New Ylides from *gem*-Dicyano Epoxides

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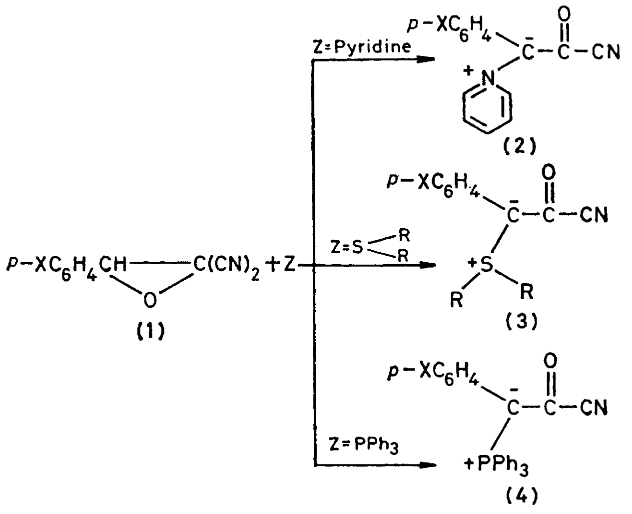
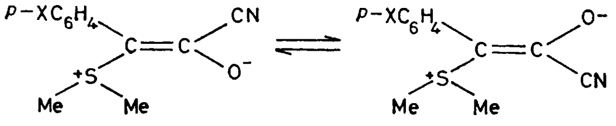
Summary A novel ring opening of trisubstituted *gem*-dicyano epoxides by pyridine, dialkyl sulphides, or triphenylphosphine has been shown to give new ylides stabilized by a COCN group.

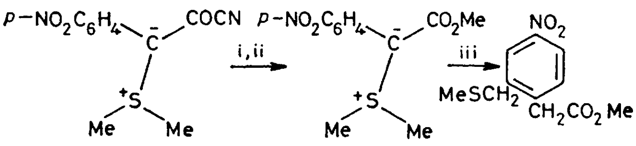
THE reaction of pyridine and dialkyl sulphides with tetracyanoethylene oxide to give the corresponding pyridinium and sulphonium dicyanomethylides and carbonyl cyanide is well-known.[1] A pyridinium ylide of the 1,3-dioxoindan type has been prepared by a similar reaction.[2]



The course of the reaction of the *gem*-dicyano epoxides (**1**) with nucleophilic compounds (pyridine, dialkyl sulphides, or triphenylphosphine) was, however, radically different. Carbonyl cyanide was not formed but the new pyridinium, sulphonium, or phosphonium ylides (**2**)—(**4**), stabilized by the reactive COCN group, were obtained. For example (**2**; X = Cl or NO_2) was obtained by refluxing (**1**) (1 g) and pyridine (10 ml) for 2 min, and (**3**; X = Cl or NO_2) was obtained by refluxing (**1**) (1 g) with dimethyl sulphide (1 g) and dry tetrahydrofuran (20 ml) for 24 h. The ylidic structures of compounds (**2**)—(**4**) are in agreement with their spectral data (see Table).[3,4]

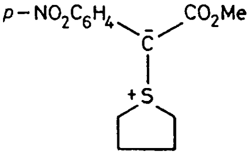

(3a) (3b)

As previously described for other stabilized sulphonium[4] or phosphonium[5,6] ylides two forms were observed by ^1H n.m.r. spectroscopy for the ylides (**3**). The ratio (**3a**) : (**3b**) (X = NO_2 or Cl), in nitrobenzene, was found to be 79 : 21; the coalescence temperatures for the methyl protons was 130 °C (X = NO_2) and 190 °C (X = Cl).



SCHEME i, CF_3CO_2H–MeOH; ii, NaOH; iii, heat, MeOH.

When 1 M NaOH was added to a methanol–trifluoroacetic acid solution of the ylides (**2**) and (**3**) the corresponding ylidic esters were obtained. For example, the sulphonium ylide (**3**; X = NO_2) gave the sulphonium ylide (**5**) [m.p. 160 °C; $\nu_{C=O}$ (Nujol) 1642 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 3·08 (6H, s), 3·75 (3H, s), and 7·86 (4H, m)] in 98% yield. Thermolysis of (**5**) gave the Sommelet–Hauser rearranged product (**6**) [m.p. 59 °C; $\nu_{C=O}$ (Nujol) 1731 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 2·05 (3H, s), 3·74 (3H, s), 3·84 (2H, s), 3·94 (2H, s), and 7·73 (3H, m)] (see Scheme). The ylidic esters (**7**) (m.p. 146 °C; yield 90%) and (**8**) (m.p. 252 °C; yield 70%) were similarly prepared from the corresponding ylides (**3**) and (**2**), respectively.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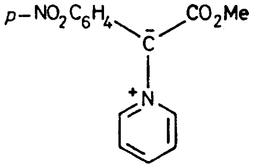
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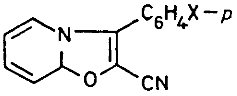
(9)

It was recently claimed that ethylene oxide and isoquinoline gave an oxazolo(3,2-*a*)isoquinoline adduct.[7] The ^{13}C

TABLE. Physical data for ylides (**2**), (**3**), and (**4**)

	X	Z	m.p. °C	Yield/%	I.r. (Nujol)/cm^{-1} $\nu_{C=O}$[a]	$\nu_{C\equiv N}$[b]
(**2**)	NO_2	Pyridine	308	86	1628	2205
	Cl	Pyridine	229	34	1621	2193
	NO_2	4-Methylpyridine	232 (decomp.)	92	1637	2198
	NO_2	3,5-Dimethylpyridine	271	67	1617	2195
(**3**)	NO_2	SMe_2	210—212 (decomp.)	81	1592	2206
	Cl	SMe_2	151—157 (decomp.)	40	1576	2208
	NO_2	Thiolan	220	65	1597 1590	2204
	H	Thiolan	169	41	1570	2197
(**4**)	Cl	PPh_3	238	22	1588	2200

[a] Medium intensity. [b] Very weak band.

n.m.r. spectrum of (**2**) is in agreement with the ylidic structure (**2**; X = Cl); δ (Me_2SO) 142 (C=O), 117 (C≡N), 120 (ylidic C), 150, 147, and 129 (pyridine C), and 136, 128, 127, and 122 (Ar C) p.p.m., and rules out the oxazolo(3,2-*a*)-pyridine structure (**9**) owing to the absence of an *sp*^{3} C–H carbon signal expected at δ *ca.* 80 p.p.m.[7]

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