a crude product which was chromatographed on 5 g of silica gel, using chloroform–ethyl acetate (3:2) as eluant, to give 76 mg (88%) of chenodeoxycholic acid (4) as colorless needles (ethyl acetate–hexane), which was identified by comparison with an authentic sample, obtained by purification of commercially available (+)-chenodeoxycholic acid, of its IR ($CHCl_3$), NMR ($CDCl_3$), and mass spectra, including optical rotation and mixture melting point test. 4: mp 143–145 °C; IR ($CHCl_3$) 1705 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 0.66 (3 H, s, CH_3), 0.92 (3 H, s, CH_3), 0.94 (3 H, d, J = 4 Hz, CH_3), 3.20–3.75 (1 H, m, $C_{3\beta}$-H), 3.75–4.00 (1 H, br s, $C_{7\beta}$-H); MS m/e 392 (M^+); $[\alpha]^{20}_D$ +11.2° (c 0.142, EtOH).

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Reductive Condensation of Methyl Arylglyoxylates. Direct Synthesis of 2,3-Bis(carbomethoxy)stilbene Oxides and Related Systems

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A number of aryl-substituted 2,3-bis(carbomethoxy)stilbene oxides have been prepared by reductive condensation of the corresponding methyl phenylglyoxylates induced with hexamethylphosphorous triamide. The stereochemical assignments to the parent isomeric phenylglycidates provided an unexpected challenge. The earlier literature in this area has been reviewed and previous structural conclusions have been reconciled. These oxiranes have been prepared in order to employ in our continuing direct, energy and electron transfer photochemical studies of such substrates. The related epoxydiphenylsuccinic anhydride and imide show particularly interesting photochemical properties.

In an expansion of our continuing research on the photochemistry of small-ring heterocyclic compounds, we became interested in preparing substituted 2,3-bis(carbomethoxy)stilbene oxides for use as potential carbene[3] and carbonyl ylide[4] precursors. From our previous observations it was apparent that stilbene oxides of this type should be photolabile, exhibit photochromic properties, and fragment to carbenes.[3,4] For example, *trans*-2,3-dicyanostilbene oxide undergoes photocleavage to phenylcyanocarbene and benzoyl cyanide.[3a,d,f,g] Huisgen[5] was the first to report that the isomeric pair of 2,3-dicyanostilbene oxides undergo *thermal* additions to a variety of dipolarophiles. We anticipated that these synthetically useful reactions which proceed by way of carbonyl ylides might be extended to the title esters and that such [2 + 3 → 5] cycloadditions perhaps could be induced thermally and/or photochemically.[6]

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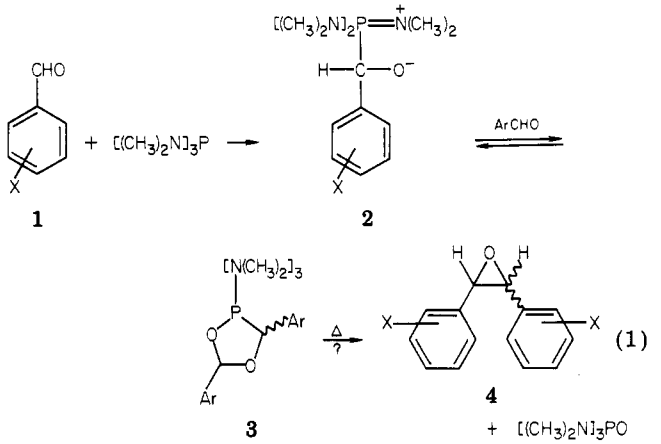
Background

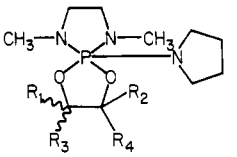
It is evident from a survey of the literature that reductive coupling of carbonyl compounds with trivalent phosphorus reagents might provide a convenient route to the desired dicarbomethoxystilbene oxides. In a publication of considerable practical significance, Mark[7a] reported that 2,3-diaryloxiranes **4** are formed in moderate to high yields upon treatment of aryl aldehydes **1** (particularly those bearing electronegative substituents) with hexamethylphosphorous triamide (eq 1). The reaction in



some instances leads to 1:1 adducts that incorporate a carbon–phosphorus bond as evidenced by spectral data. This is the case with benzaldehyde (**1**, X = H), which forms such an adduct, assigned structure **2**.

Mark[7a] contended that the anionic center on oxygen of the initial 1:1 N–P$^+$–C–O$^-$↔$^+$N=P–C–O$^-$ adduct **2** formed by attack of phosphorus at the electrophilic carbon center undergoes nucleophilic addition to a second mole of aldehyde forming another open zwitterionic intermediate that is in equilibrium with the 2:1 cyclic 1,4,2-dioxaphospholane adduct **3**. It is proposed that **3** is thermally unstable with respect to loss of hexamethylphosphoric triamide and the oxirane **4**. Ramirez and co-workers in their studies of the reductive condensation of aromatic aldehydes to give stilbene oxides with both tris(dialkylamino)phosphines[7b] and triethyl phosphite[7c,d] assert that no precedent exists for thermal decomposition of such carbonyl adducts as **3** (derived from 1:1 dipolar N–P$^+$–C–O$^-$ species including **2**) to give oxirane and amidate fragments.[7b,8] An alternate mechanism for the overall condensation is formulated by Ramirez and co-workers which entails initial attack of the trialkyl phosphites and/or tris(dialkylamino)phosphines on electron-deficient aryl aldehydes at the carbonyl oxygen site to form at the outset 1:1 zwitterionic $^-$C–O–P$^+$ adducts. The ensuing steps in the condensation mechanism advanced involve covalent binding at the carbanionic center of the 1:1 dipolar adduct with a second mole of aldehyde or ketone and cyclization to give the 1,3,2-dioxaphospholanes as the ultimate products. The resulting 1,3,2-dioxaphospholanes are often isolable and sufficiently stable to be characterized in many cases by ^{31}P NMR spectroscopy;[7b,9] however, they are in fact thermolabile and fragment to oxiranes in high yield upon warming, in contrast to their isomeric 1,4,2 counterparts.[7b]

In the case of aromatic aldehydes bearing electron-withdrawing substituents, Ramirez and co-workers[7b] found that selected *cyclic* tris(dimethylamino)phosphines yield 2:1 adducts of the type **5a**, which are stable above 20 °C and must be thermolyzed to generate stilbene oxides, unlike the comparable *acyclic* counterparts, which give oxiranes and amidates directly even at low temperatures. The structures for the 2:1 adducts were secured as 1,3,2-dioxaphospholanes by ^{31}P NMR data which confirm that a 1:1 $^+$P–O–C$^-$ bonding sequence must be established at some phase of the condensation sequence; however, no intermediates were detected in the overall condensation process, e.g., with *p*-nitrobenzaldehyde in which the cis adduct **5a** is the primary product. On the other hand, 1:1



5a, $R_1 = R_2 = O_2NPh$; $R_3 = R_4 = H$
b, $R_1 = R_2 = R_3 = R_4 = CF_3$

adducts have been isolated from reactions of tris(dialkylamino)phosphines with vicinal polycarbonyl compounds having $^+$P–O–C$^-$ structural entities. Therefore, Ramirez and co-workers concluded that such 1:1 adducts are precursors for the 2:1 *p*-nitrobenzaldehyde adducts.[7b] It is conceivable that 1:1 $^+$P–C–O$^-$ adducts may form in the case of the corresponding condensation of nitrobenzaldehydes induced by trialkyl phosphites; however, rearrangement occurs prior to subsequent condensation, although no experimental evidence (other than conjecture regarding the nature of the species responsible for development of a transient brown color at −70 °C) was advanced to support or reject this hypothesis.

o-Nitrobenzaldehyde under similar conditions behaves in a manner analogous to that observed for *p*-nitrobenzaldehyde and reacts with cyclic tris(alkylamino)phosphines to form a diastereomeric pair of stable 1,3,2-dioxaphospholanes, and the cis isomer again predominates (2.3:1). On the other hand, the interaction of cyclic triaminophosphines with *m*-nitrobenzaldehyde is atypical in that a reddish brown color develops at −70 °C in methylene chloride. Furthermore, no evidence was detected for formation of the trans phospholane, and the isolable cis epimer was formed in relatively low yield (20%), which also represents unique behavior. An examination of the crude reaction mixture by ^{31}P NMR[8] reveals the presence of three additional signals, each exhibiting negative shifts. While one of the three is assigned to the cyclic amidate fragment, the origin of the remaining pair remains obscure. The authors speculate that one signal could arise from the presence of a 1:1 adduct with $^+$P–O–C$^-$ bonds, a suggestion previously advanced by Mark[7a] to rationalize the reactions of aldehydes with hexamethylphosphorous triamide, which leads to oxiranes.[7b]

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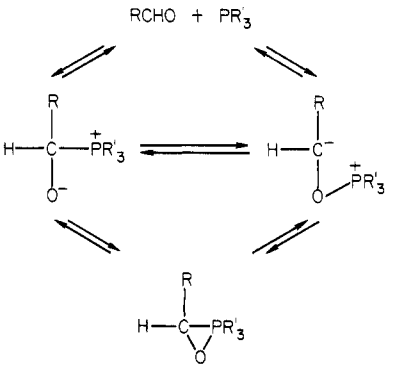
Of mechanistic significance is the fact that attack by trivalent phosphorus reagents on the oxygen atom of keto carbonyl groups is promoted by α-halo substitution. For example, hexafluoroacetone bears fluoro substituents capable of stabilizing a negative charge, which develops during formation of the 1:1 adducts, and thus enhancing the ability of phosphorus to exercise its tendency to become bonded to the oxygen of the carbonyl group. The overall course of the reaction and product stability is markedly influenced by the type as well of the structures of P(III) reagents employed.[7b,e-h,8] Trialkyl- and triarylphosphines, as well as triaminophosphines and trialkyl phosphites, condense with hexafluoroacetone under varying conditions by attack on oxygen to give 1:1 adducts incorporating a $^{-}C-O-P^{+}$ structural unit. At high temperatures such 1:1 adducts may decompose by several pathways which have been elaborated.[7e,h] Among those factors that influence the lifetime of the 1:1 adduct and dictate the course of these reactions (i.e., control subsequent addition of the 1:1 adduct to a second mole of hexafluoroacetone) include (1) the nucleophilicity of the trivalent phosphorus reagent, (2) the nucleophilicity of the carbanion which must undergo condensation with a second mole of ketone, (3) the number and type of halo substituents on the ketone, (4) the propensity of the anion to eject halide ion or phosphoryl group, and (5) the nature of the substituents on phosphorus.

