Anal. Calcd for $C_{17}H_{23}SO_5N$: C, 57.76; H, 6.51; N, 3.96. Found: C, 57.83; H, 6.49; N, 3.87 (Nagy).

***p*-Trimethylammoniumbenzhydrol *p*-Toluenesulfonate.** *p*-Dimethylaminobenzophenone (1.0 g, 0.0044 mole) and 1.5 g (0.0054 mole) of methyl *p*-toluenesulfonate were mixed and heated to 120° for a few minutes. The product was crystallized from ethyl alcohol, mp 252–253°, 1.4 g (0.0034 mole), 77% yield, ***p*-benzoylphenyltrimethylammonium *p*-toluenesulfonate.** A solution of this product in 50 ml of ethanol was treated with 0.26 g (0.0066 mole) of sodium borohydride in portions over 5 min and stirred at 75° for 1 hr. Saturated ammonium sulfate (25 ml) was added at 0°, and the mixture was evaporated to dryness. The residue was extracted with warm ethanol, the extracts were concentrated, and the residue was dissolved in ethanol and diluted with chloroform, leading to *p*-trimethylammoniumbenzhydrol *p*-toluenesulfonate, mp 183.5–184.5° from ethanol.

Anal. Calcd for $C_{23}H_{27}NO_4S$: C, 66.79; H, 6.58; N, 3.39; S, 7.74. Found: C, 66.83; H, 6.57; N, 3.54; S, 7.90 (Bernhardt).

Photoreduction of *p*-Benzoylphenyltrimethylammonium Methosulfate (Ia). Aliquots (5 ml) of a solution of 1.44 g (0.0041 mole, 0.164 *M*) of compound Ia in 25 ml of 1:1 2-propanol–water were degassed and irradiated under argon for 25 hr with the GE A3 lamp. An aliquot was concentrated and the residue, the pinacol, was washed with chloroform and dried, mp 168° dec.

Anal. Calcd for $C_{34}H_{44}N_2O_{10}S_2 \cdot 2H_2O$: C, 55.12; H, 6.53. Found: C, 54.61; H, 6.60 (Nagy).

Photoreduction of *p*-Benzoylphenyltrimethylammonium Chloride (Ib). a. A solution of 7.6 g (0.028 mole, 0.11 *M*) of Ib in 250 ml of 9:1 2-propanol–water was irradiated in a Rayonet photochemical reactor until absorption at 350 mμ disappeared, 168 hr. The solution was concentrated, and the residue was recrystallized from aqueous 2-propanol, leading to the pinacol, 6.1 g, 80% yield, mp 180–182° dec.

b. A solution of 0.138 g (0.50 mmole, 0.10 *M*) of Ib in 5 ml of 9:1 2-propanol–water was degassed and irradiated under argon for 19 hr with a GE 85w A3 lamp. The ketone was completely reduced. The pinacol was recovered as in a.

Anal. Calcd for $C_{32}H_{38}N_2O_2Cl_2 \cdot 2H_2O$: C, 65.63; H, 7.23. Found: C, 65.87; H, 7.33 (Bernhardt).

c. A solution of 0.1 *M* Ib in 0.1 *N* HCl in 1:1 2-propanol–water was irradiated with the Osram lamp and underwent photoreduction at a rate of 0.031 *M* hr^{-1}; 0.1 *M* benzophenone in 2-propanol was photoreduced at the same time at a rate of 0.051 *M* hr^{-1}. The residual solutions were photoreduced to completion, 20 hr; the acid was neutralized with 1 *N* NaOH, the solutions were taken to dryness, the residue was extracted with hot 2-propanol, the extracts were concentrated, and the new residue was crystallized, leading to the pinacol, mp and mmp 182–186° dec.

d. A solution of 0.1 *M* Ib in 0.1 *N* NaOH in 1:1 2-propanol–water was irradiated at the same time as c and underwent photoreduction at a rate of 0.020 *M* hr^{-1}. Analysis of an aliquot by alkaline decomposition after irradiation for 20 hr led to no formation of the absorption peak at 352 mμ. The fully irradiated solutions were combined, neutralized with 1 *N* HCl, and evaporated to dryness. The residue was extracted with hot 2-propanol and the extracts were concentrated. The new residue was an amorphous solid, *p*-trimethylammoniumbenzhydrol chloride, with infrared spectrum identical with that prepared from the methosulfate by conversion to the hydroxide by ion exchange and neutralization with hydrogen chloride. We were unable to crystallize either sample. It was converted to *p*-trimethylammoniumbenzhydrol *p*-toluenesulfonate, mp 184.5–185.5° from ethanol; identical with the synthesized sample.

Anal. Found: C, 66.46; H, 6.93; N, 3.27; S, 7.64 (Bernhardt).

e. A solution of 1.38 g (0.0050 mole, 0.20 *M*) of Ib in 25 ml of 1.0 *M* 2-propylamine in water was degassed and irradiated under argon for 24 hr in Thunberg tubes. The solutions were combined and lyophilized. The residue was dissolved in 20 ml of water, placed on a column of 20–50 mesh Dowex 1-XB (hydroxide form), eluted, neutralized with *p*-toluenesulfonic acid, and concentrated. The residue was crystallized from chloroform–ethanol, and from ethanol, mp and mmp 184–185°, 1.27 g (0.0031 mole), 62% yield, *p*-trimethylammoniumbenzhydrol *p*-toluenesulfonate.

