

## The Photochemical Synthesis of Alkyl 2,2-Dimethyl-3-(2-methylpropenyl)aziridine-1-carboxylates and 3,3-Dimethylaziridine-1,2-dicarboxylates from Alkyl Azidoformates

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The photolysis of alkyl azidoformates in 2,5-dimethylhexa-2,4-diene gave alkyl 2,2-dimethyl-3-(2-methylpropenyl)-aziridine-1-carboxylates (azachrysanthemates). Similarly, photolysis of the same azidoformates in alkyl 3-methylcrotonates gave dialkyl 3,3-dimethylaziridine-1,2-dicarboxylates (azacaronates). The copper-catalysed pyrolysis of ethyl azidoformate in 2,5-dimethylhexa-2,4-diene, however, led to a  $\Delta^2$ -oxazoline. An open-chain unsaturated carbamate was obtained, instead of the expected benzyl ester, on treatment of ethyl 2,2-dimethyl-3-(2-methylpropenyl)aziridine-1-carboxylate with benzyl alcohol. The novel cyclic amino-acid, 3,3-dimethylaziridine-2-carboxylic acid, was prepared by hydrolysis of dimethyl 3,3-dimethylaziridine-1,2-dicarboxylate.

THERE has been much recent interest in the addition and insertion reactions of nitrenes (*e.g.* ref. 1). Addition of alkoxy-carbonylnitrenes, prepared by the photochemical decomposition of azidoformates (1), to substituted olefins generally leads to alkyl aziridine-1-carboxylates. We report the application of this reaction to the synthesis of alkyl 2,2-dimethyl-3-(2-methylpropenyl)aziridine-1-carboxylates (2) and 3,3-dimethylaziridine-1,2-dicarboxylates (3).

The addition of nitrenes to conjugated dienes<sup>1b,2,3</sup> occurs with only one of the double bonds. The azachrysanthemates (2) were required as part of a study of pyrethrum analogues, and the initial approach to their synthesis was based on the preparation<sup>4</sup> of ethyl chrysanthemate from ethyl diazoacetate and 2,5-dimethylhexa-2,4-diene (4). Ethyl azidoformate (1; R<sup>1</sup> = Et) was added to the diene (4) under reflux in the presence of copper powder, and the heating was continued until evolution of nitrogen ceased. The isolated

product, however, was the  $\Delta^2$ -oxazoline (5), formed either by the 1,3-dipolar addition of the nitrene to the carbon-carbon double bond, or, more likely, by rearrangement of the initially formed aziridine (2; R<sup>1</sup> = Et). Compound (5) was identified on the basis of the results of Lwowski and his co-workers,<sup>1b,5</sup> who observed a similar rearrangement of ethyl aziridine-1-carboxylates on passage through a g.l.c. apparatus. The i.r. and n.m.r. spectra of compound (5) agreed well with those of the  $\Delta^2$ -oxazolines reported in ref. 5.

However, irradiation at room temperature of a 10% solution of ethyl azidoformate (1; R<sup>1</sup> = Et) in the diene (4) until the i.r. absorption at *ca.* 2150 cm<sup>-1</sup> had disappeared led in good yield to the ester (2; R<sup>1</sup> = Et), which was isolated by fractional distillation at low pressure. The methyl and allyl ( $\nu_{\max}$ , 985 and 930 cm<sup>-1</sup>) esters (2; R<sup>1</sup> = Me or CH<sub>2</sub>:CH·CH<sub>2</sub>) were similarly prepared, but although the benzyl and tetrahydrofurfuryl esters were prepared in a crude form, and identified by

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<sup>1</sup> See (a) W. Lwowski, *Angew. Chem. Internat. Edn.*, 1967, **6**, 897, and references cited therein; (b) A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.*, 1968, **33**, 481; (c) J. M. Simson and W. Lwowski, *J. Amer. Chem. Soc.*, 1969, **91**, 5107.

<sup>2</sup> C. W. Rees and R. S. Atkinson, *Chem. Comm.*, 1967, 1230.

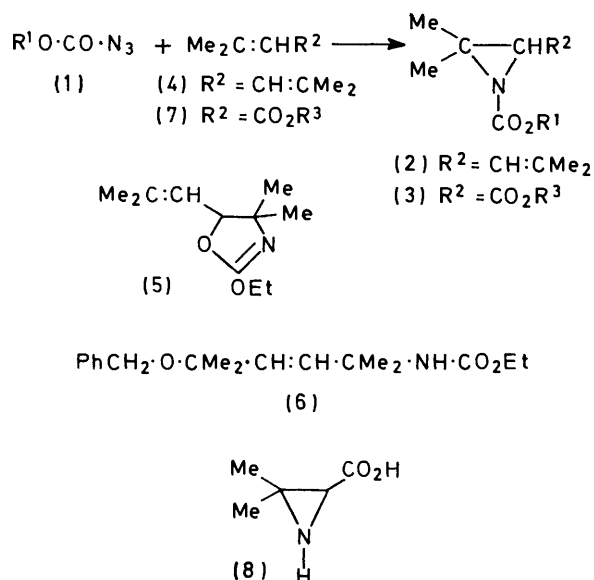
<sup>3</sup> K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Letters*, 1964, 3953.