The 2:1 adduct is stabilized by formation of the 1,3,2-dioxaphospholane ring system. It is even proposed that the driving force for all such reactions may be formation of the five-membered ring system incorporating a pentacovalent phosphorus atom.[7e] Factors that affect the degree of stability of the pentacovalent phosphorus system are (1) the electronegativity of those atoms bound to phosphorus (e.g., O > N > C) and (2) the magnitude of the steric requirements of the β-substituents (e.g., OR < NR_2 < CR_3). Increasing steric requirements for the substituents R also exert an adverse effect on the stability of the oxyphosphoranes, presumably through buttressing or crowding effects associated with the trigonal-bipyramidal configuration of pentacoordinated phosphorus.[7e]

It is noteworthy that in the absence of substituents on the carbonyl moiety capable of stabilizing a negative charge on carbon that develops during formation of the 1:1 adduct, the condensation may take an alternate course. Aliphatic monoaldehydes, for example, react with trialkyl phosphites to give 1,4,2-dioxaphospholanes structurally related to 3,[7a,i-k,8] which suggests that the degree of electrophilicity of the carbonyl group is significant. Even in the case of the aromatic aldehyde pentafluorobenzaldehyde, the initial 2:1 adduct formed [presumably via the dipolar $(CH_3O)_3P^{+}-C-O^{-}$ 1:1 adduct] has the 1,4,2-dioxaphospholane structure; however, this oxaphospholane slowly isomerizes at 25 °C to the isomeric 1,3,2-dioxaphospholane.[8] Despite the discovery of this conversion, no compelling evidence exists that 1,4,2-dioxaphospholanes constitute obligatory precursors for all or even any additional 1,3,2-dioxaphospholanes.

A reasonable alternative proposition is advanced to rationalize the disparate results obtained with substituted aliphatic aldehydes, and those observed with most aromatic aldehydes and ketones activated by electron-withdrawing substituents. It is conceivable that the reactions of phosphites with both aldehydes and ketones may involve in all cases initial formation of adducts of the $^{+}P-C-O^{-}$ type that may be interconvertible with those incorporating the $^{+}P-O-C^{-}$ bond sequence by prior reversion to aldehyde, direct interconversion, or molecular reorganization through a three-membered intermediate or transition state, perhaps even generated directly by a three-center attack of the trivalent phosphorus reagent on the carbonyl group (see Scheme I). In fact, it may even be concluded that the zwitterionic structures are electronically indistinguishable. In any event the presence of electronegative substituents on R (or C) should enhance participation by the $^{+}P-O-C^{-}$ dipolar 1:1 adduct. These distinctions are believed to become less "operationally significant" as the rate of the proposed rearrangement of the $^{+}P-C-O^{-}$ to the $^{+}P-O-C^{-}$ adducts increases and the position of equilibrium shifts toward the $^{+}P-O-C$ adduct.[7e]

Scheme I



It is postulated that the probability for the initial formation of a $^{+}P-O-C^{-}$ adduct should be considerably higher for halo ketones than for aldehydes, since the negative charge induced on the carbonyl carbon during the initial step of the reaction is stabilized by electron-withdrawing groups.[7b] Borowitz first investigated the kinetics of the Perkow reaction,[10c] a conversion of α-halo ketones such as α-chloro- and α-bromoisobutyrophenones with triethyl phosphite to the corresponding diethyl vinyl phosphate, a reaction that embraces features in common with the reductive condensation reactions under discussion.

It is argued that the rate-determining step is nucleophilic addition of trivalent phosphorus to the carbonyl carbon atom of the α-halo ketones. The series of α-chloro ketones studied reacts 1.1–2.7 times faster than the corresponding α-bromo analogues. From this kinetic scrutiny of the reaction, they conclude that ρ values for a series of chloro and bromo ketones correlate better with nucleophilic addition at the electrophilic carbon atom of the carbonyl group than with initial addition to the carbonyl oxygen atom; i.e., the rate-determining addition in the latter case should correlate with σ^{-} rather than σ^{+} values.[10c,d]

Borowitz and colleagues[10a,b] concur with Ramirez and co-workers[7f,g,8] that ketones structurally related to cyclopentadienone such as fluorenone undergo analogous reductive cyclization through initial attack of tricovalent phosphines and phosphites on the carbonyl oxygen of the substrates. In summary, despite the data presented, it appears that the controversy regarding the site of attack of phosphite phosphorus on the carbonyl groups of various aldehydes and ketones remains to be resolved if indeed a general mechanism prevails.

Newman and Blum[11a] were the first to apply the Mark

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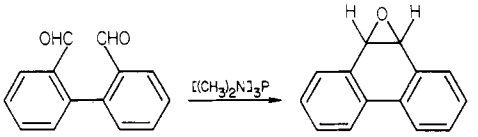
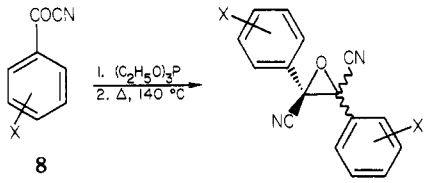
condensation[7a] in an intramolecular fashion to prepare a K-region arene oxide, namely 9,10-dihydro-9,10-epoxyphenanthrene (7) in high yield (81%) from 2,2′-diformylbiphenyl (6) (eq 2). This method has since been extended to the synthesis of a variety of other K-region oxides.[11b-c]



6 7 (2)

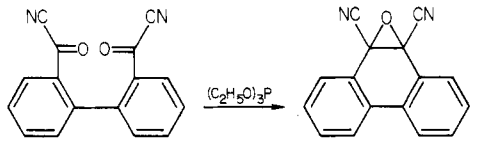
The reactivity of alkyl and aryl trivalent phosphorus reagents is substantially less in this condensation; however, Mukaiyama and co-workers had found that aroyl cyanides such as 8 undergo reductive condensation to *trans*-2,3-



8 9a, cis b, trans (3)

dicyanostilbene oxide upon treatment with triethyl phosphite (eq 3).[12a] The presumed intermediate is a 1,3,2-dioxaphospholane adduct which in turn is converted thermally to the oxiranes **9** and triethyl phosphate upon heating.

The Mukaiyama method has recently been applied in an intramolecular fashion in our laboratories for the synthesis of 9,10-dicyano-9,10-epoxyphenanthrene (11) from the diaroyl cyanide **10** (eq 4).[13,14] This arene oxide was



10 11 (4)

found to undergo the oxygen walk reaction,[13-16] a general photorearrangement first reported by our group[15] and has proven to be a superior precursor for a variety of other substrates of photochemical significance as well.[13b,14] Regardless of the fact that controversy still surrounds the reaction of carbonyl compounds with trivalent phosphorus reagents and the mechanism(s) remains to be totally resolved, there is clearly a marked tendency for such substrates as aroyl cyanides **8** bearing substituents capable of stabilizing carbanionic centers to undergo reductive condensation via phospholane intermediates (or open dipolar forms) to give oxiranes. These and related observations made a Ramirez[7e-g,8] and Borowitz[10a,b] that ketones such as tetracyclone, fluorenone, α-diketones, and *o*-quinones, which are capable of forming stable oxyphosphonium ylides, undergo condensation with trivalent phosphorus reagents suggested that the desired title bis(carbomethoxy)stilbene oxides could be formed from arylglyoxylic esters in a corresponding manner. In the case of methyl pyruvate, an aliphatic glyoxylate, reductive condensation occurs with trimethyl phosphite to give a 2:1 phospholane adduct. This adduct, however, upon subsequent heating, fails to give the expected oxirane.[17] A recent report on the reaction of α-keto acids, including phenylglyoxylic acid, is also significant in this context. The aliphatic and aromatic glyoxylic acids undergo selective reduction to α-hydroxy acids by trialkyl phosphites.[18] Fortunately, such is not a major reaction pathway with arylglyoxylate esters, at least when hexamethylphosphorous triamide is employed as the reducing agent.

Preparation of Methyl Arylglyoxylates

Two general methods were employed for the conversion of the corresponding aroyl cyanides to methyl arylglyoxylates. The most convenient method, where applicable, is that utilized by Eastham and Selman.[19] The methyl arylglyoxylates (**12a-h**) are obtained in medium to high yield by addition of hydrogen chloride gas to an ethereal solution of the aroyl cyanides containing methanol, followed by hydrolysis of the resulting imino ether, which deposits as a precipitate. In certain cases (**12f**), we also resorted to the more time-consuming method of Oakwood and Weisgerber[20a] for conversion of the aroyl cyanides to the corresponding acids, which consists of stirring the latter for 5 days with 12 N hydrochloric acid. After quenching the reaction mixture, the glyoxylic acid is isolated and esterified with methanol under acid conditions or alternatively by treatment with dimethyl sulfoxide containing sodium hydroxide.[21] The aroyl cyanides required for this study in general were prepared in turn by heating the corresponding aroyl chlorides with cuprous cyanide directly[20b] or under reflux in acetonitrile.[22]

Condensation Products of Methyl Arylglyoxylates with Trivalent Phosphorus Reagents

The proposed condensation reactions of phenylglyoxylate esters were observed to occur, and hexamethylphosphorous triamide was found to be the reagent of choice to achieve the proposed condensation of the arylglyoxylates **12** to the desired stilbene oxides **13** and/or **14** (eq 5). This reagent was originally employed by Mark to effect the conversions of aldehydes to oxiranes.[7a] Treatment of phenylglyoxylates **12a-h** with hexamethylphosphorous triamide gives as the major product 2,3-bis(carbomethoxy)stilbene oxides **13**, assigned cis stereochemistry, in moderate to high yields (Table I); however, the alternate trans isomer in each case may be detected spectroscopically (NMR) among the reaction products and the conditions may be modified and controlled to render separation of the minor adduct feasible (vide infra).