To 5 ml of another similar photolysate, there were added 0.20 g of thiosemicarbazide and 0.50 g of sodium acetate, and the tube was sealed and heated at 85° for 1 hr. Acetone thiosemicarbazone was obtained, 0.074 g (0.57 mmole), 57% yield, mp 188–189°, infrared spectrum identical with that of an authentic sample. In a blank preparation from a similar concentration of acetone the yield of thiosemicarbazone was 60%, indicating ~95% yield of acetone in the photoreduction.

The Reaction of Epoxides with Tri-*n*-butylcarbethoxymethylidenephosphorane. Formation of Unsaturated Esters

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Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. *Received May 11, 1967*

Abstract: The title ylide reacts with various epoxides in refluxing benzene to give α,β-unsaturated esters. Methylenecyclohexane epoxide and 1-octene oxide yield ethyl 3-cyclohexylpropenoate and ethyl 2-decenoate, respectively, by a process involving hydride migration. Cyclohexene oxide, 1-methylcyclohexene oxide, and cycloheptene oxide give the products of carbon migration (ring contraction). The product from styrene oxide is isomerized under these conditions to the more stable ethyl 4-phenyl-3-butenoate. Cyclopentene oxide behaves anomalously, giving by a somewhat slower reaction 6-carbethoxybicyclo[3.1.0]hexane. The mechanism is discussed.

Epoxides have previously been shown to react with certain phosphorus ylides to yield cyclopropane derivatives.[2,3] The structural requirement of an anion-stabilizing group (carbethoxy, cyano) bonded to the ylide carbon has been stressed.[3] Thus Denney, Vill, and Boskin[4] have reported the reaction (under forcing conditions, 200°) of cyclohexene oxide with triphenylcarbethoxymethylidenephosphorane to give ethyl 7-norcaranecarboxylate (**2**) in moderate yield. Comparable results were obtained with 1-octene oxide and styrene

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(1) NASA Predoctoral Trainee.

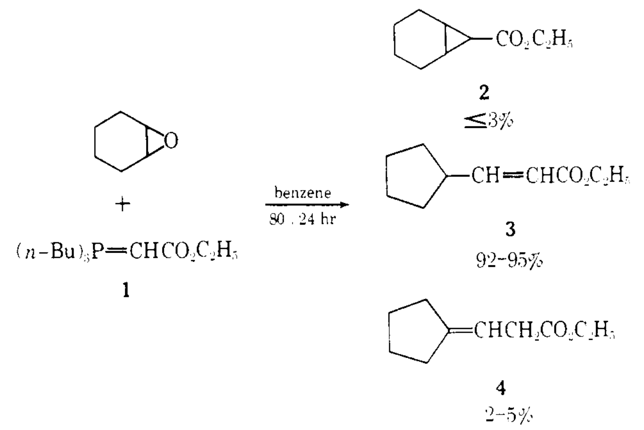
(2) D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **81**, 6330 (1959).

(3) W. S. Wadsworth, Jr., and W. D. Emmons, *ibid.*, **83**, 1733 (1961).

(4) D. B. Denney, J. J. Vill, and M. J. Boskin, *ibid.*, **84**, 3944 (1962).

oxide. These authors also noted that the analogous tri-*n*-butylphosphorane gave a cyclopropane derivative under much milder conditions (refluxing benzene).[5]

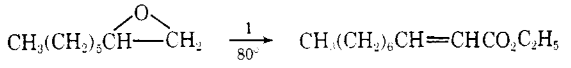
As a potential route for the stereospecific synthesis of alkyl-substituted norcaranes, we were interested in determining the limitations of this reaction. In a preliminary experiment, however, the distillable product (36%) obtained from cyclohexene oxide and tri-*n*-butylcarbethoxymethylidenephosphorane (**1**) was found to be almost exclusively ethyl 3-cyclopentylpropenoate (**3**). Only traces of the expected cyclopropyl derivative **2** were formed,[6] along with minor amounts of an isomeric unsaturated ester (**4**).



The structure of **3** was determined from its nmr spectrum, which integrated correctly and was characteristic for an α,β-unsaturated ester; the vinyl proton coupling constant (J = 16 cps) led to the assignment of the *trans* configuration for this ester. Hydrolysis of **3** gave the corresponding known acid.[8] Confirmation of this structural assignment was afforded by alternate synthesis of **3** *via* the Wittig reaction on cyclopentanecarboxaldehyde.

When this reaction was carried out in refluxing xylene (134°), the over-all yield was somewhat diminished, while the proportion of **2** increased to 6-12%. The major product under these conditions is the β,γ-unsaturated ester **4**. It was subsequently established that **3** is the initially formed material, which is isomerized to the more stable **4**. Equilibration is slow at 80° (under the standard reaction conditions), but occurs with a half-life of a few hours at 134°. At the higher temperature $K(\mathbf{4}/\mathbf{3}) = 2.45$. The greater stability of the unconjugated ester is attributed to branching at the γ-carbon.[9] The structure of **4** was established by its characteristic nmr spectrum, and further confirmed by catalytic reduction to give an ester identical with that obtained by Michael addition of cyclopentylmagnesium bromide to ethyl acrylate.

