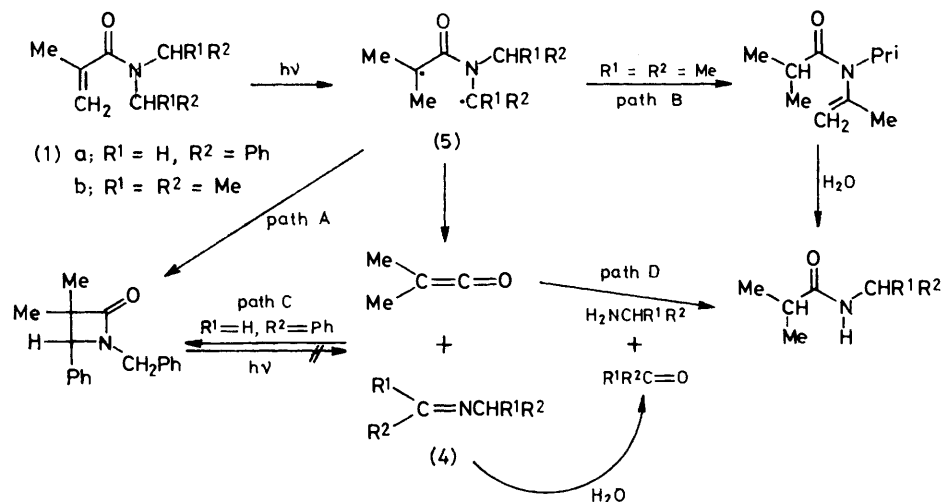
RESULTS AND DISCUSSION

First, in order to examine the intermediacy of dimethylketene in the formation of (3), we tried trapping the ketene with nucleophiles. When (1b) in benzene was irradiated in the presence of an excess of benzylamine, N-benzylisobutyramide (3a) was obtained instead of (3b). The keten was also trapped with benzyl
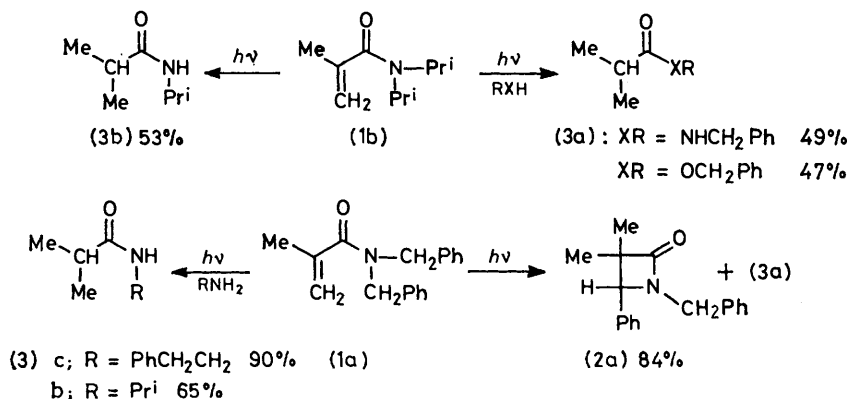

(1) a; R¹ = H, R² = Ph
    b; R¹ = R² = Me

for these reactions. However, the formation of a small amount of a saturated amide (3a) from NN-bis(benzyl)-methacrylamide (1a) could not be explained by the mechanism (path B).[1]

Recently, Mazzocchi et al. reported [2] the formation of N-monosubstituted amides in the photolysis of β-lactams. This reaction proceeds via ketens and imines which are produced by photofragmentation of the β-lactams.[2] Their investigation suggested to us that the N-monosubstituted amide (3) might be formed through path D, which involves type II-analogous cleavage of the unsaturated amide (1), and prompted us to reinvestigate the mechanism. In this investigation, (1a) and NN-di-isopropylmethacrylamide (1b) were chosen as reactants.
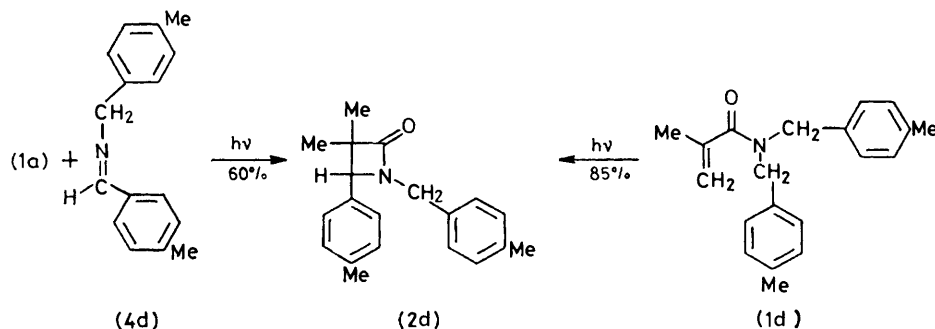
alcohol to give benzyl isobutyrate. This result disproves path B and strongly supports path D. An attempt to detect acetone, which should be produced by hydrolysis of the imine (4b), using v.p.c. was unsuccessful. However, in the case of (1a), the formation of benzaldehyde by hydrolysis of the imine (4a) was confirmed by examination of the reaction mixture with v.p.c. and n.m.r. On the basis of these results, we can conclude that the isobutyramides (3a) and (3b) were formed via path D.

