

Aliphatic Hydrazonates

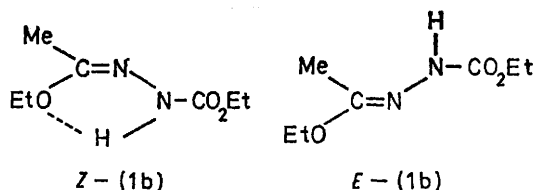
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Summary Ethoxycarbonylnitrene reacts with the N-H bond of imidates to form hydrazonates.

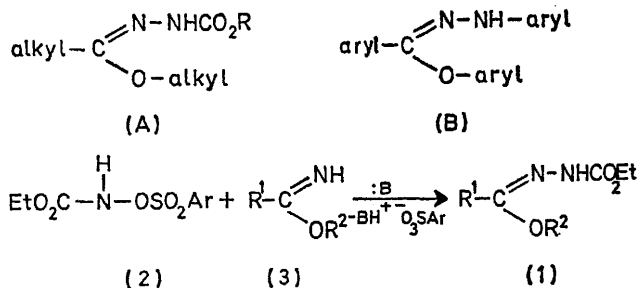
To our knowledge, aliphatic hydrazonates (A) have not been reported,¹ although some aromatic ones (B) are known.² These were obtained *via* the hydrazidic halides, Ar-CX=N-NHAr, which are readily prepared only when Ar is an aromatic group bearing electron-withdrawing substituents. We were unable to obtain aliphatic hydrazonates when we tried to use the hydrazidic halide route. We report the synthesis of (1) from ethoxycarbonylnitrene and aliphatic imidates. The base :B, employed to generate the nitrene EtO₂C-N from (2)³ can be the imidate (3) itself, but Et₃N is more useful because of its greater basicity and the insolubility of its *p*-nitrobenzenesulphonate. Best yields of (1) (*ca.* 40%) are obtained with concentrated

and ethyl carbamate from the nitrene, and 2,4,6-trialkyl-1,3,5-triazines from the imidates. The reaction mixture is worked up by evaporation *in vacuo*, addition of ether, and evaporation, followed by warming the residue at 40° at 1 mmHg to remove the excess of imidate and the triazine. An ether solution of the residue is filtered through unactivated silica gel, or crystallised at -40°. The product is recrystallised from ether-pentane (1:1). *E*- and *Z*-isomers are best separated after preparation of seed crystals by g.l.c.



The methyl hydrazone (1a)[†] (mixture of *E*- and *Z*-isomers), was obtained in 38% yield without isolation of the free methyl acetimidate; m.p. 79–80°, *m/e* 160; δ 6.8 br (1H), 4.2 (q, 2H), 3.73 (s, 3H), and 1.25 (t, 3H). Hydrolysis with 6N-HCl gave ethyl carbazate.

The *Z*- and *E*-isomers of the ethyl hydrazone (1b)[†] were separated by crystallisation. The isomer of m.p. 65–66° was assigned the *Z*-configuration⁴ because of the chemical shifts of the NH and Me signals in the n.m.r. spectrum which were at lower fields than the corresponding signals in the other isomer: δ 8.15 br (1H), 4.2 (overlapping q, 4H), 2.1 (s, 3H), and 1.35 (2t, 6H). The i.r. spectrum shows a sharp NH band at 3405 cm⁻¹ (CCl₄). The *E* isomer of (1b) has m.p. of 55–56°; δ 7.0 br (1H, NH), 4.2 (2 q,



a; Ar = *p*-NO₂·C₆H₄; R¹ = R² = Me

b; Ar = *p*-NO₂·C₆H₄; R¹ = Me; R² = Et

CH₂Cl₂ solutions and a 5–8 times excess of the imidate. By-products are formed copiously; diethylhydrazodiformate

[†] Satisfactory elemental analyses were obtained.

4H), 1.95 (s, 3H), and 1.30 (2 t, 6H), ν_{\max} 3420 br cm^{-1} (CCl_4).

The =N-H group of the imidates reacts with ethoxycarbonylnitrene markedly slower than do N-H groups of primary and secondary amines. In competition for the nitrene $\text{EtO}_2\text{C-N}$, the =N-H function of methyl acetimidate was only 2.3 times more reactive than each C-H group of cyclohexane, as measured by product analysis. Amino-groups are 40–80 times more reactive than the cyclohexane C-H groups in such competition experiments.⁵ The $\text{p}K_{\text{a}}$ value does not seem to be a decisive factor, aniline reacting about as well as do aliphatic amines. The $\text{p}K_{\text{a}}$ of imidates should be greater than 2, and even with diphenylamine ($\text{p}K_{\text{a}}$ 0.79) a 30% yield of ethyl 3,3-diphenylcarbazate was obtained.⁷ Thus, it seems to be the difference in hybridiza-

tion on nitrogen that causes the different reactivities towards the nitrene. This low reactivity of the =N-H group limits the scope of our synthesis. Since the reactivity of the benzene ring towards N-CO₂Et is *ca.* 12 times that of a C-H bond in cyclohexane,⁸ an extension of our hydrazonate synthesis to molecules containing phenyl groups does not seem promising. Indeed, the reaction of ethoxycarbonylnitrene with ethyl benzimidate gave only very small yields of the desired ethyl *N*-ethoxycarbonylbenzohydrazonate [n.m.r.: δ 8.7 br (1H), 7.5 (m, 5H), 4.2 (q, 2H), 3.95 (q, 2H), and 1.32 (t, 3H); M^+ , m/e 236].

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¹ The azine $\text{EtO-MeC=N-N=CMe-OEt}$ has been obtained in a low yield from ethyl acetimidate and hydrazine in ethanol; W. Oberhammer, *Monatsh.*, 1933, **63**, 285.

² A. F. Hegarty, J. A. Kearny, M. P. Cashman, and F. L. Scott, *Chem. Comm.*, 1971, 689; A. F. Hegarty, J. A. Kearny, and F. L. Scott, *Tetrahedron Letters*, 1972, 3211.

³ W. Lwowski and T. J. Maricich, *J. Amer. Chem. Soc.*, 1965, **87**, 3630.

⁴ G. C. McCarty in 'The Chemistry of the Carbon-Nitrogen Double Bond,' S. Patai, ed., Wiley-Interscience, New York, 1970, p. 393ff; C. I. Stassinopoulou, C. Ziodru, and G. J. Karabatsos, *Tetrahedron Letters*, 1972, 3671, and references therein.

⁵ W. Lwowski and L. H. Selman, unpublished results.

⁶ Cf. T. Okuyama, T. C. Pletcher, D. J. Sahn, and G. L. Schmir, *J. Amer. Chem. Soc.*, 1973, **95**, 1253.

⁷ G. Woods and W. Lwowski, unpublished results.

⁸ W. Lwowski and R. L. Johnson, *Tetrahedron Letters*, 1967, 891.