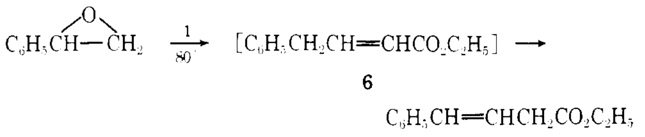
Because of the unexpected product obtained from cyclohexene oxide, the reaction of **1** with a number of other epoxides was examined. 1-Octene oxide gave as volatile product the conjugated ester **5**. The vpc behavior and integration of the nmr spectrum of this material indicated that it could contain only minor amounts of isomeric contaminants. Again the large vinyl coupling constant (J = 15.5 cps) suggests that **5** has the *trans* configuration.



$$CH_3(CH_2)_5\overset{O}{CH{-}CH_2} \xrightarrow[80°]{1} CH_3(CH_2)_6CH{=}CHCO_2C_2H_5$$

5

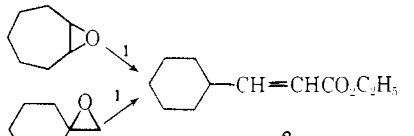
Styrene oxide and **1** react to give ethyl 4-phenyl-3-butenoate (**7**), presumably *via* initial formation and rearrangement of the isomeric α,β-unsaturated ester **6**. An authentic sample of **6**, prepared by the Wittig procedure on phenylacetaldehyde, was found to be readily (and essentially completely) isomerized to **7** under basic conditions.[10] Basic hydrolysis of **6** led to 4-phenyl-3-butenoic acid, illustrating again the relative facility with which this system rearranges. Although the equilibrium product **7** is presumed to have the *trans* configuration, the β- and γ-protons have comparable chemical shifts and consequently do not exhibit an observable coupling constant.



$$C_6H_5\overset{O}{CH{-}CH_2} \xrightarrow[80°]{1} [C_6H_5CH_2CH{=}CHCO_2C_2H_5] \longrightarrow C_6H_5CH{=}CHCH_2CO_2C_2H_5$$

6 **7**

Cycloheptene oxide reacts with **1** by a process involving ring contraction analogous to that observed with cyclohexene oxide, yielding ethyl 3-cyclohexylpropenoate (**8**). This product was identified by alternate synthesis using cyclohexanecarboxaldehyde and triphenylcarbethoxymethylidenephosphorane. Both procedures apparently give a high proportion of *trans* material (J = 16 cps). The same product (**8**) is obtained from methylenecyclohexane oxide.



8

The reaction of 1-methylcyclohexene oxide with **1** also occurs with ring contraction, leading to the unsaturated ester **9** which was identified by its characteristic nmr spectrum.

9

Cyclopentene oxide, unlike the other epoxides examined, reacts smoothly with **1** to give the cyclopropyl derivative (26%). The 6-carbethoxybicyclo[3.1.0]-

10

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[5] Reported in a footnote in ref 4, without experimental conditions. Professor Denney has informed us (personal communication) that his procedure (1-octene oxide) differs from that described in this paper in that potassium *t*-butoxide rather than butyllithium was used to generate the ylide. Our attempts to duplicate this result, using both 1-octene oxide and cyclohexene oxide, have to date been unsuccessful.

[6] Based on comparison of vpc retention times. An authentic sample of 2 was prepared by the copper powder catalyzed decomposition of ethyl diazoacetate in cyclohexene.[7]

[7] M. Mousseron, R. Jacquier, and R. Fraisse, *Compt. Rend.*, **243**, 1880 (1956).

[8] R. Roth and H. Erlenmeyer, *Helv. Chim. Acta*, **38**, 1276 (1955).

[9] For a recent study involving unsaturated acids, and references to earlier work, see K. L. Rinehart, Jr., and L. J. Dolby, *J. Org. Chem.*, **22**, 13 (1957).

[10] K. MacKenzie, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 428.

hexane (**10**) obtained under the usual reaction conditions (80°) appears (vpc and spectral evidence) to be free from all but minor amounts of impurities. Identification is based on alternate synthesis from cyclopentene and ethyl diazoacetate.[7]

Discussion

Although relatively little work has been reported on the reaction of phosphorus ylides with epoxides, the literature appears to be in accord regarding the structural features required to effect the formation of cyclopropyl derivatives by this route. Two groups have reported successful syntheses[4,11] using triphenylcarbethoxymethylidenephosphorane, and Wadsworth and Emmons[3] have obtained comparable results under milder conditions using the more reactive phosphonate carbanions, which again were substituted on the ylide carbon by an anion-stabilizing carbethoxy or cyano group. When this structural feature is absent, the few cases studied indicate that reaction may occur predominantly by a very different pathway, although cyclopropanes may be formed in minor amounts. Of particular interest in terms of the present study is the work of McEwen and co-workers,[12,13] who found that the minor products (hydrocarbons) of the reaction of methylethylphenylbenzylidenephosphorane with styrene oxide were predominantly isomeric 1,3-diphenylpropenes, along with trace amounts of *trans*-1,2-diphenylcyclopropane.[12] When triphenylbenzylidenephosphorane was used in this reaction, the hydrocarbon-forming path(s) predominated (50%), while the ratio of substituted propene to cyclopropane remained effectively constant.[13,14] Zbiral[11] has also reported that this same ylide reacts with cyclohexene oxide to give a mixture of olefin (by ring contraction) and 7-phenylnorcarane,[15] while styrene oxide yields only olefin.[17]