<sup>4</sup> I. G. M. Campbell and S. H. Harper, *J. Chem. Soc.*, 1945, 283.

<sup>5</sup> W. Lwowski and T. J. Maracich, *J. Amer. Chem. Soc.*, 1965, **87**, 3630.

their i.r. and n.m.r. spectra, they were not isolated pure, owing to their decomposition on distillation.

An alternative approach to the benzyl ester involved heating the ethyl ester on a steam-bath under reduced



pressure with an excess of benzyl alcohol, and then removing unchanged alcohol under high vacuum. This reaction, however, led to ring opening, resulting from attack of the benzyl alcohol on the isobutenyl group, to give the *trans*-olefinic carbamate (6) in quantitative yield.

The addition of alkoxy-carbonylnitrenes to  $\alpha\beta$ -unsaturated esters has not been reported previously. Irradiation of 10% solutions of azidoformates (1) in 3-methylcrotonates (7) similarly gave good yields of the diesters (3). Once again, the lower-boiling esters could

Me) with aqueous ethanolic sodium hydroxide at room temperature, and followed by adjustment of the pH to 5, gave an almost quantitative yield of the novel 3,3-dimethylaziridine-2-carboxylic acid (8). Attempts to hydrolyse and decarboxylate the ethyl ester (2; R<sup>1</sup>=Et) under similar conditions failed.

#### EXPERIMENTAL

I.r. spectra were determined for liquid films or Nujol mulls. N.m.r. spectra were determined for solutions in deuteriochloroform, with tetramethylsilane as internal reference, unless otherwise stated. Azidoformates were prepared by the method used by Lwowski and Mattingly<sup>7</sup> for the ethyl ester, and distilled before use under reduced pressure.

*Copper-catalysed Decomposition of Ethyl Azidoformate.*—2,5-Dimethylhexa-2,4-diene<sup>8</sup> (88 g, 0.8 mol) and copper-bronze (2.0 g) were heated under reflux at 120–130°C. With vigorous stirring, ethyl azidoformate (9.2 g, 0.08 mol) was added dropwise so as to maintain a rapid evolution of nitrogen. Fractionation of the product yielded 2-ethoxy-4,4-dimethyl-5-(3-methylpropenyl)- $\Delta^2$ -oxazoline (5) (8.5 g, 54%), b.p. 102.5° at 10.5 mmHg (Found: C, 66.8; H, 9.7; N, 7.4. C<sub>11</sub>H<sub>19</sub>NO<sub>2</sub> requires C, 67.0; H, 9.7; N, 7.1%),  $\nu_{\text{max}}$  1660s cm<sup>-1</sup> (C=N),  $\tau$  4.66 (1H, d, *J* 9 Hz, showing long-range splitting with two Me groups, *J* 1 Hz), 5.14 (1H, d, *J* 9 Hz, ring proton), 5.79 (2H, q, *J* 7 Hz), 8.22 and 8.30 (6H, both d, *J* 1 Hz), 8.67 (3H, t, *J* 7 Hz), 8.74 (3H, s), and 8.91 (3H, s). [Lwowski *et al.*<sup>10</sup> observed  $\nu_{\text{max}}$  1660 cm<sup>-1</sup> and  $\tau$  5.0–5.3 (1H, m, ring proton) for an analogous compound.]

*Photochemical Decomposition of Azidoformates.—General procedure.* 10% Solutions of the azidoformate in either 2,5-dimethylhexa-2,4-diene or the alkyl 3-methylcrotonate, were irradiated at room temperature by an external, low-pressure, quartz spiral mercury lamp (principal emission at 253.7 nm) through quartz. The contents were stirred vigorously under nitrogen with a wad of glass wool attached to the stirrer blade (to keep the inside surface of the flask

Aziridine esters (2) and (3)

Ester	R <sup>1</sup>	R <sup>3</sup>	B.p. (T/°C; P/mmHg)	$n_D$ (T/°C)	Found (%)			Required (%)		
					C	H	N	C	H	N
(2)	Me		96.5/11	1.4595(23)	65.2	9.5	7.7	65.5	9.35	7.65
(2)	Et		68/0.55	1.4589(19)	67.0	9.9	7.2	67.0	9.7	7.1
(2)	Allyl		118/15	1.4673(23)	69.0	9.15	6.6	68.9	9.15	6.7
(3)	Me	Me	57/0.07	1.4450(24)	51.0	7.0	7.5	51.3	7.0	7.5
(3)	Me	Et	67/0.10	1.4443(24)	54.1	7.8	7.0	53.7	7.5	7.0
(3)	Et	Me	66/0.13	1.4433(24)	54.1	7.3	6.9	53.7	7.5	7.0
(3)	Et	Et	86/0.65	1.4463(20)	56.4	8.2	6.8	56.3	8.0	6.5

be isolated in a high state of purity, but the benzyl ethyl ester (3; R<sup>1</sup>=PhCH<sub>2</sub>, R<sup>2</sup>=Et) decomposed on distillation.

