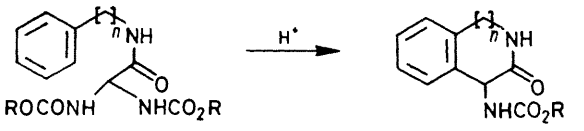
Intramolecular Amidoalkylation of Olefins

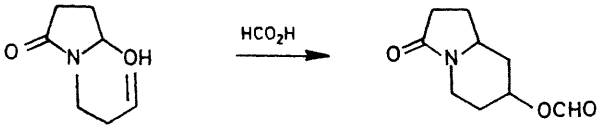
By Dov BEN-ISHAI
(*Department of Chemistry, Israel Institute of Technology, Haifa, Israel*)

Summary *N*-Allylamides and allyl esters of bisalkoxycarbonylaminoacetic acid (**5**) were found to cyclize in strong acid solutions to the five-membered pyrrolidones (**6**; Y = NH) and butyrolactones (**6**; Y = O) rather than to the corresponding six-membered piperidinones (**8**; Y = NH) or the six-membered lactones (**8**, Y = O).

AROMATIC amides of bisalkoxycarbonylamino acetic acids (**1**) were recently found to cyclize in strong acid solutions to the corresponding lactams (**2**).[1] This intramolecular amidoalkylation reaction (**1**) → (**2**) which afforded oxindoles (**2**; $n = 0$), isoquinolones (**2**; $n = 1$), and benzazepinones (**2**; $n = 2$) involves, in terms of Baldwins rules,[2] an *exo-trigonal* cyclization, and has now been extended to olefins.

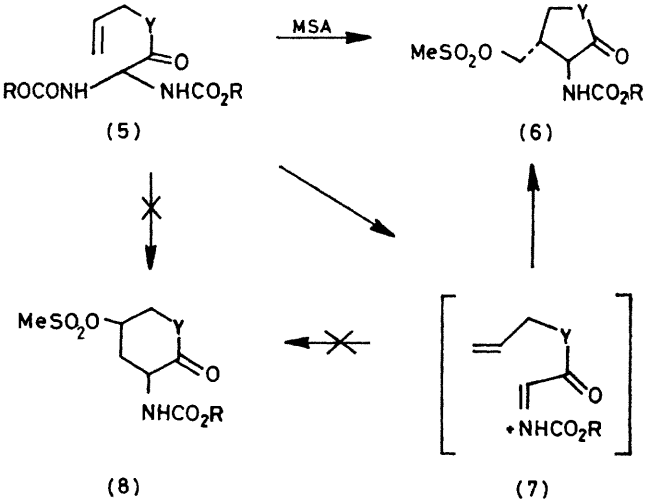


(1) (2)



(3) (4)

Intramolecular amidoalkylations of olefins were studied by Speckamp[3] using the *N*-butenylpyrrolidone series (**3**) and were found to afford the corresponding piperidine derivatives (**4**). These cyclizations (**3**) → (**4**) involve an *endo-trigonal* addition to the olefinic bond. In our case we found that the reaction of the allylamides of bisbutyloxycarbonylaminoacetic acid (**5d**) and bismethoxycarbonylaminoacetic acid (**5c**), in methanesulphonic acid (MSA) at room temperature, afforded the corresponding pyrrolidone derivatives (**6d**) (m.p. 124 °C) and (**6c**) (m.p. 148 °C) in 80 and 51% yield. Similarly the allylesters of bisbutyloxycarbonylaminoacetic acid (**5b**) and bismethoxycarbonylaminoacetic acid (**5a**) cyclized in MSA to the corresponding butyrolactones (**6b**) (oil) and (**6a**) (m.p. 118 °C) in 64 and 47% yield. We did not detect, in the crude mixture, the presence of the six-membered-ring products of type (**8**).

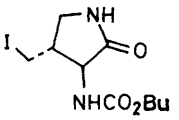


(5) (6) (8) (7)

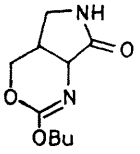
SCHEME. **a**; R = Me, Y = O
b; R = Bu, Y = O
c; R = Me, Y = NH
d; R = Bu, Y = NH

The reactive intermediates (**7**) cyclized in an *exo-exo-trigonal* fashion leading to five-membered products (**6**) rather than in an *endo-exo-trigonal* fashion which would have led to the formation of six-membered products of type (**8**) (Scheme). The number of trigonal atoms which are incorporated into the newly formed ring probably plays an important role in the stereoelectronic preferences of the reaction. The amide or ester groups in our case [Y–C(:O)–] add two trigonal atoms to the other olefinic atoms which are involved in the cyclization reaction (**7**).

The structures assigned to the reaction products (**6**) are based on their i.r., n.m.r., and mass spectra. The lactones (**6a**) and (**6b**) showed i.r. absorptions at ν (C=O) 1710 ($NHCO_2R$) and 1795 (lactone) cm^{-1}; δ 3·2 (CH_3SO_3) and 4·4 (d, 2H, $J_{3,4}$ 8·5—9·5 Hz); and M^+ and $(M - MeSO_2OCH_2)^+$ (strong) ions in the high-resolution mass spectra. An *X*-ray crystal structure analysis showed the lactone (**6a**) to have the *trans* configuration.



(9)



(10)

The pyrrolidone derivative (**6d**) was further converted on treatment with KI in refluxing methanol into the iodomethyl derivative (**9**) (m.p. 165 °C) and, on treatment with $KOBu^t$ in Bu^tOH, to the bicyclic system (**10**) (m.p. 152—153 °C).

We thank Dr. M. Kapon for the *X*-ray crystal structure determinations of compounds (**6a**) and (**10**).

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[1] D. Ben-Ishai, N. Peled, and I. Sataty, *Tetrahedron Lett.*, 1980, **21**, 569.
[2] J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.
[3] H. E. Schoemaker, J. Dijkink, and W. H. Speckamp, *Tetrahedron*, 1978, **34**, 163, 173.