The products obtained in the present work are for the most part those that would be anticipated if the epoxide has undergone electrophilic rearrangement prior to normal Wittig reaction. As analogies one might cite the reactions of methylmagnesium halide with styrene oxide and cyclohexene oxide, which give products derived from phenylacetaldehyde and cyclopentanecarboxaldehyde, respectively.[18] The ylide reaction solution contains a variety of electrophiles potentially capable of causing such rearrangement, including lithium cation, excess phosphonium salt, and phosphine oxide. Under the conditions used in this work (refluxing benzene), cyclohexene oxide remains unchanged in the presence of an equimolar amount of tri-*n*-butylphosphine oxide.[19] Some cyclohexene oxide was lost when refluxed in benzene with an equivalent amount of tri-*n*-butylcarbethoxymethylenephosphonium bromide, but the reaction was considerably slower than with the ylide, and no evidence for the formation of cyclopentanecarboxaldehyde could be obtained (vpc). Further, when the ylide reaction was carried out using a 20% excess of butyllithium (assuring the absence of phosphonium salt) the yield of **3** was identical with that obtained in earlier experiments.

Other evidence argues against the possibility of prior electrophilic rearrangement. Thus, in the reaction of cyclopentene oxide, no ethyl cyclopentylideneacetate is formed,[21] although anticipated on the basis of known examples of rearrangement of this epoxide by electrophiles.[22] 1-Methylcyclohexene oxide is reported to rearrange to 1-methylcyclopentanecarboxaldehyde at 0° with magnesium bromide; however at 60° the major product is 2-methylcyclohexanone.[23] It is therefore significant that no derivative of the latter compound was obtained in the ylide reaction (comparison of vpc retention times).

Lithium ion is not expected to shown much catalytic activity as an electrophile,[24] but conceivably the nature of the metal ion could affect the reaction of ylide with epoxide. Two runs were made with cyclohexene oxide and the ylide generated with butyllithium, one with added pulverized lithium chloride, the other with potassium chloride. In both cases the rate of disappearance of epoxide remained unaffected, and the isolated yields, although somewhat lower in the lithium chloride run, were effectively the same as in the absence of added salt. The solutions were vigorously stirred, but the low solubility of alkali metal halides in benzene prevents any definite conclusion from these results.

Schlosser and Christmann[25] have observed a rate acceleration in certain Wittig reactions when potassium *t*-butoxide–*t*-butyl alcohol complex is added to the alkyllithium-generated ylide. We have repeated their procedure, using 1.1 moles of complex per mole of ylide. The mixture (using cyclohexene oxide) was refluxed for 24 hr; no product was formed, and the epoxide remained unchanged under these conditions, as indicated by vpc.

Although prior electrophilic rearrangement of the epoxides to aldehydes cannot be conclusively ruled out, its occurrence is not supported by the available evidence. The literature contains two pieces of data directly sup-

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[11] E. Zbiral, *Monatsh.*, **94**, 78 (1963).

[12] W. E. McEwen, A. Bladé-Font, and C. A. Vanderwerf, *J. Am. Chem. Soc.*, **84**, 677 (1962).

[13] W. E. McEwen and A. P. Wolf, *ibid.*, **84**, 676 (1962).

[14] This ratio is of interest particularly because of the apparent effect of changing ligands on phosphorus observed in Denney's work (triphenyl) and the present study (tri-*n*-butyl).

[15] The ratio of products, in which olefin predominates,[11] is shown inverted in a review article by Trippett.[16]

[16] S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).

[17] Zbiral[11] has stated that the 1,3-diphenylpropene formed in the reaction with styrene oxide is "almost exclusively *cis*," and further that the major product from *p*-methoxystyrene oxide is *cis*-1-(4-methoxyphenyl)-3-phenylpropene. Professor Zbiral has informed us (personal communication) that in fact the alternate positional isomer, as anticipated from the present study, was formed (nomenclature error), and that the *cis* designation was assigned by analogy with the result from styrene oxide. In view of the rather shaky evidence for the latter, and the results of McEwen and Wolf,[13] who found the olefin to be largely *trans*, a reexamination of Zbiral's work would seem in order.

[18] For reference to these and other examples of epoxide rearrangements, see S. Winstein and R. Henderson in "Heterocyclic Compounds," Vol. I, R. C. Elderfield Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p 1.

[19] This reagent has been shown[20] to cause the isomerization of a number of epoxides to related carbonyl compounds at 160°.

[20] D. E. Bissing and A. J. Speziale, *J. Am. Chem. Soc.*, **87**, 1405 (1965).