Physical and analytical data for the pure esters (2) and (3) are listed in the Table. All the aziridine esters prepared were characterised by absorption in the i.r. at *ca.* 1315m and 800w cm<sup>-1</sup> (ring modes<sup>6</sup>) and in the n.m.r. at *ca.*  $\tau$  7 (ring proton). Yields were in the range 60–70%.

Mild hydrolysis of the dimethyl ester (3; R<sup>1</sup>=R<sup>3</sup>=

clean). Irradiation was continued until the i.r. absorption at *ca.* 2150 cm<sup>-1</sup>, characteristic of the azide function, had disappeared, and the products were isolated by fractional distillation under reduced pressure, or high vacuum. Products were characterised by their i.r. and n.m.r. spectra. Compounds prepared thus include: ethyl 2,2-dimethyl-3-(2-methylpropenyl)aziridine-1-carboxylate (2; R<sup>1</sup>=Et),  $\nu_{\text{max}}$  1725s, 1260s, and 1095m (ester), and 1330m and 800w cm<sup>-1</sup> (aziridine),  $\tau$  5.00 (1H, d, *J* 7 Hz, showing long-range splitting with two Me groups), 5.85 (2H, q, *J* 7 Hz), 7.1 (1H, d, *J* 7 Hz, ring proton), 8.22br (6H, s), and 8.69(s), 8.73 (t, *J*

<sup>6</sup> H. L. Spell, *Analyt. Chem.*, 1967, **39**, 185.

<sup>7</sup> W. Lwowski and T. W. Mattingly, *J. Amer. Chem. Soc.*, 1965, **87**, 1947.

<sup>8</sup> S. H. Harper, H. W. B. Reed, and R. A. Thompson, *J. Sci. Food Agric.*, 1951, **2**, 94.

7 Hz), and 8.77 (s) (total 9H); and *diethyl 3,3-dimethylaziridine-1,2-dicarboxylate* (3;  $R^1 = R^3 = \text{Et}$ ),  $\nu_{\text{max}}$  1760s, 1730s, 1315m, 1250s, 1190s, 1160m, 1040m, and 800w  $\text{cm}^{-1}$ ,  $\tau$  5.5–6.0 (4H, m), 7.00 (1H, s, ring proton), 8.61br (6H, s), and 8.71 (6H, t,  $J$  7 Hz).

*Action of Benzyl Alcohol on Ethyl 2,2-Dimethyl-3-(2-methylpropenyl)aziridine-1-carboxylate.*—The ester (2;  $R^1 = \text{Et}$ ) was mixed with a ten-fold excess of benzyl alcohol, and the mixture heated at 100° and 15 mmHg for 2 h. The pressure was reduced to 0.03 mmHg and heating was continued at 100° until no further volatile components were evolved. *Ethyl N-(4-benzyloxy-1,1,4-trimethylpent-trans,2-enyl)carbamate* (6) was obtained quantitatively (Found: C, 70.2; H, 8.8; N, 4.8.  $\text{C}_{18}\text{H}_{27}\text{NO}_3$  requires C, 70.8; H, 8.9; N, 4.6%),  $\nu_{\text{max}}$  3300m, 1720s, 1500s, 1245s, 1085s, and 975w  $\text{cm}^{-1}$ ,  $\tau$  4.21 (1H, d,  $J$  17 Hz), 4.40 (1H, d,  $J$  17 Hz), and 5.28br (1H, s, NH), and other bands consistent with the proposed structure.

*Hydrolysis of Dimethyl 3,3-Dimethylaziridine-1,2-dicarboxylate.*—The ester (3;  $R^1 = R^3 = \text{Me}$ ) (3.8 g, 0.02 mol)

was stirred at room temperature with a solution of sodium hydroxide (1.6 g, 0.04 mol) in ethanol (25 ml) and water (25 ml) for 20 h. Further sodium hydroxide (1.6 g) was added, the mixture was stirred for an additional 8 h until homogeneous, and left overnight. With cooling (ice-water), a solution of sulphuric acid (3.92 g, 0.04 mol) in water (15 ml) was added during 0.5 h. Carbon dioxide was evolved. Solid sodium hydrogen carbonate was added to adjust the pH to 5. Ethanol (20 ml) was added, and the solution was filtered to remove sodium sulphate. Removal of the solvent under reduced pressure (< 50°) yielded *3,3-dimethylaziridine-2-carboxylic acid* (8) (2.1 g, 91%), m.p. 190° (decomp.) (from 50% aqueous ethanol) (Found: C, 51.9; H, 7.75; N, 12.3.  $\text{C}_6\text{H}_9\text{NO}_2$  requires C, 52.2; H, 7.8; N, 12.2%),  $\nu_{\text{max}}$  3100–2200vbr, 1600s,br, 1430s, and 1140s  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{D}_2\text{O}$ ) 6.42 (1H, s) and 8.43 and 8.50 (6H, both s of equal intensity).

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