

ν -Triazolines. Part V.¹ Rearrangement of Triazolines from Cyclopropyl-enamines and Toluene-*p*-sulphonyl Azide

By Donato Pocar * and Pasqualina Trimarco, Istituto di Chimica Organica della Facoltà di Farmacia, Università di Milano, Viale Abruzzi 42, 20131 Milano, Italy

The reactions of tosyl azide with enamines bearing a cyclopropyl group in the α -position (1) afford, *via* unstable triazolines (2), zwitterionic intermediates (3) which can lead (i) through C-C cleavage to diazo-compounds (6) and amidines (5) and (ii) through nitrogen loss and rearrangement to amidines (7).

DURING our work on the reactions of arenesulphonyl azides with enamines²⁻⁹ evidence has been found showing that unstable 5-amino- ν -triazoline intermediates (2) are formed which react according to the paths (i) and/or (ii). Path (i) is followed where $R^1 = R^2 = H$,^{3,4,7} and where R^1 , R^2 , and R^3 are alkyl the rearrangement reaction is preferred.^{2,4,5,8} We now report the corresponding reactions of enamines bearing a cyclopropyl group in the α -position. The possibility of interaction of the cyclopropyl group with a carbocation centre at the β -position and its great ability to migrate are well documented.¹⁰ We were also interested in examining the influence of β -substituents on the course of reaction.

The reactions between the enamines (1a-f) and tosyl azide were performed at room temperature in benzene solution. All the enamines have the cyclopropylvinyl structure¹¹ and their configurations are as indicated in Table 1. The enamine (1f) was used as the

equilibrium mixture with its tautomer. The amidines (5a, b, and f) and (7a-f) formed are listed in Table 1, along with the ratio in which they were formed and their

TABLE I
Reactions of enamines (1) with tosyl azide

Enamine	Amidines produced	Ratio (5) : (7)	Yield [(5) + (7)](%)
(1a)	(5a) and (7a)	75 : 25	80
(1b) (<i>E</i> : <i>Z</i> 7 : 3)	(5b) and (7b)	30 : 70	74
(1c)	(5a) and (7c)	25 : 75	91
(1d)	(5a) and (7d)	10 : 90	82
(1e) (<i>E</i>)	(5a) and (7e)	60 : 40	90
(1f) (<i>E</i> : <i>Z</i> 6 : 4)	(5f) and (7f)	40 : 60	50

overall yields. The formation in appropriate cases of the diazo-compound was inferred from the isolation of the corresponding amidine (5) [path (i)]; and no effort was made to isolate it. The structures of all amidines

¹ Part IV, R. Stradi, D. Pocar, and G. Bianchetti, *Org. Magnetic Resonance*, 1972, **4**, 247.

² R. Fusco, G. Bianchetti, and D. Pocar, *Gazzetta*, 1961, **91**, 933.

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

⁴ G. Bianchetti, D. Pocar, P. Dalla Croce, and A. Vigevani, *Chem. Ber.*, 1965, **98**, 2715.

⁵ G. Bianchetti, P. Dalla Croce, and D. Pocar, *Ist. Lomb. Acc. Sci. Lett.*, 1965, **A99**, 259.

⁶ G. Bianchetti, D. Pocar, and P. Dalla Croce, *Ist. Lomb. Acc. Sci. Lett.*, 1965, **A99**, 316; *Gazzetta*, 1965, **95**, 1220.

⁷ P. Ferruti, D. Pocar, and G. Bianchetti, *Gazzetta*, 1967, **97**, 110.