[21] This was demonstrated by comparison of vpc retention times with an authentic sample prepared *via* the Wittig procedure on cyclopentanone.

[22] For instance, when cyclopentene oxide is subjected to Reformatsky conditions (zinc and ethyl bromoacetate), the product is that derived from cyclopentanone: G. R. Clemo and J. Ormston, *J. Chem. Soc.*, 362 (1933).

[23] S. M. Naqvi, J. P. Horwitz, and R. Filler, *J. Am. Chem. Soc.*, **79**, 6283 (1957).

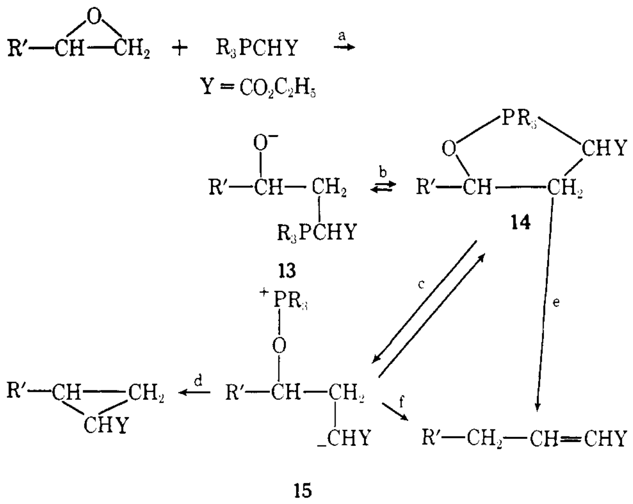
[24] For example, phenyllithium (unlike the Grignard reagent) reacts normally with cyclohexene oxide, giving *trans*-2-phenylcyclohexanol: J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936).

[25] M. Schlosser and K. F. Christmann, *Angew. Chem. Intern. Ed. Engl.*, **3**, 636 (1964).

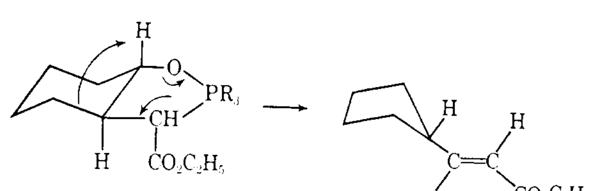
porting the premise that the initial step in epoxide–ylide reactions involves nucleophilic displacement of oxygen by the carbanionic center of the ylide. McEwen and his co-workers[12] have isolated the lithium iodide adduct of the betaine from styrene oxide and methylethylphenylbenzylidenephosphorane, formed by attack at the less hindered primary position of the epoxide. Also, Denney[4] has shown that the reaction of optically active styrene oxide with triphenylcarbethoxymethylidenephosphorane yields active ethyl *trans*-2-phenylcyclopropanecarboxylate; subsequent determination of the absolute configuration of this acid[26] has confirmed Denney's suggestion that inversion of configuration is involved.[27]

The data obtained here indicate that the structure of the unsaturated ester product is also predictable (from an unsymmetrical epoxide) on the basis of nucleophilic attack at the least hindered carbon. A mechanism involving common intermediates for both cyclopropane and unsaturated ester formation is shown.

We have found that triphenylcarbethoxymethylidenephosphorane (generated with butyllithium) does react with cyclohexene oxide in benzene at 80°. Although the epoxide is consumed under these conditions, only a very small amount (3%) of volatile product (mainly **3**) is formed. It may be that the lithium ion offers electrophilic assistance by complexing with the epoxide oxygen, with this complex subsequently undergoing nucleophilic attack to give **13**. The intermediate **13** can be involved in a number of reactions which are apparently[12] very dependent on the structure of the ylide. Closure of **13** to the heterocycle **14**, followed by heterolytic opening to **15**, has been suggested[2,3] as the most probable pathway to cyclopropane, and this mechanism certainly accounts for the function of the anion-stabilizing group Y.



At least two plausible routes to the α,β-unsaturated ester involving formation of **14** may be drawn; subsequent decomposition could be concerted (path e, illustrated for the reaction of cyclohexene oxide, **16**), or may also involve the intermediate **15**. A concerted mechanism would require a good deal of conformational control in the formation and/or reactivity of heterocycle **14** to explain the very strong preponderance of *trans* olefinic product.[28] The ring-opened intermediate **15**, on the other hand, may readily assume the conformation giving *trans* product (**17**). Path f, in the mechanistic scheme, may in fact not be a single-step process; a number of plausible routes to the unsaturated ester are possible.[29]



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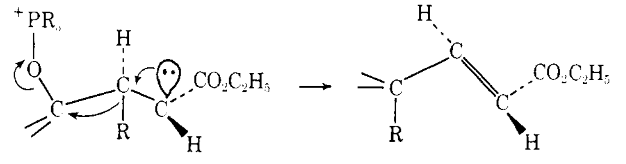

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The formation of cyclopropyl derivative from **15** (path d) requires a *trans* coplanar alignment of the anionic center and the leaving phosphine oxide moiety (assuming a concerted reaction). In the cyclohexyl system, this is possible only if the involved groups assume the diaxial conformation. This conformational effect may play an important role in determining the ratio of cyclopropane to olefin formed in a given reaction, although its application is not obvious for acyclic epoxides.

