**Tetrahedron Letters No.36, pp. 2479-2482, 1964. Pergamon Press Ltd.
Printed in Great Britain.**

# REACTIONS OF AZIDOFORMATES WITH FUNCTIONAL GROUPS

T. J. Prosser, A. F. Marcantonio and D. S. Breslow
Research Center, Hercules Powder Company ,
Wilmington, Delaware 19899

(Received 17 July 1964 )

Although the literature is practically devoid of any mention of the reaction of azidoformates with functional groups, we have found them to react with functional groups in several different ways: by a rate-determining loss of nitrogen to yield a nitrene, i.e., an intermediate with an electron-deficient nitrogen atom; by displacement of the azide group; or by formation of an unstable intermediate.

Examples of the first type are illustrated in Table I. These runs were carried out with n-octadecyl azidoformate, measuring the increase in pressure at constant volume (1). The relatively small effect of solvent structure on rate (less than four-fold compared to diphenyl ether as standard) is a reasonably good indication that the rate-determining step in each case is loss of nitrogen from the azide and formation of a nitrene:

$$\mathrm{ROCON_3} \xrightarrow{\Delta} \mathrm{ROCO}\ddot{\underset{\cdot\cdot}{\mathrm{N}}} + \mathrm{N_2}$$

Subsequent reactions are then a function of the substrate.

Tetramethylene bis(azidoformate) reacts with n-butanol to give a 90% yield of butyraldehyde, identified as its 2,4-dinitrophenylhydrazone; tetramethylene bis(carbamate),

TABLE I

Decomposition of n-Octadecyl Azidoformate in Various Solvents[a]

| Solvent | $k_1 \times 10^4$ sec.$^{-1}$ | Relative rate | Gas evolved % of theory |
|---|---|---|---|
| Diphenyl Ether | 2.40 | 1 | 100 |
| n-Octanol | 7.40 | 3.08 | 107 |
| n-Heptaldehyde[b] | 1.99 | 0.83 | 1850 |
| Dimethyl Sulfoxide | 3.34 | 1.39 | *ca.* 150 |
| Dimethylaniline | 9.10 | 3.80 | 100 |
| Pyridine[c] | 1.42 | 1.78 | 100 |

a - 0.1 *M* at 120° b - 0.006 *M* at 120° c - 0.018 *M* at 110°

identified by comparison with a known species, was also isolated.

$$N_3COO(CH_2)_4OCON_3 + 2C_4H_9OH \xrightarrow{\Delta} 2C_3H_7CHO + NH_2COO(CH_2)_4OCONH_2 + 2N_2$$

The slight excess of gas formed in the reaction of n-octadecyl azidoformate with n-octanol was explained by studying the reaction of the azidoformate with heptaldehyde. Here an almost twenty-fold excess of gas was evolved, which by mass spectroscopic analysis was found to consist of nitrogen, large amounts of carbon monoxide, and n-hexane. The simplest explanation would appear to be that the reaction involves a free-radical chain decomposition of aldehyde catalyzed by the nitrene reacting in its triplet state.

$$ROCON_3 \xrightarrow{\Delta} ROCO\overset{\cdot\cdot}{\underset{\cdot}{N}}\cdot + N_2 \qquad \text{rate determining}$$

$$ROCO\overset{\cdot\cdot}{\underset{\cdot}{N}}\cdot + CH_3(CH_2)_5CHO \longrightarrow ROCO\overset{\cdot\cdot}{\underset{\cdot}{N}}H + CH_3(CH_2)_5\underset{\cdot}{C}O$$

$$CH_3(CH_2)_5\underset{\cdot}{C}O \longrightarrow CH_3(CH_2)_4CH_2\cdot + CO$$

$$CH_3(CH_2)_4CH_2\cdot + CH_3(CH_2)_5CHO \longrightarrow CH_3(CH_2)_4CH_3 + CH_3(CH_2)_5\underset{\cdot}{C}O$$