(12) (a) T. Mukaiyama, I. Kuwajima, and K. Ohno, *Bull. Chem. Soc. Jpn.* **38**, 1954 (1965); (b) the treatment of benzoyl cyanides with alkylene methyl phosphites gives stable 1,3,2-dioxophosphoranes with spiro structures which decompose at 120–160 °C to give **9b** and cyclic phosphates. See I. V. Konovalova, E. Kh. Ofitserova, N. P. Anoshina, and A. N. Pudovik, *Zh. Obshch. Khim.*, *45*, 2119, (1975); *J. Gen. Chem. USSR (Engl. Ed.)*, *45*, 2088 (1975).

(13) N. E. Brightwell, dissertation submitted in partial fulfillment for the Ph.D. requirements of the University of New Orleans, New Orleans, LA, 1974.

(14) G. W. Griffin, S. K. Satra, N. E. Brightwell, K. Ishikawa, and N. S. Bhacca, *Tetrahedron Lett.*, 1239 (1976).

(15) N. E. Brightwell and G. W. Griffin, *J. Chem. Soc., Chem. Commun.*, 37 (1973).

(16) (a) D. M. Jerina, B. Witkop, C. L. McIntosh, and O. L. Chapman, *J. Am. Chem. Soc.*, **96**, 5578 (1974); (b) T. Okamoto, K. Shudo, and N. Miyata, *Chem. Pharm. Bull.*, **21**, 2809 (1974).

(17) F. Ramirez, N. B. Desai, and N. Ramanathan, *Tetrahedron Lett.*, 323 (1963).

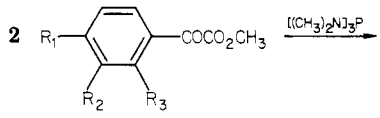
(18) T. Saegusa, S. Kobayashi, Y. Kimura, and T. Yokoyama, *J. Org. Chem.*, **42**, 2797 (1977).

(19) J. F. Eastham and S. Selman, *J. Org. Chem.*, **26**, 293 (1961).

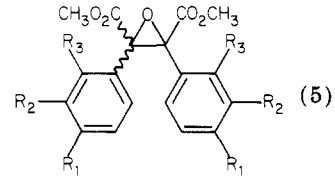
(20) (a) T. S. Oakwood and C. A. Weisgerber, "Organic Synthesis", Coll. Vol. III, E. D. Horning, Ed., Wiley, New York, 1955, p 114; (b) *ibid.*, p 112.

(21) R. G. Gillis, *Tetrahedron Lett.*, 1413 (1968).

(22) J. F. Normant and C. Piechucki, *Bull. Soc. Chim. Fr.*, 2402 (1972).



12



13, cis
14, trans

After the appearance of our original communication on reductive coupling of arylglyoxylic esters to stilbene oxides[2a] it was discovered and later acknowledged in a corrigendum note[2b] that the ratio of cis and trans epimers formed is markedly dependent on temperature (vide infra). In the course of surveying the reliability of additional data tabulated in the initial communication, significant discrepancies were uncovered in the experimental data. This is readily apparent upon comparison of the individual entries compiled in Table I of this paper with those found in our original communication.[2a] For example, the melting point and NMR data reported for the *p,p'*-dinitro- and dichlorostilbene oxides (of previously undesignated stereochemistry) have significantly lower melting points than those now reported for the individual isomers (**13** and **14b** and **c**, respectively) now separated, purified and characterized stereochemically (Table I). We attribute the differences observed to the difficulties encountered earlier by D.M.G. in achieving complete separation of isomers particularly in the case of the nitro derivatives (**13a** and **14b**), which provides the more difficult technical challenge. However, we offer no excuses other than carelessness for our inability to observe the NMR signals and discern that the products originally reported were inhomogeneous. The chemical shift differences are of such magnitude (**13b–14b**, 14 cps, **13c–14c**, 22 cps) that contamination by the alternate isomer in each case is detected unless exceedingly low concentrations of the trans epimers in each case suffice to reduce the melting point dramatically of the favored cis products. Furthermore, much higher yields (89%) have now been achieved in the condensation of methyl (*p*-methylphenyl)glyoxylate (**12e**) than originally reported by D.M.G. (~2%).[2a]

It is also noteworthy that the direct condensation of ortho-substituted arylglyoxylates have proven unsuccessful and that difficulty has been encountered in reproducing the earlier results reported by D.M.G. for the condensation of methyl *o*-chloro- as well as (*o*-iodophenyl)glyoxylates.[2a] It is conceivable that these substrates will condense under modified conditions from those originally described. On the other hand, an adventitious modification in procedure and/or contaminant may account for the success originally reported.[2a]

To cite a specific case, for example, when **12a** is treated with hexamethylphosphorous triamide, an exothermic reaction ensues and a white crystalline solid, ultimately identified as *cis*-2,3-bis(carbomethoxy)stilbene oxide (**13a**) (CH_3O, δ 3.77) is obtained. A signal for the methoxy protons at higher field (δ 3.36) observed in the NMR spectrum of the crude condensate of **12a** (eq 5) provided the first indication that the alternate trans isomer **14a** is formed and that the glyoxylate condensation reaction is not highly stereospecific. The ratio of **13a** to **14a** formed at 23 °C using hexamethylphosphoric triamide as the solvent is 3.8:1.0 although this ratio is subject to variations as a function of temperature. In benzene at the reflux, for example, temperature stereorandomization increases to 1.22:1 (Table II).

Attempts to replace the phosphorous triamide with triethylphosphite in the condensation reaction proved unprofitable despite the successful use of the latter with the analogous aroyl cyanides.[12a] In fact, no evidence for condensation to oxiranes could be detected with the limits of conventional 60-MHz NMR techniques upon treatment of the methyl (*p*-chloro- and *p*-methylphenyl)glyoxylates (**13c**, **14c** and **13e**, **14e**) with triethyl phosphite under conditions used to induce the condensation of the corresponding aroyl cyanides **8** to **9** (eq 3).[2c,12] It is noteworthy too that among the latter reactions the yield of oxirane is affected markedly by the nature of the para substituents on the aroyl cyanides. Relatively high yields of oxiranes are obtained with benzoyl cyanide and its *p*-nitro derivative. In contrast, the yields of oxiranes are substantially lower with such substrates as *p*-methyl- and *p*-chlorobenzoyl cyanide. In fact, Mukaiyama and co-workers[12a] obtained 1,3-dicyano-*p,p'*-dimethoxystilbene rather than the oxirane (64%) as the major product upon treatment of *p*-methoxybenzoyl cyanide with triethyl phosphite. The corresponding 1,3,2-dioxaphospholane was not observed as an intermediate, as is the case with other triethyl phosphite-induced condensations of this type. By way of comparison, methyl (*p*-methoxy-, *p*-chloro, and *p*-methylphenyl)glyoxylates proved unreactive with triethylphosphite under Mukaiyama's conditions;[2c,12a] however, all condense ultimately to give oxiranes with hexamethylphosphorous triamide, presumably via phospholane intermediates that are not isolable. It is evident from our failures to achieve condensation of methyl (*o*-chloro- and *o*-iodophenyl)glyoxylates with hexamethylphosphorous triamide[2d,e] that ortho substituents may exert an adverse effect on the reaction with hexamethylphosphorous triamide. This lack of reactivity may be attributed to the intervention of adverse steric effects that accrue in the carbon–carbon bond-formation step. The corresponding meta-substituted methyl (chloro- and bromophenyl)glyoxylates (**12g** and **12h**, respectively) condense readily to the oxides **13g**, **14g**, and **13h**, **14h**, respectively, in high yield in accordance with this proposal.

Stereochemistry of Oxirane Adducts

Confirmation of the gross structure of the oxirane adduct derived from **12a** and presumed to be 2,3-bis(carbomethoxy)stilbene oxide (**13a** or **14a**) was accomplished by oxidation and accompanying hydrolysis of diphenylfumaro or malenonitrile with basic sodium tungstate and hydrogen peroxide.[23] Subsequent esterification gave a common oxirane (mp 126–127 °C) in low yield (<10%) identical in all respects with the product of unknown structure obtained from **12a**. While this observation, in addition to the NMR, IR (Table I), and mass spectral and combustion analytical data support the gross skeletal structures **13a** (or **14a**) assigned to the adduct, no a priori deductions regarding stereochemistry in either case could be made with certainty from these results since the oxidation is clearly nonstereospecific, a fact that was confirmed in control experiments.

Establishing the stereochemistry of **13a**, the major condensation product obtained from **12a**, to our satisfaction proved to be more than a trivial problem. In particular, our efforts to correlate the structure of **13a** with

(23) G. B. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 54 (1959).