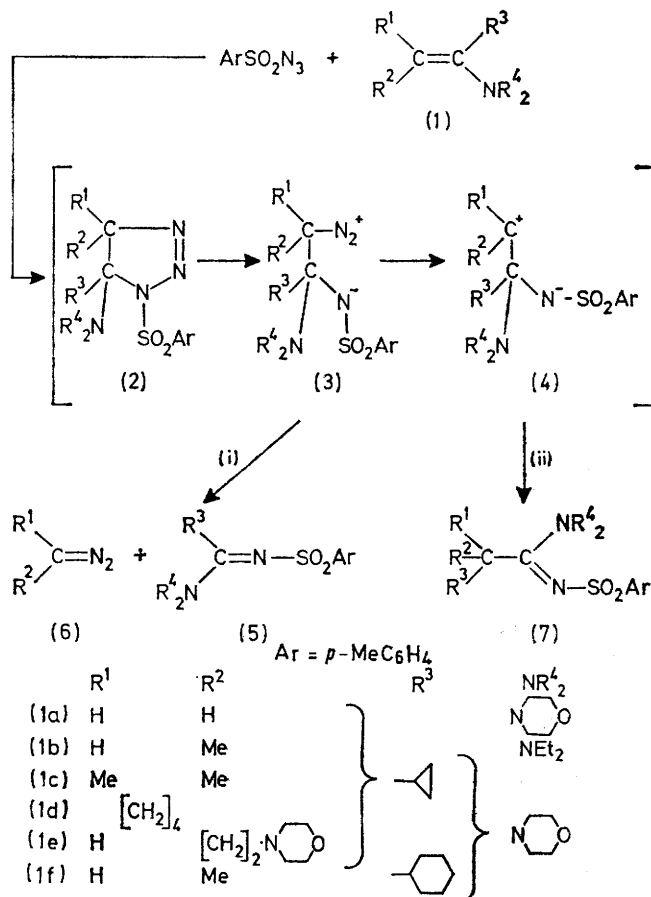
⁸ D. Pocar, G. Bianchetti, and P. Ferruti, *Gazzetta*, 1967, **97**, 597; P. Dalla Croce and R. Stradi, *Ist. Lomb. Acc. Sci. Lett.*, 1967, **A101**, 692.

⁹ P. Dalla Croce, D. Pocar, and R. Stradi, *Ist. Lomb. Acc. Sci. Lett.*, 1967, **A101**, 680.

¹⁰ For a review, see J. Haywood-Farmer, *Chem. Rev.*, 1974, **74**, 315.

¹¹ D. Pocar, R. Stradi, and P. Trimarco, *Tetrahedron*, 1975, **31**, 2427.

were assigned on the basis of their ^1H n.m.r. spectra (solvent C_6D_6).



The results show that both paths (i) and (ii) are operative at the same time. This behaviour has been

(7).^{*} A possible explanation is related to the ability of alkyl substituents to stabilize the carbocation (4), thus making path (ii) easier. Mechanism (ii) is a general pathway for the reactions of azides bearing strongly electron-withdrawing substituents¹² with strained or unstrained olefins and vinyl ethers.¹³ In the particular case of enamines, path (i) becomes important probably because cleavage of the C-C bond to give the diazo-compound can be assisted by the amino-substituent. However, it seems that the basicity of the amine residue has little influence on ratio of the products (5) and (7).¹⁴

Finally, the presence of the α -cyclopropyl group does not affect particularly the pathway of the reaction with tosyl azide. Also, the migratory aptitude of the cyclopropyl group in our systems is similar to that of the cyclohexyl group [enamine (1f)] and that of the isopropyl group.⁴

EXPERIMENTAL

Enamines.—The enamines (1a, b, d, and e) were prepared as previously described;¹¹ (1c) was obtained by the same procedure from cyclopropyl isopropyl ketone¹⁵ as a liquid, b.p. 85°C at 4 Torr (yield 50%). The enamine (1f) was prepared according to the same method from cyclohexyl ethyl ketone, morpholine, and titanium tetrachloride in light petroleum as a liquid, b.p. $95\text{--}97^\circ\text{C}$ at 0.3 Torr (yield 50%). Compound (1f) is obtained along with its tautomer, 1-cyclohexylidene-1-morpholinopropane, as the equilibrium mixture which, according to its ^1H n.m.r. spectrum (solvent C_6D_6) contains about 70% of (1f).