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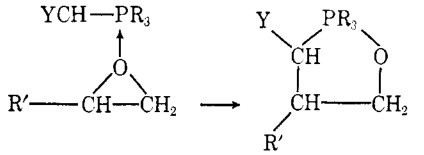
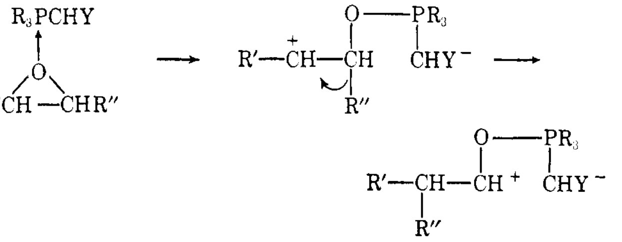
(26) I. Tomoskozi, *Tetrahedron*, **19**, 1969 (1963).

(27) In the present work an alternate first step, involving electrophilic attack of ylide phosphorus on oxygen followed by ring closure (to give **11**), cannot be discounted in all systems. It appears to be highly unlikely, though, in view of the products formed from 1-octene oxide and 1-methylcyclohexene oxide, and also the formation of cyclopropyl derivative from cyclopentene oxide.



11

Another mechanism which deserves consideration involves electrophilic attack by the ylide phosphorus without direct ring closure to **11**, but with concurrent or subsequent migration of either hydride or ring carbon to give the species **12**. The latter would of course react further to yield the normal Wittig product of the corresponding aldehyde.



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Two aspects of the present work, however, do not appear to be adequately explained by this mechanism: first, the absence of other than a single rearrangement product (*e.g.*, from 1-methylcyclohexene oxide), and second, the abrupt change in the course of the reaction observed with cyclopentene oxide.

(28) It is assumed that the high percentage of *trans* olefin is not due to equilibration of *cis* material, as it has been shown in the case of cyclohexene oxide that complete equilibration leads to mainly the β,γ isomer. The more rapid equilibration *cis–trans* than α,β–β,γ cannot be excluded, however.

(29) One possibility, direct elimination to give the β,γ unsaturated enolate ion ($R_2C{=}CHC{=}C(O^-)OC_2H_5$), with product determined by the position of subsequent protonation, may be ruled out since a mixture of α,β and β,γ isomers would be anticipated (as direct reaction products). Also, this mechanism would not lead to the observed products in the reactions of the cyclic epoxides.

Also, the formation of *relatively* more cyclopropane with the triphenyl ylide may be partially explained on this basis, in view of the higher temperatures required for this reaction. As noted previously, the proportion of cyclopropyl derivative from cyclohexene oxide using the tributyl ylide increased somewhat on changing the reaction temperature from 80 to 135°. However, it appears that the nature of the substituents on phosphorus must also play an important role to account for the large differences in product composition observed in Denney's work[4] and the present study.

The formation of cyclopropyl derivative from cyclopentene oxide is of particular interest; the *trans*-fused heterocycle **14** in this case may suffer considerable strain, leading to ready opening to **15**. The latter, because of steric interactions, may show an appreciable preference for the *trans* coplanar conformation favoring closure to cyclopropane. Formation of a strained cyclobutane ring and unfavorable geometry are undoubtedly also factors in preventing ring contraction or cyclopentanone-derived product (by hydride migration).

Most of the reactions described in this paper were carried out under standard conditions (see Experimental Section) to allow more direct comparison of required reaction times and yields. The latter were only fair (25–45%) under these conditions, and some experiments were carried out to effect improvement. Using cyclohexene oxide, a twofold excess of ylide raised the yield negligibly, from 36 to 41%. Interestingly, threefold dilution (reagents in 1:1 ratio) gave a comparable yield (31%) after 24 hr. No cyclohexene oxide remained at this time. The yield of product prevents any definite conclusion regarding kinetic order, but it is striking that the rate of reaction was not visibly depressed by dilution. This suggests that the initial opening of the epoxide is not the rate-controlling step; however, prolonged heating (60 hr) failed to give a significant increase in yield, as anticipated if appreciable amounts of an intermediate species had built up in solution.

The reaction promises to be of some utility for the preparation of unsaturated esters, particularly where the precursor aldehyde normally used in the Reformatsky or other similar condensation procedure is difficult to obtain. Although the yields are not impressive under the standard conditions used here, the products are in general obtained in a high state of purity.

Further work is in progress to determine both the limitations and the mechanism of the reaction of epoxides with ylides.

Experimental Section

Tri-*n*-butylcarbethoxymethylenephosphonium Bromide. This salt was prepared by the method of Speziale and Bissing.[30]

Epoxides. Cyclohexene oxide and styrene oxide were obtained from commercial sources. Cyclopentene oxide (bp 99–100°),[31] cycloheptene oxide [bp 70–72° (46 mm)],[32] 1-octene oxide [bp 86–87° (47 mm)],[31] 1-methylcyclohexene oxide (bp 137–138°),[33] and methylenecyclohexane epoxide (bp 145–146°)[34] were all prepared in moderate yields from the corresponding olefins using *m*-chloroperbenzoic acid in ether.