Table I. *cis*- and *trans*-2,3-Bis(carbomethoxy)stilbene Oxides

substituents for 13 and 14	yield of adduct,[a] %	mp, °C	NMR ($CDCl_3$), δ	IR (Nujol), cm^{-1}
13a		126-127 (benzene-hexane) polymorphic 134-135 (CH_2Cl_2-hexane)	3.77 (s) 7.1 (m)	1735, 1310, 1288, 1245, 1177, 1044, 1008, 968, 824, 751, 735, 698
a, $R_1 = R_2 = R_3 = H$	50			
14a		114-115 (CH_2Cl_2-hexane)	3.36 (s) 7.5 (m)	1745, 1300, 1245, 1211, 1179, 1088, 1023, 975, 937, 910, 840, 795, 760, 708, 670
13b		174 (methanol)	3.82 (s) 7.20 (d) 7.97 (d)	1765, 1745, 1620, 1535, 1450, 1365, 1250, 1053, 1007, 868, 860, 795, 744, 711
b, $R_1 = NO_2$; $R_2 = R_3 = H$	73			
14b		222 (CH_2Cl_2-methanol)	3.58 (s) 8.17 (d) 855 (d)	1755, 1740, 1610, 1530, 1250, 1285, 1240, 1111, 1043, 1029, 1020, 868, 856, 789, 745, 709
13c		126 (CH_2Cl_2-methanol)	3.94 (s) 7.4 (m)	1750, 1500, 1293, 1244, 1172, 1100, 1047, 1003, 800
c, $R_1 = Cl$; $R_2 = R_3 = H$	91			
14c		136 (CH_2Cl_2-methanol)	3.42 (s) 7.30 (d) 7.62 (d)	1740, 1274, 1240, 1095, 1039, 1020, 920, 910, 848, 814, 782
13d		138 (CH_2Cl_2-methanol)	3.95 (s) 7.55 (m)	1765, 1600, 1295, 1245, 1206, 1172, 1081, 1047, 1006, 848, 817, 795, 781
d, $R_1 = Br$; $R_2 = R_3 = H$	94			
14d		135 (CH_2Cl_2-hexane)	3.57 (s) 7.78 (s)	1760, 1590, 1400, 1285, 1245, 1072, 1033, 1014, 905, 844, 777
13e		106 (CH_2Cl_2-methanol)	2.27 (s) 3.90 (s) 7.18 (d) 7.48 (d)	1750, 1530, 1435, 1307, 1284, 1240, 1207, 1170, 1049, 1005, 970, 912, 840, 819, 770
e, $R_1 = CH_3$; $R_2 = R_3 = H$	89			
14e		149 (CH_2Cl_2-methanol)	2.42 (s) 3.54 (s) 7.42 (d) 7.87 (d)	1745, 1520, 1300, 1241, 1207, 1188, 1173, 1034, 1015, 915, 852, 840, 797, 765
13f		93 (CH_2Cl_2-methanol)	3.70 (s) 3.81 (s) 6.73 (d) 7.29 (d)	1750, 1620, 1570, 1520, 1300, 1262, 1233, 1173, 1120, 1046, 1021, 1007, 939, 918, 850, 833, 820, 811, 800, 770
f, $R_1 = OCH_3$; $R_2 = R_3 = H$	70			
14f		116 (CH_2Cl_2-methanol)	3.55 (s) 3.94 (s) 7.14 (d) 7.90 (d)	1760, 1620, 1515, 1310, 1265, 1246, 1182, 1119, 1045, 1021, 920, 851, 824, 806, 770
13g		112 (benzene-methanol)	3.92 (s) 7.4 (m)	1740, 1590, 1570, 1435, 1370, 1300, 1276, 1210, 1180, 1090, 1053, 1028, 890, 833, 781, 772, 710, 685
g, $R_2 = Cl$; $R_1 = R_3 = H$	82			
14g		108 (benzene-methanol)	3.53 (s) 7.8 (m)	1760, 1610, 1575, 1318, 1298, 1278, 1257, 1210, 1179, 1108, 1041, 1028, 970, 893, 842, 788, 740, 695
13h		126 (benzene-methanol)	3.92 (s) 7.4 (m)	1740, 1600, 1570, 1445, 1370, 1303, 1230, 1207, 1178, 1080, 1050, 1021, 1002, 913, 900, 888, 830, 792, 773, 690
h, $R_2 = Br$; $R_1 = R_3 = H$	89			
14h		128 (benzene-methanol)	3.56 (s) 7.7 (m)	1750, 1600, 1565, 1440, 1230, 1075, 1020, 1000, 910, 895, 803, 780, 718, 690

[a] Produced after 10 min at the reflux temperature of benzene.

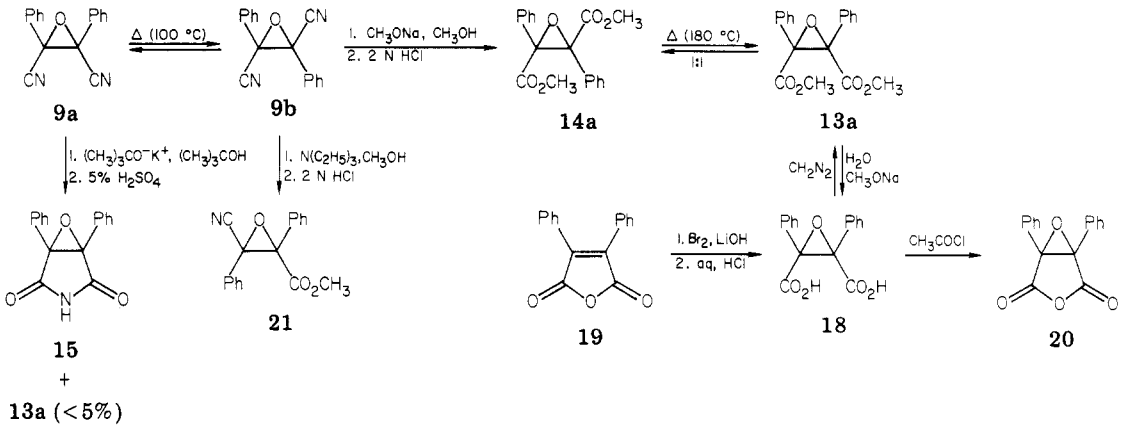
the corresponding dicyanostilbene oxide **9a** or **9b** (X = H) proved more arduous than anticipated. In fact, the original stereochemical assignment for *trans*-2,3-dicyanostilbene oxide (**12a**) had been challenged.[24] This complicated our task since prior confirmation of this structure was required and kindled an evaluation of the literature data in this area, which was in a state of confusion. A summary of our analysis is warranted and is presented here for clarification purposes.

Solely on the basis of steric arguments, trans stereochemistry was assigned to an isolable 1,3,2-dioxaphospholane obtained by Mukaiyama and co-workers[12a] upon condensation of benzoyl cyanide 8 (X = H) with triethyl phosphite under relatively mild conditions (50 °C, 0.5 h). This 2:1 adduct (mp 117 °C) upon thermolysis (140 °C) decomposed with loss of triethyl phosphate into a dicyanostilbene oxide (**9a** or **9b**, X = H; mp 162 °C, 70%), which was designated as trans (i.e., **9b**). This assignment was advanced on the basis that deoxygenation with tri-*n*-butylphosphine (150 °C), a process believed to occur with inversion,[25,26] gave a 1,2-dicyanostilbene (48%) whose melting point (158–160 °C) was consistent with that reported in the old literature for the *Z* configurational isomer.[27a]

(24) J. H. Boyer and R. Selvarajan, *J. Org. Chem.*, **35**, 1229 (1970).

(25) G. Wittig and W. Hagg, *Chem. Ber.*, **88**, 1654 (1955).
(26) M. J. Boskin and D. B. Denney, *Chem. Ind. (London)*, 330 (1959).

Scheme II



Subsequent work in this area was conducted by Boyer and Selvarajan[24] presumably in an attempt to achieve direct deoxygenation of benzoyl cyanide 8 (X = H) to phenylcyanocarbene with triethyl phosphite. Under the more drastic conditions employed (80 °C, 72 h) a dicyanostilbene oxide (mp 166–166.5 °C, 26%) as well as a dicyanostilbene (mp 161.5–162 °C, 23%) were formed. Although a 1,3,2-dioxaphospholane was not isolated in this case, such a 2:1 adduct was proposed as an intermediate.[24]

The *Z* configuration assigned earlier to the 1,2-dicyanostilbene, mp ~160 °C, obtained by Mukaiyama and co-workers[12a,27a] and thus the trans stereochemistry of the precursor stilbene oxide (mp 162 °C), however, were challenged by Boyer[24] on the basis of X-ray crystallographic data available in the literature.[27b] This reference was conceivably overlooked earlier and/or rejected by Mukaiyama, perhaps because the results were preliminary in nature. In addition, Boyer[24] cites published chemical and ultraviolet data that the alleged diphenylmaleonitrile (*Z* configuration) is in reality the *E* configurational isomer diphenylfumaronitrile.[27c] The facile acid-induced cyclization of the latter to diphenylmaleic anhydride proved to be a key factor in leading to the original erroneous assessment and reversal of configuration assignments,[27d] despite the recognition by early workers that hydrolysis could be accompanied by inversion.[27a]

The synthesis of authentic diphenylmaleonitrile (mp 134 °C)[27c] was ultimately achieved, and the results were published shortly in advance of the appearance of Mukaiyama's work;[12a] however, the refined and definitive X-ray data published on the *E* isomer (mp 161 °C)[27e] were apparently overlooked by both groups.[12a,24] Indeed, this question of the stereochemistry of the isomeric dicyanostilbenes represents a classic problem whose final solution spanned a period of over 70 years.

Certainly the reluctance exercised by Boyer[24] in accepting Mukaiyama's assessment of configuration for the pivotal dicyanostilbene, mp 161 °C, upon which the *cis*-2,3-dicyanostilbene oxide structural assignment rested at that time was justified.[24] This, in turn, cast doubt on the validity of the precursor oxirane stereochemistry designated as trans by Mukaiyama (i.e., **9b**) in order to accommodate the inversion anticipated on deoxygenation.[25,26] Boyer,[24] applying similar reasoning, was led to conclude that the oxirane should in fact be assigned cis rather than trans stereochemistry.[24]

The stereochemistry of the oxirane **9** (X = H, mp 166 °C) obtained by Boyer[24] remained to be secured, however, and became the primary question of significance in this context. The tentative cis assignment, as noted, was based solely upon the premise that the deoxygenation to the stilbene invariably proceeds with inversion;[25,26] however, isomerization under the reaction conditions had not been precluded. This matter was finally resolved when it was found that dipole moment data (**9a**, cis, μ = 6.5 D; **9b**, trans, μ = 0.87 D)[5b] were found to be at variance with Boyer's assignment of cis stereochemistry **9a** (X = H) to the 2,3-dicyanostilbene oxide (mp 166 °C),[24] which must in fact be the trans isomer **9b**, X = H, as originally contended by Mukaiyama. These results, in turn, have been verified by a Russian group[28] who found that the isomer **9b** (X = H, mp 159–160 °C) prepared by Konovalova and Ofitserova[12b] has a dipole moment of 0.32 D, which conforms more closely to that calculated for the trans epimer (0.49 D) than that for the cis (6.49 D).[28] In the interim period, we demonstrated that the (*Z*)-1,2-dicyanostilbene, mp 134 °C does partially undergo thermal isomerization to the alternate isomer mp 161 °C under the deoxygenation conditions employed by Mukaiyama[12a] with the oxirane **9b**. Thus, it should be recognized that these original assignments proved correct only as a consequence of a set of compensating errors. Although initially (*Z*)-2,3-dicyanostilbene may be formed as a result of inversion, equilibration prior to or during the deoxygenation may occur to give the *E* isomer as noted above. Consequently, the trans stereochemistry deduced for the oxirane by Mukaiyama[12a] from what he believed was the *Z* stilbene proved correct. In contrast, Boyer[24] correctly assigned trans stereochemistry to the stilbene although he was therefore in error in his assignment of cis stereochemistry to the oxirane.