Next, NN-bis(benzyl)methacrylamide (1a) was irradiated in the presence of phenethylamine. In this case, contrary to expectation, not only the formation of (3a) but also that of the lactam (2a) were completely suppressed and N-phenethylisobutyramide (3c) was

obtained in high yield. Photolysis of (1a) in the presence of isopropylamine gave a similar result. These results indicate that dimethylketen is also the intermediate in the formation of the lactam (path C). It is

while (4a) reacts directly with the keten predominantly to give the lactam (2a). The different reactivities in the imines are understandable, because it is known that 1 : 1 cycloadditions of ketens and imines have been

(3b) 53%   (1b)   (3a) : XR = NHCH₂Ph   49%
                              XR = OCH₂Ph   47%

(3) c; R = PhCH₂CH₂ 90%   (1a)   (2a) 84%
    b; R = Prⁱ 65%

well known that dimethylketen reacts with imines to give β-lactams.[3] It is also conceivable that the lactam is formed through path A and is photochemically equilibrated with the keten–imine pair, since photochemical cleavage of β-lactams to ketens and imines has been reported.[4] However, this possibility can be eliminated because the lactam (1a) was inert toward photolysis in the presence of benzylamine. The mechanism (path C) was further supported by the following experiments.

limited to aromatic imines with few exceptions.[4] The cleavage of (1) to the keten and the imine is the first example of a type II reaction of aliphatic olefins, although there has been one report concerning type II reaction of a phenyl-substituted olefin.[5]

Finally, the behaviour of the biradical (5) formed in the photoreaction is worth noting. As described above the biradical undergoes only cleavage and no cyclization. This behaviour is of interest in view of the facts that (a)

(4d)   (2d)   (1d)

When (1a) was irradiated in the presence of an excess of 4-methylbenzyl-N-(4-methylbenzylidene)amine (4d), the β-lactam (2d) which was produced by addition of dimethylketen to (4d) was obtained instead of (2a). The structure of (2d) was elucidated by spectral data and elemental analysis, and further confirmed by an independent synthesis from NN-di-(p-tolylmethyl)methacrylamide (1d). These results lead to the conclusion that (2a) was produced by addition of dimethylketen to benzyl(benzylidene)amine (4a). Contribution via path A to the formation of (2a) must be negligibly small because (2a) could not be detected in the photolysis of (1a) in the presence of the amine as described above.

In conclusion, both (1a) and (1b) undergo intramolecular hydrogen abstraction by the β-carbon atom followed by cleavage of the C–N bond giving dimethylketen and the imine (4). The imine (4b) is readily hydrolysed and the resulting isopropylamine reacts with the keten to yield N-isopropylisobutyramide (3b),

similar 1,4-biradicals [(6) and (7)] undergo cyclization exclusively [6] and (b) an amide CO–N bond has partial double-bond character.[7] In spite of the double-bond character, the dissociation energy of the CO–N bond is presumed to be comparable with that of ordinary C–C bonds because C–N bonds are generally weaker than C–C bonds (C–N, ca. 70 kcal mol⁻¹; C–C, ca. 85 kcal mol⁻¹).[8] The failure of the biradicals (6) and (7) to undergo cleavage has been ascribed to the perpendicular orientation of the p orbital of the allylic radical site to the C(2)–C(3) σ bond.[6] The orientation is due to the conjugation of the p orbital with the adjacent double bond. Therefore, the conjugation of the C(α) p orbital of (5) with the amide carbonyl group is presumed to be weak (the radical-stabilizing effect of an ester carbonyl group is known to be very weak [9]). The biradical (8) which is produced in photolysis of isopropyl benzoylformate undergoes only cleavage.[10] This is consistent with the above consideration. On the other hand, the

biradical (9) which is very similar to (5) undergoes both cyclization and cleavage.[11] However, the problem is
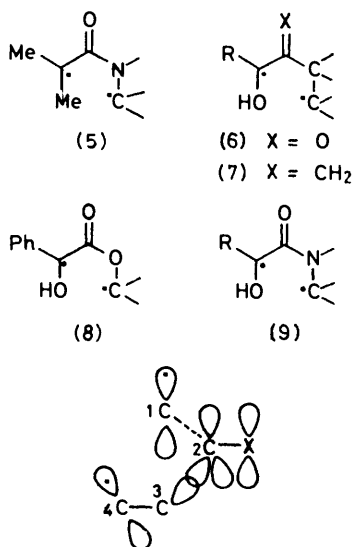
less simple in this case because of the presence of another competitive process, i.e., 1,4-hydrogen migration.