Analysis of the off-gas gives a clue to the nature of the reaction of n-octadecyl azidoformate with dimethyl sulfoxide. The excess gas consists of carbon dioxide, dimethyl sulfide, and nitric oxide in the ratios of 3.1:1.15:1. Apparently, therefore, the initial step is abstraction of an oxygen from dimethyl sulfoxide, followed by decomposition of the resulting nitrite.

$$\mathrm{ROCON_3 \xrightarrow{\Delta} ROCO\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} + N_2} \qquad \text{rate determining}$$

$$\mathrm{ROCO\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} + (CH_3)_2SO \longrightarrow ROCONO + (CH_3)_2S}$$

$$\mathrm{ROCONO \longrightarrow RO\dot{C}O + NO}$$

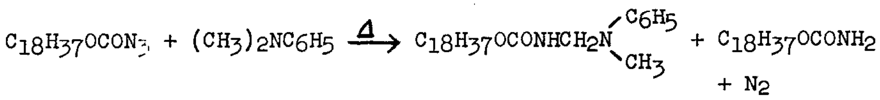
$$\mathrm{RO\dot{C}O \longrightarrow R\cdot + CO_2}$$

This sequence of reactions does not explain the excess of carbon dioxide. A solid separated which is probably the sulfoximine, $\mathrm{C_{18}H_{37}OCON\overset{O}{S}(CH_3)_2}$, although it was not isolated as a pure compound. An analogous material was obtained in rather low yield by Horner and Christmann (2) from the photochemical reaction of a sulfonyl azide with a sulfoxide.

There are many reactions, however, which do not go through a nitrene intermediate. Thus, no gas is evolved when a primary amine is reacted with an azidoformate; the reaction is one of nucleophilic displacement, the azide salt being stable at the reaction temperature.

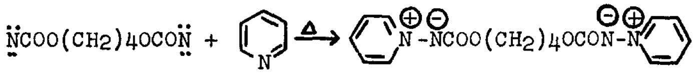
$$\mathrm{ROCON_3 + 2R'NH_2 \longrightarrow ROCONHR' + R'NH_3^+\ N_3^-}$$

With secondary aliphatic amines the amount of gas is less than theoretical, indicating some nucleophilic displacement, but the gas evolved comes off at 20-100 times the expected rate, indicating the formation of an intermediate less stable than the azidoformate. With tertiary aliphatic amines the calculated quantity of gas is evolved, but at ten times the expected rate. Dimethylaniline reacts more normally (Table I). According to Hafner (3) the major reaction is one of insertion into the methyl group and this insertion has been confirmed. Some octadecyl carbamate is also formed.



$$C_{18}H_{37}OCON_3 + (CH_3)_2NC_6H_5 \xrightarrow{\Delta} C_{18}H_{37}OCONHCH_2N\begin{matrix}\nearrow C_6H_5\\ \searrow CH_3\end{matrix} + C_{18}H_{37}OCONH_2 + N_2$$

The reaction of n-octadecyl azidoformate with pyridine is first order at the expected rate and therefore involves a nitrene intermediate. The product from pyridine and tetramethylene bis(azidoformate) is the ylid, the reaction being similar to that reported for sulfonyl azides (4).



Triphenylphosphine and trimethyl phosphite, however, react with azidoformates at room temperature.

$$C_2H_5OCON_3 + PX_3 \longrightarrow C_2H_5OCON{=}PX_3 + N_2$$

Although the mechanism is unknown (5), there can be little doubt that the reaction does not involve a nitrene intermediate.

## REFERENCES

1. T. J. Prosser, A. F. Marcantonio, C. A. Genge and D. S. Breslow, Tetrahedron Letters
2. L. Horner and A. Christmann, Chem. Ber., 96, 388 (1963).
3. K. Hafner, private communication.
4. J. N. Ashley, G. L. Buchanan and A. P. T. Easson, J. Chem. Soc., 60 (1947).
5. J. E. Leffler and Y. Tsuno, J. Org. Chem., 28, 902 (1963).