After repeated attempts, we were finally successful in achieving the conversion of the readily accessible trans epoxy dinitrile **9b**[12a] (μ = 0.87 D)[5b] to the diester **14a** (mp 114–115 °C) in high yield (87%). This product is isomeric with, but not identical with, the polymorphic diester **13a** (mp 126–127 °C, C_6H_6–C_6H_{14}; 134–135 °C; CH_2Cl_2–C_6H_{14}) obtained as the major condensation product from methyl phenylglyoxylate (**12a**). The trans dinitrile **9b** (X = H) was initially transformed into a bis(imino ether) by treatment with sodium methoxide in methanol, which in turn was hydrolyzed in dilute, aqueous, methanolic hydrochloric acid to **14a** (Scheme II). This method for the efficient conversion of epoxynitriles to esters may be of

(27) (a) L. Chalanay and E. Knoevenagel *Ber. Dtsch. Chem. Ges.* **25**, 289 (1892); (b) C. J. Timmons and S. C. Wallwork, *Chem. Ind. (London)*, 62 (1955); (c) M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 2222 (1964); (d) D. G. Coe, M. M. Gale, R. P. Linstead, and C. J. Timmons, *J. Chem. Soc.*, 123 (1957); (e) S. C. Wallwork, *Acta Crystallogr.*, **14**, 375 (1961).

(28) S. G. Vul'fson, A. I. Donskova, and A. N. Vereshchagin, *Izv. Akad. Nauk. SSSR, Ser. Khim*, **24**, 72 (1975); *Bull. Acad. Sci., USSR, (Engl. Ed.), Div. of Chem. Sci.*, **24**, 63 (1975).

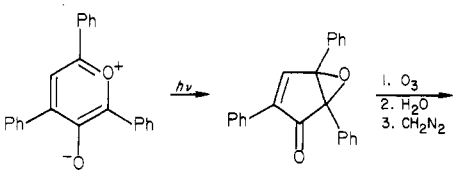
broad synthetic utility and was first reported by Kohler and Brown.[29]

Subsequently it was found that thermal isomerization of the cis diester adduct **13a** occurs upon heating in the absence of solvent at 180 °C for 24 h to give a 1:1 equilibrium mixture of **13a** and **14a**, which remains unchanged in composition after 44 h of additional heating. Similar results were obtained upon thermal equilibration of the trans diester **14a** available in turn by the alternate route involving methanolysis of the trans dicyanooxirane **9b** in the presence of sodium methoxide (Scheme II).[29] Separation of the equilibrium isomeric mixtures by thick-layer chromatography on silica gel (PF 254) was achieved by using 1:1 ether–hexane as the eluent mixture. As expected, the signals for the methoxy protons in the NMR spectrum of **14a** are found at higher field (δ 3.41) in accordance with predictions based upon the assigned configurations.[30]

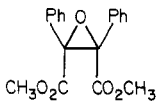
It is not unexpected that our attempts at methanolysis of the *cis*-dinitrile **9a** (X = H) (prepared by thermal equilibration of **9b**)[31] under conditions similar to those employed with **9b** (sodium methoxide or triethylamine in methanol) should prove more complex in view of the proximity of the reactive centers. In fact, the corresponding imide **15** (mp 156–157 °C; CH_2Cl_2–C_6H_{14}) is the primary product; however, this proved to be a substrate of considerable photochemical significance.[4f] Tedious thick-layer chromatographic separation permitted isolation of accompanying small amounts (<5%) of the desired cis diester **13a** identical in all respects with that obtained from **12a**. This completed the structural correlation of the diesters **13a** and **14a** with the dinitriles **9a** and **9b** (X = H), respectively, whose structures in turn had been secured by dipole moment measurements on the oxiranes[5b,28] and X-ray crystallographic data on the dicyanostilbenes.[27c]

These assignments for the epoxide **13a** are corroborated by data available that previously escaped our attention and were omitted from our preliminary communication.[2a] This was due in part to our original confusion regarding the structural assignment for **13a** and to the secondary importance attached in the literature to an earlier synthesis of this diester, which was simply a product of a degradative structural determination.[32]

Ozonolysis of the photobleached isomer **17** of the photochromic system **16**–**17** in the absence of hydroxylic solvents followed by oxidative workup provided a dibasic acid, presumably **18**. Upon esterification with diazomethane, this product gave a crystalline diester (mp 129–130 °C) (eq 6) presumably **13a** whose structure was deduced from spectral data [IR ($CHCl_3$ 1745 (C=O), 1220 (COC) cm^{-1}; NMR δ 7.30 (10 H, Ar H), 3.83 (6 H, OCH_3); *m/e* 312]. It is justifiable to assume from the similarity in melting points that **13a** (which is known to be polymorphic) and the ozonolysis product **13a** derived from **16** (eq 6) are the same, particularly since the recrystallization solvent is not reported and may differ from that employed in our studies. A comparison of the NMR and infrared spectral data reported for the oxirane derived from **17** with that of **13a** (despite slight differences in conditions), validates our contention that **13a** obtained independently



16 **17**



(6)

13a

from **12a** by treatment with hexamethylphosphorous triamide is the cis modification and that the stereochemistry assigned the diester precursor **9a**, as well as **9b**, is secure and in agreement with the dipole moment data.[5b]

Finally, an alternate route to the cis dibasic acid **18**, and thus ultimately the cis diester **13a**, was also developed involving treatment of diphenylmaleic anhydride with bromine in dimethylformamide containing lithium hydroxide which gives *cis*-diphenylepoxysuccinic acid (**18**), presumably through cyclization of an intermediate bromohydrin and accompanying hydrolysis of the anhydride. The dibasic acid **18** obtained from the cis diester **13a** or diphenylmaleic anhydride (**19**) is converted to the epoxy diphenylsuccinic anhydride **20** upon treatment with acetyl chloride. This self-consistent series of interconversions leaves no doubt that our structural assignments for **13a** and **14a** are firm.

The oxiranes **13a** and **14a** proved surprisingly resistant to deoxygenation using tri-*n*-butylphosphine[25,26] or the method of Dowd and Kang,[33] in sharp contrast to the results obtained with the corresponding dicyano analogue **9b** and a variety of other oxiranes. This precluded the use of deoxygenation techniques in our efforts at structural elucidation of **13a** and **14a**. Furthermore, while conversion of the dinitrile **9b** to the corresponding diamide with basic hydrogen peroxide is successful, subsequent nitrosation with nitrosyl chloride proved unsuccessful in generating the diacid, which would have provided additional structural information.

Temperature Effects on the Reductive Condensation of Methyl Phenylglyoxylates

A dramatic effect of variations in reaction temperature on the adduct stereochemistry of the phenylglyoxylates condensation noted above was observed. As the temperature is increased, the rate of condensation increases while the cis/trans ratio of 13:14 decreases; i.e., the condensation mixture becomes increasingly enriched with the trans isomer. This variation in isomer composition with temperature cannot be attributed to stereoepimerization of the isomeric oxiranes to the more stable isomer by way of ylide intermediates since those studied, and presumably the others, are stable at the temperature range employed (−10 to 80 °C). The pertinent data for the condensation of the glyoxylates **12a**, **12c**, and **12d** are displayed in Table II. Therefore the temperature dependence must have its origin at a stage in the condensation reaction that remains to be discerned. Perhaps formation of an initial 2:1 adduct is reversible[7e] and subject to steric and/or electronic factors of sufficient magnitude to exert control on the mode of interaction in the transition state leading to overall condensation. Conceivably, open-chain zwitterions formed reversibly and leading to transient 1,3,2- (or less likely 1,4,2-) dioxaphospholanes, may be responsible for the ob-

(29) E. P. Kohler and F. W. Brown, *J. Am. Chem. Soc.*, **55**, 4299 (1933).

(30) V. R. Valente and J. L. Wolfhagen, *J. Org. Chem.*, **31**, 2509 (1966); L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, New York, 1959, pp 85, 125.

(31) Huisgen and co-workers[5b] also achieved this equilibration **9b** to **9a** although the physical properties, aside from the dipole moment, of **9a** such as the melting point and infrared spectral data, remain to be published.

(32) E. F. Ullman, *J. Am. Chem. Soc.*, **85**, 3529 (1963).

(33) P. Dowd and K. Kang, *J. Chem. Soc. D*, 384 (1974).

Table II. Effects of Temperature on the Ratio of Epimers Formed upon Reductive Condensation with HMPT

solvent	temp, °C	ratio (yield; time, h) 13a:14a	13c:14c	13d:14d
toluene	−10	10.1:1 (32%; 15)		
hexamethylphosphoric triamide	23	3.78:1 (49%; 3)		
benzene	23	3.56:1 (55%; 3)	4.45:1 (88%; 0.5)	2.94:1 (90%; 1)
benzene	80	1.22:1 (50%; 0.16)	1.32:1 (91%; 0.16)	1.09:1 (91%; 0.16)

served selective stereochemical dependence on the temperature. In view of the synthetic utility associated with controlling oxirane stereochemistry in this manner, further studies are warranted in order to discern the origin of the observed effect.

