Tetrahedron Letters No. 25, pp. 1753-1755, 1963 Pergamon Press Ltd.
Printed in Great Britain.

A NEW RING-EXPANSION REACTION FROM ENAMINE AND DICHLOROCARBENE

Masaji Ohno
Basic Research Laboratories, Toyo Rayon Co. Ltd.,
Kamakura, Japan

(Received 6 August 1963)

Reaction of enamines with various electrophilic reagents opened quite interesting fields of organic syntheses, introducing various substituents at β-position to the amino-groups.[1]

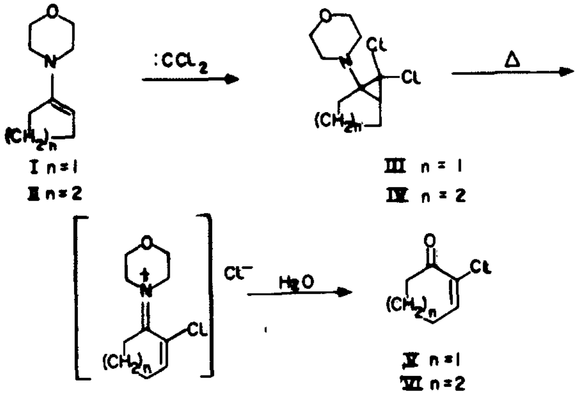
However, it is also an interesting problem to utilize the double bond itself of enamine, on which considerable investigations recently are focussed.[2,3,4,5]

We wish to report a new ring-expansion reaction from morpholine enamines and dichlorocarben.

Reaction of 1-morpholino-1-cyclopentene (I) with chloroform in the presence of excess of potassium t-butoxide in tetrahydrofuran at -45~-40° followed by removal of the solvent at 30~40° under reduced pressure after complete washing of the base, gave an unsaturated ketone, m.p. 70-71°, in 50% yield based on the enamine. The structure of the ketone has proved to be 2-chloro-2-cyclohexen-1-one (V) from its analysis (Calcd. for C_6H_7ClO: C, 55.18; H, 5.40; Cl, 27.27. Found: C, 54.88; H, 5.44; Cl, 26.96), and infrared and ultraviolet spectra which show the presence of α,β-unsaturated ketone at 1695 cm^{-1}(strong) and 1612 cm^{-1}(weak), and 242 mμ(ε,12,000), respectively.

The nuclear magnetic resonance spectra of V and its 2,4-dinitrohenylhydrozone, with m.p. 178-179° and orange color, are in full agreement with those expected from the structure showing an olefinic proton in a triplet centered at $\tau = 2.83$ with J = 6 cps and at $\tau = 3.36$ with J = 3 cps, respectively. The structure has furthermore been confirmed by converting into α-chlorocyclohexanone by catalytic hydrogenation (5% Pd-C in methanol), which is identical with authentic sample[6] spectroscopically and vapor phase chromatographically.

Analogous reaction of 1-morpholino-1-cyclohexene (II) at -20~-10° gave a stable adduct (IV),[7] m.p. 84-85°, in 85% yield, in which no olefinic



proton or double bond was observed in its N.M.R. or infrared spectra (Calcd. for $C_{11}H_{17}Cl_2NO$: C, 53.0; H, 6.81; Cl, 28.40; N, 5.60; O, 6.38. Found: C, 52.89; H, 6.87; Cl, 28.56; N, 5.61; O, 6.76). Gradual thermal decomposition of of IV 120-130° in xylene for 3 hours gave an oily product (VI) in 17% yield after chromatography on neutral alumina and morpholine hydrochloride, m.p. 171-173°, with recovery of 30% of the starting material. Prolonged heating caused the yield to decrease since the oily product was very unstable to form a tar which was difficult to identify. The structure of VI follows from its infrared and ultraviolet spectra which show the presence of α,β-unsaturated ketone at 1692 cm^{-1}(strong) and 1612 cm^{-1}(weak), and 245 mμ (ε, 6,770), respectively. The unstable ketone was converted into stable 2,4-dinitrophenylhydrazone, with m.p. 198-199° and red-purple color, which corresponds with ring-expanded structure (VI) from its analysis (Calcd. for $C_{13}H_{13}N_4ClO_4$: C, 48.05; H, 4.03; N, 17.26; Cl, 10.94; O, 19.72. Found: C, 48.15; H, 4.10; N, 17.08; Cl, 10.51; O, 20.15) and N.M.R. spectra showing an olefinic proton in a triplet centered at $\tau = 3.00$ with J = 4 cps.

Thermal decomposition of IV in boiling tetralin caused an abrupt evolution of chlorine gas and a tarry material was obtained which was also difficult to identify.

By analogy,[8,9] formation of compound (V) could be explained bv the rearrangement of an initial adduct such as III, but we have not as yet been able to prove the existence of this intermediate. However, the facile ring-expansion under such mild condition would reasonably be understood from releasement of the strained structure of biyclo[3.1.0.] hexane system besides ammonium ion participation.

General scope of this reaction is now being surveyed and will be published soon.

REFERENCES

1 See, for instance, G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovitz and R. Terell, J. Amer. Chem. Soc. **85**, 207 (1963).

2 G. Stork and I. J. Borowitz, J. Amer. Chem. Soc. **84**, 313 (1962).

3 R. Fusco, G. Bianchetti, D. Pocar and R. Ugo, Chem. Ber. **96** 802 (1963).

4 G. Opitz and F. Zimmermann, Ann. Chem. **662**, 178 (1963).

5 A. G. Cook and E. K. Fields, J. Org. Chem. **27**, 3686 (1962).

6 M. S. Newman, Org. Syn. Coll. Vol. III, John Wiley & Sons, Inc., New York, (1955), p. 188.

7 G. Stork, Amer. Chem. Soc. Meeting Abstracts of papers, p. 45Q Sept. 1961.

8 J. Sonnenberg and S. Winstein, J. Org. Chem. **27**, 148 (1962).

9 L. Ghosez and P. Haroche, Proc. Chem. Soc. **1963**, 90.