# Ethoxalylnitrene

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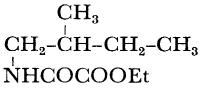
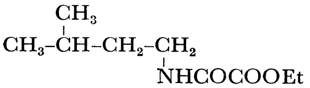
Thermolysis of ethoxalyl azide (I) in ethanol gave quantitatively ethoxycarbonylurethane (III) *via* isocyanate (II),[1] the Curtius rearrangement product, whereas photolysis of I, with the light of a low-pressure mercury arc at −78°C, in a solution of dichloromethane with alcohols yielded *N*-alkoxyethoxalamides (IV) and ethoxalamide (V) in addition to the corresponding urethanes (III). Similarly, the photolysis of I with saturated hydrocarbons gave *N*-alkyl- or *N*-cycloalkyl ethoxalamides (VI), V and II under the same experimental condition (Table 1). The formation of IV, V and VI suggests that the reaction involves a carbonyl nitrene, ethoxalylnitrene (VII), as an intermediate in a similar manner to the cases of ethyl azidoformate[2] and pivaloyl azide.[3]



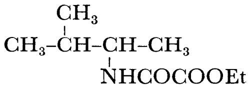
$$\underset{\text{NHCOCOOEt}}{\mathrm{CH_2}}\text{-}\overset{\mathrm{CH_3}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\text{-}\mathrm{CH_3}$$

(VIa, 2.1%)



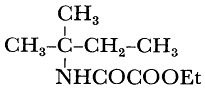
$$\mathrm{CH_3}\text{-}\overset{\mathrm{CH_3}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\text{-}\underset{\text{NHCOCOOEt}}{\mathrm{CH_2}}$$

(VIb, 0.8%)



$$\mathrm{CH_3}\text{-}\overset{\mathrm{CH_3}}{\mathrm{CH}}\text{-}\underset{\text{NHCOCOOEt}}{\mathrm{CH}}\text{-}\mathrm{CH_3}$$

(VIc, 4.2%)



$$\mathrm{CH_3}\text{-}\overset{\mathrm{CH_3}}{\underset{\text{NHCOCOOEt}}{\mathrm{C}}}\text{-}\mathrm{CH_2}\text{-}\mathrm{CH_3}$$

(VId, 14%)

In the reaction with 2-methylbutane, the product (VI) was observed to be a mixture of four kinds of isomers (VIa—VId).

The relative reactivity of ethoxalylnitrene toward primary (1°), secondary (2°) and tertiary (3°) C–H bonds in 2-methylbutane is shown to be 1 : 6.6 (±10%) : 44 (±13%). The results indicate that the reactivity of ethoxalylnitrene is more selective than that of ethoxycarbonylnitrene[2] owing to the resonance stabilization (Table 2).

TABLE 2. RELATIVE REACTIVITIES OF CARBONYLNITRENES TOWARD THE C–H BONDS IN 2-METHLBUTANE

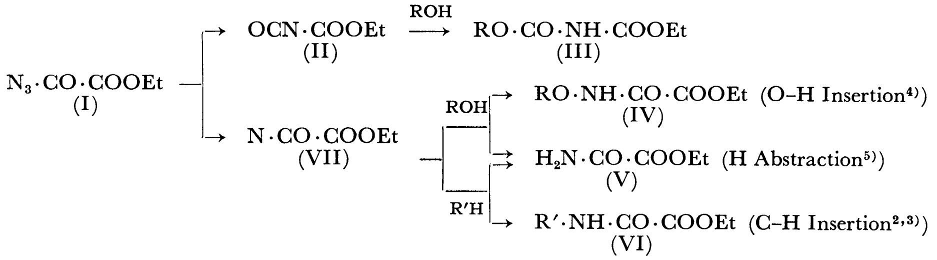
| Nitrene | 1° | : | 2° | : | 3° |
|---|---|---|---|---|---|
| N·CO·COOEt | 1 | : | 6.6(±10%) | : | 44(±13%) |
| N·COOEt | 1 | : | 9(±10%) | : | 34(± 5%) |
| N·CO·C$(CH_3)_3$ | 1 | : | 8.6(±10%) | : | 160(±25%) |

The mechanism of the insertion of ethoxalylnitrene into C–H bonds will be discussed elsewhere.

TABLE 1. PHOTOLYSIS OF ETHOXALYL AZIDE IN DICHLOROMETHANE

| Substrate | Product (mol%) | | | |
|---|---|---|---|---|
| | OCN·COOEt (II) | RO·NH·CO·COOEt (IV) | R′·NH·CO·COOEt (VI) | $H_2N$·CO·COOEt (V) |
| Ethanol | 45* | 26 | — | 10 |
| 2-Propanol | 45* | 22 | — | 16 |
| Cyclohexane | 41 | — | 16 | 4 |
| Cyclopentane | 45 | — | 17 | 4 |
| 2-Methylbutane | 47 | — | 21 | 9 |

* The yield of II shows that of urethanes derived from II.



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[1] P. A. S. Smith, "Organic Reactions," Vol. 3, ed. by D. Adams, John Wiley & Sons, New York (1962), p. 337; "Molecular Rearrangements," Vol. 1, ed. by P. de Mayo, Interscience Publishers, New York (1963), p. 528.

[2] W. Lwowski, *Angew. Chem.*, **79**, 922 (1967).

[3] G. T. Tisue, S. Linke and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 6303 (1967).

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