Experimental Section

General Procedures. Proton magnetic resonance spectra were obtained on a Varian A-60 or Hitachi Perkin-Elmer R-20B spectrometer generally with $CDCl_3$ as the solvent with 1% tetramethylsilane as the internal standard. All melting points were established on a Thomas Hoover or a Buchi capillary melting point apparatus and are uncorrected. Silica gel G (PF_{254}; Brinkman Co.) was used for thin- and thick-layer chromatographic separations. Resolution was visualized by exposure of the chromatogram to shortwave ultraviolet radiation with a UVS-11 Ultraviolet Products (San Gabriel, CA) hand scanning lamp. Microanalyses were performed primarily by Galbraith Laboratories, Inc., Knoxville, TN, and by Integral Microanalytical Laboratories, Inc., Raleigh, NC, as well as on occasion by Chemanalytics, Inc., Tempe, AZ. Combustion analyses for C, H, N, and halogen, with rare exception, fell within acceptable limits of the theoretical values.

Preparation of the Substituted Benzoyl Cyanides (8a–h). The aroyl cyanides employed in this study were prepared by heating a mixture of the corresponding aroyl chloride with curpous cyanide as described by Oakwood and Weisgerber[20b] or under reflux in acetonitrile.[22] The latter method of Normant and Piechucki[22] is exemplified for the conversion of *m*-bromobenzoyl chloride into the previously unknown *m*-bromobenzoyl cyanide (**8h**) (vide infra).

***cis*- and *trans*-2,3-Bis(carbomethoxy)stilbene Oxide (13a and 14a, Respectively).** To 2.5 g (15 mmol) of methyl phenylglyoxylate [bp 88–90 °C (0.5 torr) (lit.[34] 110–111 °C (6 torr))] prepared according to the method of Eastham and Selman[19] was added dropwise hexamethylphosphorous triamide (1.3 g, 8.0 mmol). A spontaneous exothermic reaction ensues, and a dark yellow oil is produced. Trituration of this oil with an ethanol–water mixture resulted in crystallization of 1.1 g (49%) of **13a**: mp 126–127 °C (benzene–hexane); NMR ($CDCl_3$) δ 3.77 (s, 6 H, OCH_3), 7.0–7.4 (m, 10 H, Ar H); IR (Nujol) 1734, 1288, 1245, 1044, 735, 698 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16; O, 25.61. Found: C, 69.26; H, 5.10; O, 25.50. Recrystallization of this oxirane from CH_2Cl_2–hexane gave a polymorphic modification, mp 134–135 °C.

Under these conditions the trans isomer **14a** is formed in low yield (~14%); however, the yield of **14a** relative to **13a** is temperature dependent as is apparent from the data summarized in Table II. The trans isomer **14a** was separated from the alternate cis epimer by utilizing silica gel TLC (1:1 ether–hexane) and recrystallized; mp 114–115 °C (hexane–CH_2Cl_2); NMR ($CDCl_3$) δ 3.41 (s, 6 H, OCH_3), 7.2–7.8 (m, 10 H, Ar*H*). The infrared spectrum of the diester **14a** was identical with that of a sample prepared from **9b** by methods described below upon which a combustion analysis was obtained; IR (Nujol) 1745, 1300, 1245, 1023, 760, 708 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 69.47; H, 5.31.

Methyl (*p*-Nitrophenyl)glyoxylate (12b). *p*-Nitrobenzoyl cyanide (**8b**) [mp 114 °C (lit.[22] mp 114 °C)] was converted into the glyoxylate ester **12b**. A solution of the aroyl cyanide (2.0 g, 11 mmol) in anhydrous ether (30 mL) and methanol (0.2 mL) was stirred while hydrogen chloride gas was introduced through a gas-dispersion tube (1 h). Hydrolysis of the imino ether precipitate that forms during methanolysis affords 1.4 g (52%) of the pure glyoxylate **12b**; mp 105 °C (methanol–water) NMR ($CDCl_3$) δ 3.97 (s, 3 H, CH_3), 8.18 (s, 4 H, Ar H); IR($CHCl_3$) 3100, 3025, 2940, 1730, 1690, 1520, 1340, 1200, 1000, 750 cm^{-1}.

Anal. Calcd for $C_9H_7NO_5$: C, 51.68; H, 3.37; N, 6.70; O, 38.25. Found: C, 51.78; H, 3.31; N, 6.85; O, 38.10.

***cis*- and *trans*-2,3-Bis(carbomethoxy)-*p*,*p*′-dinitrostilbene Oxide (13b and 14b, Respectively).** Hexamethylphosphorous triamide (0.16 g; 1.0 mmol) was added dropwise to a solution of benzene (10 mL) and methyl *p*-nitrophenylglyoxylate (**12b**) (0.4 g; 1.9 mmol) under reflux. The reaction mixture was then heated under reflux for an additional 10 min. These cis and trans diesters (**13b** and **14b**, respectively) (0.28 g, 73%) were isolated by using TLC silica gel chromatography (benzene). The cis–trans product ratio (**13b**/**14b**) of 1.78 was determined by NMR analysis of the crude reaction mixture.

Cis diester **13b**: mp 174 °C (methanol); NMR ($CDCl_3$) δ 3.82 (s, 6 H, OCH_3), 7.20 (d, J = 9.0 Hz, 4 H, Ar H), 7.97 (d, 4 H, Ar H); IR (Nujol) 1765, 1745, 1250, 1053, 1007, 868, 860, 795 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}N_2O_9$: C, 53.74; H, 3.51; N, 6.96. Found: C, 53.58; H, 3.42; N, 7.23.

Trans diester (**14b**): mp 222 °C (CH_2Cl_2–methanol); NMR ($CDCl_3$) δ 3.58 (s, 6 H, OCH_3), 8.17 (d, J = 9.4 Hz, 4 H, Ar H), 8.55 (d, 4 H, Ar H); IR (Nujol) 1755, 1740, 1250, 1043, 868, 856, 789 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}N_2O_9$: C, 53.74; H, 3.51; N, 6.96. Found: C, 53.60; H, 3.34; N, 6.92.

Methyl (*p*-Chlorophenyl)glyoxylate (12c). The method previously described for the conversion of **8b** to **12b** was used for the transformation of *p*-chlorobenzoyl cyanide (**8c**)[20b] [mp 39–41 °C (lit.[35] mp 40–41.5 °C)] into the glyoxylate ester **12c**. *p*-Chlorobenzoyl cyanide (3.0 g, 18 mmol) dissolved in an ether–methanol solution saturated with hydrogen chloride gas was converted to 2.4 g (67%) of white crystalline ester **12c**: mp 65–66 °C (methanol–water); NMR ($CDCl_3$) δ 3.90 (s, 3 H, OCH_3), 7.32 (d, J = 8.5 Hz, 2 H, Ar H), 7.79 (d, 2 H, Ar H); IR ($CHCl_3$) 3010, 2920, 1730, 1680, 1580, 1190, 1170, 1080, 1000, 900, 840, 810 cm^{-1}.

Anal. Calcd for $C_9H_7ClO_3$: C, 54.42; H, 3.55; Cl, 17.85. Found: C, 54.38; H, 3.44; Cl, 17.98.

***cis*- and *trans*-2,3-Bis(carbomethoxy)-*p*,*p*′-dichlorostilbene Oxide (13c and 14c, Respectively).** The method employed for the preparation of **13a** and **14a** was used to synthesize the isomeric stilbene oxides **13c** and **14c**. The reaction of methyl (*p*-chlorophenyl)glyoxylate (**12c**) (0.10 g; 0.5 mmol) with hexamethylphosphorous triamide (0.04 g; 0.25 mmol) was conducted in 4 mL of benzene and the mixture subsequently heated under reflux for 10 min. Diesters **13c** and **14c** (87 mg, 91%) were obtained by separation on silica gel by using a sequential two-step TLC process in which the solvent systems of choice were 1:1 hexane–CH_2Cl_2 followed by 1:1 ether–hexane after isolation and reapplication to a second plate. The cis/trans ratio (**13c**/**14c**) was 1.32. When this reaction was conducted at 23 °C in benzene for 30 min, the cis/trans ratio increases (**13c**/**14c** = 4.45), but the total yield of **13c** and **14c** (88%) does not change appreciably.

Cis diester **13c**: mp 126 °C (CH_2Cl_2–methanol); NMR ($CDCl_3$) δ 3.78 (s, 6 H, OCH_3), 7.4 (m, 8 H, Ar H): IR (Nujol) 1750, 1500, 1244, 1100, 1047, 1003, 800 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}O_5Cl_2$: C, 56.71; H, 3.70; Cl, 18.60. Found: C, 56.95; H, 3.66; Cl, 18.50.

Trans diester (**14c**): mp 136 °C (CH_2Cl_2–methanol); NMR ($CDCl_3$) δ 3.42 (s, 6 H, OCH_3), 7.30 (d, J = 9 Hz, 4 H, Ar H), 7.62 (d, 4 H, Ar H); IR (Nujol) 1740, 1274, 1095, 1020, 848, 782 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}O_5Cl_2$: C, 56.71; H, 3.70; Cl, 18.60. Found: C, 56.63; H, 3.76; Cl, 18.68.

(34) E. Baer and M. Kates, *J. Am. Chem. Soc.*, **67**, 1482 (1945).

(35) R. L. Soulen, S. C. Carlson and F. Lang, *J. Org. Chem.*, **38**, 479 (1973).

Methyl (*p*-Bromophenyl)glyoxylate (12d). The method described above for the preparation of **12b** was used to convert *p*-bromobenzoyl cyanide (**8d**)[20b] [mp 63 °C (lit.[36] mp 56–62 °C)] to the ester **12d**. Hydrogen chloride gas was introduced into a solution containing *p*-bromobenzoyl cyanide (3 g, 14 mmol) in 30 mL of anhydrous ether and 0.2 mL of anhydrous methanol for 1 h. Hydrolysis of the precipitate that deposited during this time afforded 2.86 g (82%) of glyoxylate **12d**: mp 63 °C (methanol–water); NMR ($CDCl_3$) δ 3.91 (s, 3 H, OCH_3), 7.63 (d, J = 8.5 Hz, 2 H, Ar H), 7.90 (d, 2 H, Ar H); IR ($CHCl_3$) 3100, 2980, 1740, 1680, 1590, 1480, 1400, 1260, 1200, 1170, 1070, 1000 cm^{-1}.

