Reactions of Aryl Glyoxylic Esters with Trivalent Phosphorus Compounds; the Preparation of αβ-Dimethoxycarbonylstilbene Oxides

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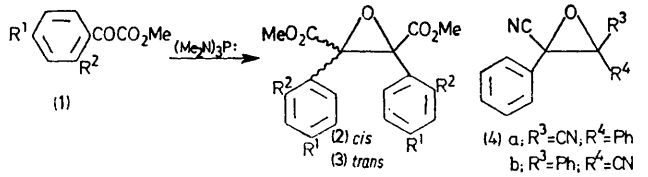
Summary A number of substituted αβ-dimethoxycarbonylstilbene oxides has been prepared by reductive condensation of the corresponding methyl phenylglyoxylates with hexamethylphosphorous triamide; these oxirans undergo [3 → 2 + 1] photocycloelimination to give aryl methoxycarbonylcarbenes and exhibit photochromic behaviour at 77 K in rigid matrices, indicative of carbonyl ylide formation.

From previous observations it appears that αβ-dimethoxycarbonylstilbene oxides of the type (2) and (3) should be photolabile, exhibit photochromic properties, and fragment to carbenes.[1,2] In addition, Huisgen has reported that both isomeric αβ-dicyanostilbene oxides (4) undergo thermal additions to a variety of dipolarophiles.[3] Mukaiyama and his co-workers[4] have shown that reductive condensation of benzoyl cyanide occurs with triethyl phosphite, to give a 1,3,2-dioxaphospholan adduct, which in turn is converted thermally into the *trans*-αβ-dicyanostilbene oxide (**4b**) and triethyl phosphate. This result suggested that the desired oxirans (**2**) and (**3**) could be formed from aryl glyoxylic esters (**1**).[5]



The proposed reaction was shown to occur, hexamethylphosphorous triamide being the best reagent to achieve the condensation of the aryl glyoxylates (**1a**—**g**)[6]. The αβ-dimethoxycarbonylstilbene oxides (**2a**—**g**), assigned *cis* stereochemistry, were obtained in moderate to high yields (Table).† Use of triethyl phosphite in the condensation gave reduced yields of the oxirans. The yield of oxiran also drops markedly if the substituent on the aryl glyoxylate is not electron withdrawing (Table).

The stereochemistry of the oxiran (**2a**) was determined by correlation with that of the related dinitriles (**4a**) and (**4b**)[3]‡ The dinitrile (**4b**) was converted into a diester (**3a**), m.p. 114—115 °C, in high yield (87%) which is isomeric with (**2a**), m.p. 126—127 °C from C_6H_6–C_6H_{14}; m.p. 134—135 °C from CH_2Cl_2—C_6H_{14}.§ Thermal isomerization of (**3a**) occurs in the absence of solvent at 180 °C to give a 1 : 1 equilibrium mixture of (**2a**) and (**3a**) in 24 h which remains unchanged after 44 h. The signals for the methoxy protons in the

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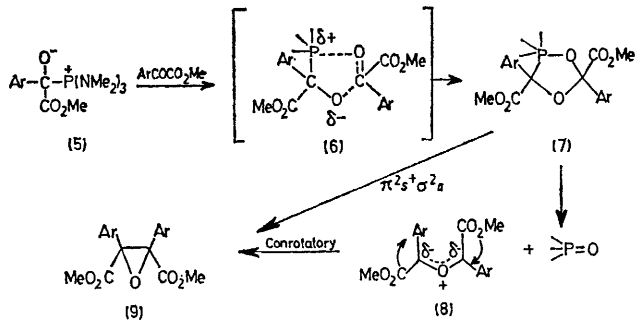
† All new compounds with the exception of (**1e**) gave satisfactory combustion analyses and in all cases the mass spectra are consistent with the proposed structures.

‡ The stereochemistry of the major condensation product (**4b**) obtained from benzoyl cyanide was originally designated as *trans* on the basis of the fact that deoxygenation with a phosphine, a reaction believed to occur with inversion, gave dicyanostilbene, m.p. 161 °C, thought to be *cis* (m.p. 134 °C).[4] This configurational assignment was later questioned (J. H. Boyer and R. Selvarajan, *J. Org. Chem.*, 1970, **35**, 1229) on the basis of *X*-ray crystallographic data available on the dicyanostilbene, m.p. 161 °C, which had apparently been overlooked earlier or rejected perhaps because of the quality which was admittedly poor. More recently, the original assignments of (**4b**) and thus (**4a**)[4] have been reaffirmed by dipole moment measurements.[3] It should be noted, however, that the dicyanostilbene, m.p. 134 °C, undergoes isomerization under the deoxygenation conditions to that isomer, m.p. 161 °C. Thus the original assignments proved correct only as a consequence of compensating errors arising from what we believe was a misleading experimental interpretation coupled with an incorrect assignment.

§ The *trans*-dinitrile (**4b**) was initially transformed to a bis-iminoether, m.p. 158–159 °C, by treatment with NaOMe in MeOH which in turn was hydrolysed in dilute, aqueous, methanolic HCl to (**3a**) [ν_{max} (Nujol) 1740 s, 1242 s, 1078 m, 1020 s, 902 m, 830 m, 789 m, 750 s, 745 s, and 697 s cm^{-1}; δ 3·36].

n.m.r. spectrum of (**3a**) are at higher field (δ 3·36), *i.e.*, shielded relative to those of the *cis* isomer (**2a**) (δ 3·77) in accord with predictions based upon the assigned configurations.