EXPERIMENTAL

General Procedure for Photochemical Reactions of Methacrylamides.—A solution of the amide (1) (100 mg) in benzene (40 ml) was irradiated in a quartz vessel under argon with a 50-W low-pressure mercury lamp for 20—30 h in the presence or absence of the additives (300 mg). After removal of the solvent, the residue was chromatographed on silica gel.

Irradiation of NN-*di-isopropylmethacrylamide* (1b) *in the presence of benzylamine.* This yielded N-benzylisobutyramide (3a), identical with authentic material.[12] Analysis of the reaction mixture by n.m.r. indicated the absence of N-isopropylmethacrylamide (3b).

Irradiation of (1b) *in the presence of benzyl alcohol.* This yielded benzyl isobutyrate, identical with authentic material. A small amount of (3b) was also detected.

Irradiation of NN-*Bis(benzyl)methacrylamide* (1a) *in the presence of phenethylamine.* This yielded N-phenethylisobutyramide (3c), m.p. 91—92 °C; $\nu_{max.}$ (KBr) 3 280 and 1 638 cm^{-1}; δ(CDCl$_3$) 1.15 (6 H, d, J 6.6 Hz, CHMe_2),

2.28 (1 H, septet, J 6.6 Hz, CHMe$_2$), 2.80 (2 H, t, J 6 Hz, PhCH_2), 3.46 and 3.56 (total 2 H, each t, J 6 Hz, NCH$_2$), and 7.24 (5 H, s, aromatic protons) (Found: C, 75.50; H, 8.95; N, 7.40. C$_{12}$H$_{17}$NO requires C, 75.35; H, 8.95; N, 7.32%). The lactam (2a) and (3a) were not detected in the reaction mixture (n.m.r. and t.l.c.).

Irradiation of (1a) *in the presence of isopropylamine.* This yielded N-isopropylisobutyramide (3b), identical with authentic material. Compounds (2a) and (3a) were not detected in the reaction mixture (n.m.r. and t.l.c.).

Irradiation of (1a) *in the presence of* 4-*methylbenzyl-*N-(4-*methylbenzylidene*)*amine* (4d). This yielded 3,3-dimethyl-4-(*p*-tolyl)-1-(*p*-tolylmethyl)azetidin-2-one (2d), b.p. 145—150 °C at 3 torr (bath temp.); $\nu_{max.}$ (film) 1 750 cm^{-1}; δ(CDCl$_3$ 0.78 (3 H, s, 3-Me), 1.31 (3 H, s, 3-Me), 2.31 (3 H, s, Ph–*Me*), 2.35 (3 H, s, Ph–*Me*), 3.81 and 4.91 (2 H, AB quartet, J 15 Hz, NCH$_2$), 4.11 (1 H, s, 4-H), and 7.1—7.45 (8 H, m, aromatic protons) Found: C, 81.80; H, 7.90; N, 5.10. C$_{20}$H$_{23}$NO requires C, 81.89; H, 7.90; N, 4.77%). Although some unidentified by-products were produced, compounds (2a) and (3a) were not detected.

Irradiation of NN-*di*(p-*tolylmethyl*)*methacrylamide* (1d). This yielded a product identical with that obtained in the preceding experiment.

REFERENCES

[1] T. Hasegawa, M. Watabe, H. Aoyama, and Y. Omote, *Tetrahedron*, 1977, **33**, 485; T. Hasegawa, H. Aoyama, and Y. Omote, *Tetrahedron Letters*, 1975, 1901.
[2] P. H. Mazzocchi, M. W. Bowen, and J. Kachinsky, *J.C.S. Chem. Comm.*, 1977, 53.
[3] (a) H. Staudinger, *Ber.*, 1907, **40**, 1149; (b) J. C. Martin, K. C. Brannock, R. D. Burpitt, P. G. Gott, and V. A. Hoyle, jun., *J. Org. Chem.*, 1971, **36**, 2211; (c) W. Kirmse, *Angew. Chem.*, 1959, **71**, 531.
[4] Ref. 3b and references cited therein.
[5] J. M. Hornback, *J. Amer. Chem. Soc.*, 1974, **96**, 6773.
[6] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.
[7] J. Zabicky, ' The Chemistry of Amides,' Interscience, London, 1970.
[8] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 466.
[9] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 1972, **94**, 7495.
[10] E. S. Huyser and D. C. Neckers, *J. Org. Chem.*, 1964, **29**, 276.
[11] H. Aoyama, T. Hasegawa, M. Watabe, H. Shiraishi, and Y. Omote, *J. Org. Chem.*, 1978, **43**, 419.
[12] H. Staudinger, H. W. Klever, and P. Kober, *Annalen*, 1910, **374**, 1.