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REACTION OF OXALYL CHLORIDE WITH CHRYSANTHEMAMIDE.

(STUDIES ON CHRYSANTHEMIC ACID. II.)

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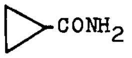
Reaction of oxalyl chloride with primary amides has been reported as a facile and general preparative method of acyl isocyanates with the exception of reaction with cyclopropanecarboxamide (I) which affords γ-chlorobutyroyl isocyanate (II) (1-3). From our interest in the reactivity of chrysanthemic acid (2,2-dimethyl-3-isobutenylcyclopropane carboxylic acid)(4), we examined the reaction of oxalyl chloride with chrysanthemamide (III) to obtain no isocyanate but instead a novelly rearranged product (IV).

Twice excess amount of oxalyl chloride was added to a solution of III (5) in methylene chloride at 0° and the mixture was stirred for 3 hrs, while being allowed to warm to room temperature, under exclusion of atmospheric moisture. Removal of the excess amounts of oxalyl chloride and methylene chloride left a brownish residue, the infrared spectrum of which showed no absorption band at around 2150 cm^{-1}, indicating no isocyanate was produced. Crystallization of the residue from methylene chloride afforded colorless needles of mp 136-139° (recrystallized from aqueous acetone) in about 10 % yield. The mass spectrum (M^+ at m/e 257) and elemental analysis established the molecular formula $C_{12}H_{15}O_3NCl$ and the structure of this compound was assigned as IV, oxazolidine-4,5-dione-2-spiro-1'-(2'-isopropenyl-3'-chloro-4',4'-dimethyl)-

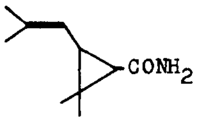
cyclopentane from the following spectral data: Ultraviolet (EtOH) λ_{max} 230 mμ (ε 6,170), Infrared (KBr) ν_{max} 3220 (NH), 1800 and 1745 (C=O), 1640 and 900 (C=CH$_2$) cm^{-1} and nmr signals (CD$_3$SOCD$_3$) at τ 4.83 and 5.14 (each for 1 H, broad singlet, C=CH$_2$), 5.72 and 6.93 (each for 1 H, AB-type quartet, $J = 13.0$ cps, $J/\Delta\tau = 0.0165$, Cl-CH-CH-C=C, the latter signal was slightly broader than the former), 7.74 (2 H, singlet, -CH$_2$-), 8.23 (3 H, singlet, C=CCH$_3$), 8.78 and 8.83 (6 H, each singlet, C(CH$_3$)$_2$)(6). The mass spectrum had peaks at m/e 257 (M^+, relative intensity 0.484 % to the base peak at m/e 154), 215 ($M^+ + 2 - 44$, 12.4 %) and 213 ($M^+ - 44$, 39.3 %); the ratio of the latter two peaks was 31.6 % which is very close to the natural abundance of Cl^{37} (32.6 %), although M^+ peak was too weak to observe $M^+ + 2$ peak (7).



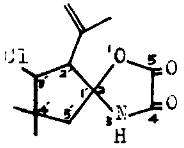
I

ClCH$_2$CH$_2$CH$_2$CO-N=C=O

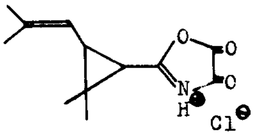
II



III



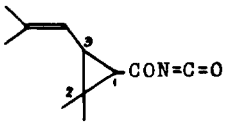
IV



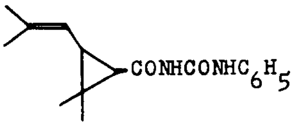
V

When the reaction was carried out in 1,2-dichloroethane at a refluxing temperature, formation of a very small amount of isocyanate was confirmed by the appearance of infrared absorption band at 2250 cm^{-1} in the reaction mixture, but the isolation of the isocyanate was not successful. In order to examine the minor possibility that IV could be an intermediate for the acyl isocyanate formation, heating IV at 120-140° under reduced pressure at 23 mmHg resulted in recovering IV from the sublimed portion. These facts might indicate that the postulated precursor for the acyl isocyanate formation (2), V in this case could be decomposed in two ways depending on the reaction temperature: at a higher temperature liberation of carbon monoxide occurs prior to or after cyclopropane ring cleavage with the liberated hydrogen chloride to afford acyl isocyanate and at a lower temperature the cyclopropane ring cleavage might be followed by recyclization to give the spiro derivative, IV.

On the other hand, chrysanthemoyl isocyanate (VI) was prepared in a moderate yield (about 50 %) by the reaction of chrysanthemoyl chloride (8) with silver cyanate in ether as a liquid of bp 60.5-61.5°/1.0 mmHg. Since VI was too sensitive towards atmospheric moisture to be microanalyzed, it was characterized by the spectral data and by the conversion to the acyl urea derivative VII. The infrared spectrum of VI had strong absorption bands at 2250 (N=C=O) and 1710 (C=O) cm^{-1} and the nmr spectrum ($CDCl_3$) had the signals at τ 5.02 (1 H, broad doublet, J = 8.5 cps, C=CH), 7.74 (1 H, unsymmetrical quartet, J = 8.5 and 6.0 cps, C-3-H), 8.24 (6 H, singlet, $C=C(CH_3)_2$), 8.45 (1 H, doublet, J = 6.0 cps, C-1-H), 8.67 and 8.78 (6 H, each singlet, gem-dimethyls at C-2)(9). Reaction of VI with aniline gave VII of mp 150-154° (from acetone) in a quantitative yield. Compound VII had a satisfactory analysis and exhibited strong infrared absorption bands at 3240 and 3140 (NH), 1700 (C=O), 1680 and 1555 (NHCONH), 1600 and 760 (phenyl) cm^{-1} (KBr).



VI



VII

Further studies on the mechanism of formation of IV and the other systems which would give spiro derivative of oxazolidine-4,5-dione by the reaction of oxalyl chloride with primary amides are in progress.

ACKNOWLEDGMENT

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REFERENCES AND NOTES

1. A. J. Speziale and L. R. Smith, J. Org. Chem., **27**, 3742 (1962).
2. A. J. Speziale and L. R. Smith, ibid., **28**, 1805 (1963).
3. A. J. Speziale, L. R. Smith, and J. E. Fedder, ibid., **30**, 4306 (1965).
4. T. Sasaki, S. Eguchi, and M. Ohno, ibid., **32**, No. 12 (1967) in press.
5. A mixture of cis- and trans-isomers (1 : 1) was used.
6. Molecular model (Dreidens) studies and the value of $J_{C-2'-H,C-3'-H}$ predicted cis-relationship of the isopropenyl- to the chloro-group, though further studies to establish the stereochemistry of IV is necessary.
7. Some other peaks related to chlorine atom appeared at m/e 201 (8.81 %) and 199 (28.6 %), 172 (10.1 %) and 170 (29.1 %).
8. The trans-isomer was used.
9. For a more detailed discussion on the nmr data of chrysanthemic acid and its derivatives, see reference 4 and references cited there.