Reactions with Tosyl Azide.—A solution (ca. 10%) of the enamine in anhydrous benzene at room temperature was treated dropwise with an equimolar amount of a solution (ca. 20%) of tosyl azide in anhydrous benzene. Stirring was continued until the end of the reaction, normally indicated by quantitative evolution of nitrogen.[†] The crude reaction mixtures were analysed by t.l.c. and the

TABLE 2

Compd.	M.p. ($^\circ\text{C}$)	Recryst. from	Formula	Analysis (%) [*]		
				C	H	N
(5a)	156—158	Pr^1OH	$\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$	58.2 (58.45)	6.4 (6.55)	9.1 (9.1)
(5b)	79—81	Pr^1_2O	$\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$	60.9 (61.2)	7.3 (7.5)	9.75 (9.5)
(5f)	(Oil)		$\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_3\text{S}$	61.3 (61.7)	7.5 (7.5)	7.9 (8.0)
(7a)	(Oil)		$\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_3\text{S}$	59.3 (59.6)	6.55 (6.9)	8.5 (8.7)
(7b)	76—78	Pr^1_2O	$\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_3\text{S}$	63.05 (63.35)	7.9 (8.15)	8.4 (8.7)
(7c)	137—139	Pr^1_2O	$\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_3\text{S}$	62.05 (61.7)	7.55 (7.5)	7.85 (8.0)
(7d)	116	Pr^1_2O	$\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_3\text{S}$	64.1 (63.8)	7.3 (7.5)	7.6 (7.45)
(7e)	(Oil)		$\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_3\text{S}$	62.5 (63.0)	8.0 (7.95)	9.85 (10.0)
(7f)	156	Pr^1_2O	$\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_3\text{S}$	63.4 (63.45)	8.15 (8.0)	7.2 (7.4)

^{*} Required values in parentheses. The structures of the products were confirmed by ^1H n.m.r. (solvent C_6D_6 or CDCl_3 ; Me_4Si standard).

observed previously only in the case of enamines derived from methyl isopropyl and methyl isobutyl ketone.⁴ The ratio between the products (5) and (7) appears to depend on the nature of the β -substituents; in the series of enamines (1a—d and f) increasing β -substitution leads to increasing amounts of rearrangement products

^{*} The complexity of the structure of the enamine (1e) makes it difficult in this case to rationalize the ratio of (5) to (7).

[†] Compound (1f) was used as the equilibrium mixture with its tautomer, yielding at least four products from which (5f) and (7f) were isolated and identified.

products were isolated by one of the following methods; their properties are collected in Table 2.

¹² P. Scheiner, 'Triazoline Decomposition in Selective Organic Transformations,' ed. B. S. Thyagarajan, vol. 1, Wiley-Interscience, 1970, p. 327; R. A. Wohl, *J. Org. Chem.*, 1973, **38**, 3862; R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, 1972, **105**, 1324; M. E. Hermes and F. D. Marsh, *J. Org. Chem.*, 1972, **37**, 2969; R. S. McDaniel and A. C. Oehlschlager, *Tetrahedron*, 1969, **25**, 1381.

¹³ R. A. Abramovitch, G. N. Knaus, M. Pavlin, and W. D. Holcomb, *J.C.S. Perkin I*, 1974, 2169 and references therein.

¹⁴ R. Stradi and P. Dalla Croce, personal communication.

¹⁵ S. C. Bunce, *J. Amer. Chem. Soc.*, 1955, **77**, 6616.

(a) *Enamines* (1a, and c—e). The crude solution was evaporated to dryness and a first crop of the less soluble amidine was obtained by recrystallization (from di-isopropyl ether or propan-2-ol). The mother liquors were evaporated and the residue was chromatographed on a silica column (Kieselgel 60; Merck),

with benzene-ethyl acetate containing 25—60% benzene as eluant.

(b) *Enamines* (1b and f). The crude mixture was evaporated and chromatographed directly on a silica column, eluted as in (a).

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