Ethyl 3-Cyclopentylpropenoate (3). A 500-ml, three-necked flask was equipped with a stirrer, dropping funnel, condenser, and nitrogen inlet. To 36.9 g (0.1 mole) of the phosphonium salt in 140 ml of anhydrous benzene, 70.0 ml of 1.48 *M* butyllithium in hexane solution (0.1 mole) was slowly added. Cyclohexene oxide, 9.8 g (0.1 mole), was then added rapidly and the solution refluxed. Samples were withdrawn at intervals to follow the course of the reaction by vpc. No detectable time lag was apparent between loss of epoxide and formation of product, *i.e.*, no evidence supporting a stable intermediate under these conditions was obtained. The epoxide was totally consumed after 19 hr, after which the solution was cooled and washed three times with water. After drying (sodium sulfate), the solvent was removed by distillation, leaving an amber residue which was directly subjected to vacuum distillation; 6.0 g (36%) of colorless liquid, bp 84–86° (3.5 mm), was obtained.

The nmr spectrum of this material integrated correctly and showed vinyl proton chemical shifts characteristic for an α,β-unsaturated acid derivative.[35] The α-proton appears as a doublet ($J = 16$ cps, with indications of further 1,3 coupling, $J \simeq 1.5$ cps) centered at 5.90 ppm (TMS = 0); the β-proton exhibits a doublet of doublets ($J = 16, 7.8$ cps) centered at 7.10 ppm. Vpc of this material indicated that it contained only minor amounts of impurities (isomeric ester and cyclopropyl derivative, as described in the text).

Hydrolysis of **3** in aqueous base followed by acidification gave the previously described 3-cyclopentylpropenoic acid, mp 46–48° (lit.[8] mp 48–50°). Nmr confirmed that this was the unrearranged acid, as the vinyl region showed the same splitting features as the ester; vinyl proton absorptions were centered at 6.17 and 7.53 ppm.

Compound **3** was identical in all respects (vpc, infrared, nmr) with material prepared from cyclopentanecarboxaldehyde and triphenylcarbethoxymethylidenephosphorane in ether solution.

Ethyl 3-Cyclopentylidenepropionate (4). A minor product from the reaction in benzene was found to predominate when refluxing xylene solvent was used (134°, the boiling point being lowered somewhat by the hexane from the butyllithium solution). A sample of this material was isolated by vpc; nmr characteristics included a doublet (α-CH_2, $J = 7.1$ cps) centered at 2.89 ppm, and a triplet (β-vinyl proton) centered at 5.37 ppm. Both **3** and **4** were catalytically hydrogenated to ethyl 3-cyclopentylpropionate, an authentic sample of which was synthesized in low yield by inverse addition of cyclopentylmagnesium bromide to ethyl acrylate.

Equilibration of 3 and 4. An experiment was carried out in the manner described for cyclohexene oxide above, except xylene was used as the solvent, while the pot temperature was maintained at 80°. After 24 hr (all of the epoxide had disappeared) the solution was refluxed, while samples were removed intermittently for vpc analysis. The peak corresponding to **3** (which comprised, as in the benzene runs, nearly all of the product at 80°) steadily decreased, while a concurrent increase in the peak corresponding to **4** was observed. Equilibrium was attained after about 8 hr, at which point integration of the vpc peaks indicated 71% **4** and 29% **3** ($K = 2.45$).

Ethyl 2-Decenoate (5). This and subsequent reactions were carried out using the molar amounts and conditions described in the preparation of **3**. 1-Octene oxide gave 26% of a colorless liquid, bp 120–124° (4 mm).[36] The nmr spectrum showed a doublet ($J = 15.5$ cps) centered at 5.71 ppm (α-proton), with each peak further split into a partially defined triplet ($J = \sim 1.5$ cps, coupling with γ-CH_2 group); the β-proton exhibited a well-defined doublet of triplets ($J = 15.5, 7.8$ cps) centered at 6.86 ppm. Integration established a minimum purity of >85% for ethyl *trans*-2-decenoate.

Ethyl 4-Phenyl-3-butenoate (7). Styrene oxide after 20 hr gave 29% of colorless liquid, bp 135–137° (2 mm).[37] The vinyl protons have comparable chemical shifts and consequently do not exhibit observable coupling. The β-proton appears as a triplet (coupling with α-CH_2), $J = 6$ cps, centered at 6.32 ppm. The lower field leg of this triplet is obscured by the singlet γ-proton at 6.40 ppm. The α-methylene group shows a sharp doublet ($J = 6$ cps), centered at 3.17 ppm. Basic hydrolysis of **7** gave crude 4-phenyl-3-butenoic acid, mp 78–80° (lit.[38] mp 87°), with nmr coupling characteristics similar to those described for the ester.[39]

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When phenylacetaldehyde was treated with triphenylcarbethoxymethylidenephosphorane in benzene the product was largely the α,β-unsaturated ester **6**; prolonged heating, however, caused extensive rearrangement to **7**. The sensitivity of **6** was further demonstrated by the fact that basic hydrolysis led to the acid derivative of **7** (mp 80–84°), rather than unrearranged 4-phenyl-2-butenoic acid.[33] Warming a solution of **6** and sodium ethoxide in ethanol for a short time led to essentially complete (by nmr) rearrangement to **7**. Attempts to distinguish **6** and **7** by vpc were unsuccessful. Characteristic features of the nmr spectrum of **6** were a doublet of doublets (J = 6.5, 1.7 cps) for the γ-methylene centered at 3.38 ppm, and a doublet of triplets (J = 15.5, 1.7 cps) for the α-proton centered at 5.67 ppm. The lower field triplet of the β-proton was obscured by the aromatic proton absorption.