Anal. Calcd for $C_9H_7BrO_3$: C, 44.47; H, 2.90; Br, 32.88. Found: C, 44.26; H, 2.77; Br, 32.88.

***cis*- and *trans*-2,3-Bis(carbomethoxy)-*p*,*p*'-dibromostilbene Oxide (13d and 14d, Respectively).** Hexamethylphosphorous triamide (0.14 g, 0.86 mmol) was added dropwise to a solution of methyl (*p*-bromophenyl)glyoxylate (**12d**) (0.43 g, 1.7 mmol) in 10 mL of benzene under reflux. After 10 min the solution was allowed to cool and was concentrated, and the resulting diesters **13d** and **14d** (**13d**/**14d** = 1.09) were separated on silica gel (benzene) (0.39 g; 94%). When this conversion was run at 23 °C the yield of the diester mixture (**13d** and **14d**) was reduced to 90%, although the cis–trans ratio (**13d**/**14d**) increased dramatically to 2.94.

Cis diester (**13d**): mp 138 °C (CH_2Cl_2–methanol); NMR ($CDCl_3$) δ 3.79 (s, 6 H, OCH_3), 7.4 (m, 8 H, Ar*H*); IR (Nujol) 1765, 1295, 1245, 1172, 1081, 1047, 1006 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}O_5Br_2$: C, 45.98; H, 3.00; Br, 34.00. Found: C, 46.14; H, 3.12; Br, 32.26.

Trans diester (**14d**): mp 135 °C (CH_2Cl_2–hexane); NMR ($CDCl_3$) δ 3.43 (s, 6 H, OCH_3), 7.78 (s, 8 H, Ar H); IR (Nujol) 1760, 1285, 1245, 1072, 1033, 1014 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}O_5Br_2$: C, 45.98; H, 3.00; Br, 34.00. Found: C, 46.00; H, 2.73; Br, 34.33.

Methyl (*p*-Methylphenyl)glyoxylate (12e). The method of Eastham and Selman[19] was used to convert *p*-methylbenzoyl cyanide (**8e**)[20b] [mp 47–49 °C (lit.[35] mp 49.0–49.5 °C)] (8.0 g, 55 mmol) into 4.38 g (44%) of **12e**, bp 100 °C (0.4 torr); NMR ($CDCl_3$) δ 2.39 (s, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 7.15 (d, J = 8.0 Hz, 2 H, Ar H), 7.75 (d, 2 H, Ar H); IR ($CHCl_3$) 3010, 2940, 1730, 1680, 1600, 1430, 1310, 1200, 1160, 1000, 900, 830 cm^{-1}.

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.03; H, 5.65.

***cis*- and *trans*-2,3-Bis(carbomethoxy)-*p*,*p*'-dimethylstilbene Oxide (13e and 14e, Respectively).** The diesters (**13e** and **14e**) were prepared by treatment of glyoxylate **12e** (0.42 g, 2.4 mmol) with hexamethylphosphorous triamide (0.2 g, 1.2 mmol) in benzene (10 mL) at the reflux temperature by the same method employed for the preparation of **13b**. The mixture of **13e** and **14e** was separated by utilizing TLC on silica gel with benzene as the eluent. The combinded yield of diesters (**13e** and **14e**) was 0.36 g (90%); cis–trans ratio (**13e**/**14e**) was found to be 1.81.

Cis diester (**13e**): mp 106 °C (CH_2Cl_2–methanol); NMR ($CDCl_3$) δ 2.27 (s, 6 H, CH_3), 3.90 (s, 6 H, OCH_3), 7.18 (d, J = 8.8 Hz, 4 H, Ar H), 7.48 (d, 4 H, Ar H); IR (Nujol) 1750, 1435, 1284, 1240, 1170, 1049, 1005 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.58; H, 5.92. Found: C, 70.79; H, 6.09.

Trans diester (**14e**): mp 149 °C (CH_2Cl_2–methanol); NMR ($CDCl_3$) δ 2.42 (s, 6 H, CH_3), 3.54 (s, 6 H, OCH_3), 7.42 (d, J = 8.8 Hz, 4 H, Ar H), 7.87 (d, 4 H, Ar H); IR (Nujol) 1745, 1300, 1241, 1173, 1015, 915 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.58; H, 5.92. Found: C, 70.85; H, 5.79.

Methyl (*p*-Methoxyphenyl)glyoxylate (12f). The method of Oakwood and Weisgerber[20a] was used for the hydrolysis of *p*-methoxybenzoyl cyanide (**8f**)[20b] [mp 57–59 °C (lit.[35] mp 58–60 °C] (5.0 g, 31 mmol) to give (*p*-methoxyphenyl)glyoxylic acid (3.5 g, 63%). Esterification of this acid (3.5 g, 19 mmol) with *p*-toluenesulfonic acid as a catalyst gave 3.3 g (87%) of **12f**, mp 49 °C (methanol) (lit.[19] mp 50–51 °C).

***cis*- and *trans*-2,3-Bis(carbomethoxy)-*p*,*p*'-dimethoxystilbene Oxide (13f and 14f, Respectively).** The method described above for the preparation of **13b** was used to prepare *cis*- and *trans*-2,3-bis(carbomethoxy)-*p*,*p*'-dimethoxystilbene oxide (**13f** and **14f**, respectively) from the reductive condensation of methyl (*p*-methoxyphenyl)glyoxylate (**12f**) induced by hexamethylphosphorous triamide.

The amide (0.17 g, 1.0 mmol) was added dropwise to a solution of benzene (10 mL) and the glyoxylate **12f** (0.4 g, 2.0 mmol) heated at the reflux temperature for a period of 10 min. After evaporation of benzene in vacuo, diesters **13f** and **14f** were isolated. Some difficulty was encountered in separating **14f** from **13f** by TLC on silica gel; however, a sequential two-step TLC process was found to be effective in which the solvent initially used was CH_2Cl_2, followed by isolation and reapplication to a plate and subsequent elution with 1:1 ether–hexane. The total yield of diesters **13f** and **14f** was 0.27 g (70%) (**13f**/**14f** = 2.30).

Cis diester (**13f**): mp 93 °C (CH_2Cl_2–methanol); NMR ($CDCl_3$) δ 3.70 (s, 6 H, $COOCH_3$), 3.81 (s, 6 H, OCH_3), 6.73 (d, J = 8.7 Hz, 4 H, Ar H), 7.29 (d, 4 H, Ar H); IR (Nujol) 1750, 1620, 1520, 1262, 1233, 1173 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.38; H, 5.55.

Trans diester (**14f**), mp 116 °C (CH_2Cl_2–methanol); NMR ($CDCl_3$) δ 3.55 (s, 6 H, $COOCH_3$), 3.94 (s, 6 H, OCH_3), 7.14 (d, J = 9.1 Hz, 4 H, Ar H), 7.90 (d, 4 H, Ar H); IR (Nujol) 1760, 1620, 1515, 1310, 1265, 1246, 1182 cm^{-1}.

Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.38; H, 5.65.

Methyl (*m*-Chlorophenyl)glyoxylate (12g). *m*-Chlorobenzoyl cyanide (**8g**) [bp 100–110 °C (10 torr) (lit.[37] bp 114–117 °C (20 torr))] (3.0 g, 18 mmol) was converted to 1.3 g (36%) of **12g**, mp 45 °C (hexane) according to the method of Eastham and Selman.[19] NMR ($CDCl_3$) δ 4.11 (s, 3 H, OCH_3), 7.7–8.3 (m, 4 H, Ar H). IR (Nujol) 1740, 1695, 1228, 1189, 1023, 895 cm^{-1}.

Anal. Calcd for $C_9H_7ClO_3$: C, 54.42; H, 3.55; Cl, 17.85. Found: C, 54.21; H, 3.39; Cl, 18.11.

***cis*- and *trans*-Bis(carbomethoxy)-*m*,*m*'-dichlorostilbene Oxide (13g and 14g, Respectively).** The method previously described for the preparation of **13b** and **14b** conducted in benzene as a solvent was used for the syntheses of **13g** and **14g**. The glyoxylate **12g** (0.33 g, 1.6 mmol) was heated in benzene (10 mL) under reflux. To this solution hexamethylphosphorous triamide (0.15 g, 0.9 mmol) was added dropwise, and heating was continued for 10 min. The diesters (**13g** and **14g**) (0.26 g, 82%) cis/trans ratio, **13g**/**14g** = 1.38) were isolated by thick-layer chromatography on silica gel utilizing benzene as an eluent.

Cis diester (**13g**): mp 112 °C (benzene–methanol); NMR ($CDCl_3$) δ 3.92 (s, 6 H, OCH_3), 7.2–7.7 (m, 8 H, ArH); IR (Nujol) 1740, 1300, 1210, 1180, 1053, 1028 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}O_5Cl_2$: C, 56.71; H, 3.70; Cl, 18.60. Found: C, 56.81; H, 3.60; Cl, 18.55.

Trans diester (**14g**): mp 108 °C (benzene–methanol); NMR ($CDCl_3$) δ 3.53 (s, 6 H, OCH_3); 7.6–8.0 (m, 8 H, Ar H); IR (Nujol) 1760, 1298, 1257, 1179, 1041, 1028 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}O_5Cl_2$: C, 56.71; H, 3.70; Cl, 18.60. Found: C, 56.95; H, 3.69; Cl, 18.65.

***m*-Bromobenzoyl Cyanide (8h, X = *m*-Br).** *m*-Bromobenzoyl chloride (10 g, 45 mmol) was heated with cuprous cyanide (12 g, 130 mmol) in acetonitrile (50 mL) at the reflux temperature for 1 h. The cyanide, 8.3 g (86%) (mp 55 °C, petroleum ether), was isolated and purified by distillation (120–123 °C (8 torr)), NMR ($CDCl_3$) δ 7.3–8.2 (m, Ar H); IR (Nujol) 1675, 1295, 1245, 988, 888, 812 cm^{-1}.

Anal. Calcd for C_8H_4BrNO: C, 45.74; H, 1.92; N, 6.67; Br, 38.05. Found: C, 45.61; H, 1.66; N, 6.51; Br, 37.87.