No stereochemical studies have been conducted on the remaining condensation products from the series (**1b**—**g**) but all give spectra (i.r., n.m.r.) consistent with that of the *cis* epoxide (**2a**). Formation of *cis*-oxirans may be rationalized by assuming initial formation of a zwitterion (**5**) by nucleophilic attack of the trivalent phosphorus reagent at the electrophilic glyoxylate carbonyl carbon atom. If this dipolar species then interacts with a second mole of glyoxylate in a transition complex (**6**) which minimizes the steric interaction between the aryl groups while maximizing the attractive forces between the phosphonium and oxido centres, a *trans*-diphenyl-1,4,2-dioxaphospholan derivative (**7**) would be obtained. Ample precedent exists for the proposal that 1:1 adducts of the type (**5**) are implicated as intermediates in the formation of 2:1 adducts assigned 1,4,2-dioxaphospholan structures such as (**7**).[7] A concerted symmetry-allowed retrograde $_{\pi}2_s + {}_{\pi}4_s$ cycloaddition (also designated as a [5 → 3 + 2] cycloelimination reaction) involving (**7**) would give the carbonyl ylide (**8**). Conrotatory cyclization of (**8**), would then lead to the *cis* oxirans (**9**).[1a]

In contrast, the triethyl phosphite-induced condensations of benzoyl cyanides lead ultimately to isolable 1,3,2-dioxaphospholans which may arise directly or by rearrangement of the 1,4,2-counterparts invoked as intermediates. No direct thermal mechanism exists for a concerted cycloelimination process for the former compounds to give a carbonyl ylide such as (**8**) and the accompanying opportunity for conrotatory cyclization to *cis*-oxirans is absent; however, as noted,[1a¶] a concerted $_{\pi}2_s + {}_{\sigma}X_a$ retrocycloaddition pathway such as that proposed for the 1,4,2-dioxaphospholans (**7**) should still be available and provide a potential route for the production of the *cis*-dinitriles. Their absence as major products leads us to favour the ylide mechanism, which may not be operational in the case of the benzoyl cyanides because the proposed 1,4,2- to 1,3,2-dioxaphospholan rearrangement is fast. The adverse dipolar interactions between the *cis*-nitrile groups also may provide the driving force for thermodynamic equilibration to the *trans*-isomers at some stage in the reaction.

The low-temperature photochemical properties of the 2,3-diaryloxirans (**2a**—**g**) are consistent with those of other *vic*-diaryloxirans.[1,8] Upon irradiation of (**2a**), (**2c**), and (**2d**) for example in 2-methyltetrahydrofuran at 77 K violet to purple colours are observed with λ_{max} at 560, 520, and 535 nm, respectively. Furthermore, irradiation of a degassed solution [(**2a**) (0·01 M) in 2,3-dimethylbut-2-ene through quartz (19 h; 40 °C)] gives the phenylmethoxycarbonyl carbene adduct 2,2,3,3-tetramethyl-1-phenylmethoxycarbonylcyclopropane (26%), and 3,3,4,4-tetramethyl-2-phenylmethoxycarbonyloxetan (63%) identical in properties to authentic samples of these compounds obtained by an

TABLE

Substituents for (**1**), (**2**), and (**3**)	Yield (%) of (**2**)	M.p./°C (recryst. solvent)	N.m.r. (δ values)
a; $R^1 = H$; $R^2 = H$	46·2 Polymorphic	126—127 (C_6H_6–C_6H_{14}) 134—135 (CH_2Cl_2–C_6H_{14})	3·77 (3H, s) 7·02 (5H, m)
b; $R^1 = NO_2$; $R^2 = H$	59·4	152—154 (EtOH–H_2O)	3·82 (3H, s) 7·20 (4H, m) 7.98 (4H, m)
c; $R^1 = Cl$; $R^2 = H$	80·4	120—121 (C_6H_6–C_6H_{14})	3·82 (3H, s) 7·23 (4H, m)
d; $R^1 = Br$; $R^2 = H$	81·6	105—106 (C_6H_6–C_6H_{14})	3·79 (3H, s) 7·30 (4H, m)
e; $R^1 = Me$; $R^2 = H$	2·0	—	2·32 (s) 3·66 (s) 7·10 (m)
f; $R^1 = H$; $R^2 = Cl$	50·2	106—107 (C_6H_6–C_6H_{14})	3·62 (s) 7·42 (m)
g; $R^1 = H$; $R^2 = I$	45·3	215—216 (C_6H_6–C_6H_{14})	3·41 (s) 7·50 (m)

¶ Alternatively, the *cis* oxirans (**9**) may arise directly from the 1,4,2-dioxaphospholan (**7**) without intervention of the ylide (**8**) as a consequence of the inversion necessary in a thermally allowed $_{\pi}2_s + {}_{\sigma}2_a$ retrograde cycloaddition. The latter mechanism may be applied equally well if in fact a 1,3,2-dioxaphospholan is implicated.

alternative route.[1d] In contrast to results obtained with (**4a**) and (**4b**) no thermal adducts of (**2a**) and (**2b**) with alkenes and alkynes have yet been obtained.

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