Ethyl 3-Cyclohexylpropenoate (8). Cycloheptene oxide, after 76 hr, gave 32% of colorless liquid, bp 105–108° (5.5 mm).[40] Integration of the nmr spectrum (α-proton, J = 15.5, 1.3 cps, doublet of doublets centered at 5.62 ppm; β-proton, J = 15.5, 6.2 cps, doublet of doublets at 6.78 ppm) indicated a purity of >95% for ethyl *trans*-3-cyclohexylpropenoate. Vpc analysis showed only one peak.

The same product (identical in vpc and spectral characteristics) was obtained from methylenecyclohexane oxide (22%) after 24 hr.

Confirmation of the structure of **8** was obtained by alternate synthesis from cyclohexanecarboxaldehyde and triphenylcarbethoxymethylidenephosphorane. The nmr was identical, indicating that this procedure also leads to essentially pure *trans* product.

Ethyl 3-(1-Methylcyclopentyl)propenoate (9). After 24 hr, 1-methylcyclohexene oxide gave 35.7% of a liquid product, bp 94–98° (5.0 mm). The structure of **9** was deduced from its nmr spectrum; α-proton, J = 16.0 cps, doublet centered at 5.64 ppm; β-proton, J = 16.0 cps, doublet at 6.92 ppm; methyl group, singlet at 1.13 ppm. (This singlet obscures the high-field leg of the triplet from the ethyl ester group.)

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 9.95. Found: C, 72.68; H, 10.03.

Ethyl 2-methylcyclohexylideneacetate was prepared in low yield by refluxing triphenylcarbethoxymethylidenephosphorane and 2-methylcyclohexanone in benzene for 72 hr. The nmr of the product was satisfactory. The vpc retention time of this compound indicated that it was not formed in the reaction of 1-methylcyclohexene oxide with the tri-*n*-butyl ylide.

6-Carbethoxybicyclo[3.1.0]hexane (10). Cyclopentene oxide, after 76 hr, gave 26% of a colorless liquid, bp 71–73.5° (5 mm). This product showed no nmr absorption in the vinyl region, and was homogeneous by vpc analysis.

A sample of authentic **10** was prepared by copper (powdered) catalyzed decomposition of ethyl diazoacetate in refluxing cyclopentene. Both *exo* and *endo* isomers are formed in this reaction, as indicated by the facile isomerization of the *endo* to the *exo* isomer when a sample of the mixture was refluxed in a solution of sodium ethoxide in anhydrous ethanol. Although the reaction of the tri-*n*-butyl ylide with cyclopentene oxide yields the *exo* isomer, isomerization to this product cannot be ruled out, as traces of the *endo* isomer are present.

Ethyl cyclopentylideneacetate was prepared in low yield by refluxing triphenylcarbethoxymethylidenephosphorane and cyclopentanone in benzene for 72 hr. The nmr of the product was satisfactory. The vpc retention time of this product indicated that it was not formed in the reaction of cyclopentene oxide with the tri-*n*-butyl ylide.

Effect of Added Potassium *t*-Butoxide. The tri-*n*-butyl ylide (0.05 mole) was prepared in the manner described above. The potassium *t*-butoxide–*t*-butyl alcohol complex (1:1) was prepared by allowing 2.2 g (0.055 mole, 1.1 equiv) of potassium to react with excess dry *t*-butyl alcohol. The excess *t*-butyl alcohol was then distilled off, and the resultant slurry pumped to dryness. The fresh ylide solution was then added directly to the powdered complex and stirred for 0.5 hr. Cyclohexene oxide, 4.95 g (0.05 mole) was then added, and reflux started. After 24 hr, no product had formed, and loss of epoxide was negligible (vpc analysis).

Reaction of Triphenylcarbethoxymethylidenephosphorane with Cyclohexene Oxide. Triphenylcarbethoxymethylphosphonium bromide,[41] 21.4 g (0.05 mole), was suspended in 150 ml of benzene and 35 ml of 1.48 *M* *n*-butyllithium solution (0.05 mole) (in hexane) added slowly under nitrogen. The phosphonium salt slowly dissolved as the base was added, and the characteristic red color developed. To the ylide solution was added 4.95 g (0.05 mole) of cyclohexene oxide and the system was brought up to reflux. The epoxide was totally consumed after 24 hr, after which the solution was cooled and washed three times with water. After drying over sodium sulfate, the solvent was removed by distillation, leaving an amber residue which was vacuum distilled; 0.25 g (3%) of colorless material, bp 82–86° (3.5 mm), was obtained. The nmr and infrared of this material were identical in every way with those of **3**.

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