Methyl (*m*-Bromophenyl)glyoxylate (12h). The method of Eastham and Selman[19] was used for the transformation of *m*-bromobenzoyl cyanide (4.0 g, 19 mmol) dissolved in an ether–methanol solution saturated with hydrogen chloride into 1.8 g (39%) of **12h**: mp 53 °C (CH_2Cl_2–hexane) NMR ($CDCl_3$) δ 4.07 (s, 3 H, OCH_3), 7.4–8.4 (m, 4 H, Ar**H**); IR (Nujol) 1740, 1600, 1220, 1074, 1018, 899, 825, 782 cm^{-1}.

Anal. Calcd for $C_9H_7BrO_3$; C, 44.47; H, 2.90; Br, 32.88. Found: C, 44.65; H, 2.75; Br, 33.12.

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***cis*- and *trans*-Bis(carbomethoxy)-*m*,*m*'-dibromostilbene Oxide (13h and 14h).** The method employed for the preparation of **13g** and **14g** was used to prepare **13h** and **14h** from the reaction of **12h** (0.42 g, 1.7 mmol) with hexamethylphosphorous triamide (0.14 g, 0.86 mmol). The diesters **13h** and **14h** were isolated and separated by TLC on silica gel with benzene; 0.36 g (89%) (cis/trans ratio, **13h**/**14h** = 1.38).

Cis diester (**13h**): mp 126 °C (benzene–methanol); NMR ($CDCl_3$) δ 3.92 (s, 6 H, OCH_3), 7.1–7.8 (m, 8 H, Ar H); IR (Nujol) 1740, 1303, 1230, 1207, 1178, 1080, 1050, 1021 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}Br_2O_5$: C, 45.98; H, 3.00; Br, 34.00. Found: C, 46.28; H, 2.89; Br, 34.16.

Trans diester (**14h**): mp 108 °C (benzene–methanol); NMR ($CDCl_3$) δ 3.56 (s, 6 H, OCH_3), 7.3–8.2 (m, 8 H, Ar H); IR (Nujol) 1740, 1230, 1075, 1020, 1000, 780 cm^{-1}.

Anal. Calcd for $C_{18}H_{14}Br_2O_5$: C, 45.98; H, 3.00; Br, 34.00. Found: C, 36.30; H, 2.85; Br, 34.10.

***cis*-2,3-Dicyanostilbene Oxide (9a, X = H).** The *cis*-oxirane **9a** was prepared by thermal equilibration of the available trans isomer and separation. Huisgen and co-workers[5b] have also achieved this equilibration although the physical properties, aside from the dipole moment, such as the required melting point and IR spectral data, to our knowledge, remain to be published. *trans*-2,3-Dicyanostilbene oxide (**9b**) (X = H) (3.7 g, 15 mmol) was heated under reflux in dioxane (80 mL) for 3.5 h. After removal of dioxane under reduced pressure, the cis-oxide **9a** (X = H) was separated from the residual epimer **9b** (X = H) by column chromatography on silica gel (CH_2Cl_2–hexane): yield 0.57 g (15%); mp 146–147 °C (CH_2Cl_2–hexane); NMR ($CDCl_3$) δ 7.28 (s, Ar H); IR (Nujol) 1220, 1085, 1017, 988, 922, 905, 800, 775, 737, 715, 708 cm^{-1}.

Anal. Calcd for $C_{16}H_{10}N_2O$: C, 78.04; H, 4.09; N, 11.38. Found: C, 77.83; H, 3.98; N, 11.25.

Conversion of *trans*-2,3-Dicyanostilbene Oxide (9b, X = H) to *trans*-2,3-Bis(carbomethoxy)stilbene Oxide (14a). A suspension of *trans*-2,3-dicyanostilbene oxide (**9b**, X = H) (1.2 g, 4.9 mmol) in a solution of sodium methoxide (0.10 g, 2.0 mmol) and methanol (30 mL) was stirred at ambient temperature for a period of 2 h. The reaction was then quenched with 2 N hydrochloric acid (10 mL), stirring was continued for an additional 2 h to ensure complete hydrolysis of the bis(imino) ether. The solid that deposited was collected on a filter and air dried; 1.3 g (85%), mp 114 °C (CH_2Cl_2–hexane).

The infrared and NMR spectra of the product were identical in all essential respects with those of a sample of the diester **14a** prepared from **12a**.

Thermolysis of *cis*-2,3-Bis(carbomethoxy)stilbene Oxide (13a). A 60-mg (0.19 mmol) in sample of the cis diester **13a** was heated at 180 °C for 18 h in a Griffin–Worden pressure vessel (Kontes Glass Co., Vineland, NJ). The separation of the mixture was achieved on silica gel (TLC) by elution with ether–hexane mixtures, and 26 mg (43%) of the trans diester **14a** was obtained in addition to 26 mg of recovered cis-diester **13a**.

Thermolysis of *trans*-2,3-Bis(carbomethoxy)stilbene Oxide (14a). A 60-mg (0.19 mmol) sample of trans-diester **14a** was heated at 180 °C for 24 h in a vessel of the type used with **13a**. The separation of the reaction mixture was achieved on silica gel (TLC) by elution with ether–hexane mixtures, and 21 mg (35%) of the cis diester **13a** was obtained in addition to 24 mg of recovered trans diester **14a**.

Epoxydiphenylsuccinimide (15). *cis*-2,3-Dicyanostilbene oxide (**9a**, X = H) (50 mg, 0.20 mmol) was added to a solution of potassium *tert*-butoxide (50 mg, 0.44 mmol) in *tert*-butyl alcohol (3 mL). After the solution was stirred at ambient temperature for 2.5 h, 2 mL of 5% sulfuric acid was added and the resulting mixture stirred for an additional 0.5 h. Epoxydiphenylsuccinimide (**15**) was isolated from this reaction mixture by extraction with ethyl acetate and separated from other components by using TLC (silica gel, 40%, ether–CH_2Cl_2): yield, 40 mg (74%); mp 157–158 °C (CH_2Cl_2–hexane); NMR ($CDCl_3$) δ 7.25 (s, Ar H); IR (Nujol) 3260, 1800, 1740, 1510, 1335, 1165, 1007, 760, 696, 627 cm^{-1}.

Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28. Found: C, 72.19; H, 3.99; N, 5.10.

Formation of *trans*-2-(Carbomethoxy)-3-cyanostilbene Oxide (21) from *trans*-2,3-Dicyanostilbene Oxide (9b, X = H). A solution of *trans*-dicyanostilbene oxide (**9b**, X = H) (0.74 g, 3.0 mmol) in methanol (20 mL) containing 0.9 g (8.9 mmol) of triethylamine was stirred at ambient temperature for a period of 6 h, after which time no remaining starting material could be detected in the reaction mixture by TLC. The volatile solvents were then removed under reduced pressure, and the resulting monoimino ether was then treated with 2 mL of 2 N hydrochloric acid in 20 mL of methanol at room temperature for 1.5 h. Water was then added and the resulting precipitate of cyanoester (0.56 g; 67%) was collected on a filter; mp 110 °C (CH_2Cl_2–hexane) NMR ($CDCl_3$) δ 3.46 (s, 3 H, OCH_3), 7.5 (m, 10 H, ArH); IR (Nujol) 1750, 1278, 1243, 1215, 1022 cm^{-1}.

Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.01. Found: C, 73.39; H, 4.80; N, 4.90.

***cis*-Epoxydiphenylsuccinic Acid (18).** *cis*-2,3-Bis(carbomethoxy)stilbene oxide (**13a**) (0.30 g, 1.1 mmol) was stirred overnight in a solution of 1 N sodium methoxide in methanol to which was added water (0.2 mL) at ambient temperature. The resulting solid was dissolved completely by addition of water. After prior acidification with hydrochloric acid, the dibasic acid **17** was extracted with ether. A white solid (0.29 mg; 95%, based on the availability of a molar equivalent of water) was obtained after removal of ether in vacuo; mp 125–126 °C (water) softens at 98 °C; NMR (acetone-d_6), δ 6.07 (s, COOH), 7.0–7.4 (m, Ar H); IR (Nujol) 3550, 1745, 1700, 1278, 1237, 1197, 960, 920, 840, 743, 692, 650 cm^{-1}. That no empimerization occurs during hydrolysis of **13a** was confirmed by esterification of the dibasic acid **17** with diazomethane in ether, which regenerates **13a** in quantitative yield.

Anal. Calcd for $C_{16}H_{12}O_5 \cdot H_2O$: C, 63.57; H, 4.67. Found: C, 63.74; H, 4.64.

Alternate Preparation of *cis*-2,3-Bis(carbomethoxy)stilbene Oxide (13a) from 2,3-Diphenylmaleic Anhydride (19). 2,3-Diphenylmaleic anhydride (0.10 g, 0.40 mmol) was dissolved in a solution of dimethylformamide (5 mL), lithium hydroxide monohydrate (1.0 g, 0.24 mmol), and water (0.3 mL). The resulting solution was then stirred at ambient temperature for 0.5 h, while bromine (3.0 g, 19 mmol) was added dropwise. Stirring was continued for an additional 6 h period, and the resulting solution was quenched with hydrochloric acid. The dibasic acid was extracted with ether and esterified with diazomethane. After removal of the ether, the cis diester **13a** [51 mg (41%) mp 126 °C] was isolated. The infrared and NMR spectra of the product are identical in all essential respects with that of a sample of **13a** prepared from **12a**. The trans diester **14a** was not formed as a product in this reaction, at least within the limits detectable by conventional NMR techniques.

Epoxydiphenylsuccinic Anhydride (20). Epoxydiphenylsuccinic acid (**18**) (0.30 g, 1.9 mmol) was heated in acetyl chloride (10 mL) under gentle reflux for 2 h. After removal of acetyl chloride under reduced pressure while maintaining the temperature below 20 °C, the residual white solid was recrystallized from $CHCl_3$–hexane, mp 146–147 °C; (0.24 g, 91%), NMR ($CDCl_3$), δ 7.30 (s, Ar H); IR (Nujol) 1845, 1810, 1250, 1160, 1100, 969, 942, 921, 773, 758, 745, 699, 627 cm^{-1}.

Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79. Found: C, 72.17; H, 3.78.

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