REACTION OF CARBETHOXYCARBENE WITH 2-PHENYLOXIRANE AND 2-PHENYLOXETANE¹

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(Received in Japan 23 May 1966; accepted for publication 8 June 1966)

Abstract—Thermal or photochemical decomposition of ethyl diazoacetate in 2-phenyloxirane gave a complex mixture, the analysis of which indicated that the reaction of carbethoxycarbene had proceeded according to the scheme summarized in Fig. 1. The reaction probably involves intermediate formation of an oxygen-ylide (IV), thus accounting for the observed oxygen-transfer and oxetane formation. Copper-catalysed thermal decomposition resulted in a more selective distribution of products, second-ary reactions as well as the tar-formation being drastically reduced. The action of other carbenes such as dihalo-, phenyl- and diphenyl-carbene yielded less or no oxygen-transfer products and the formation of oxetane was not observed. In some cases, especially in the reaction of bis(benzene-sulphonyl)carbene, the major product was cyclic dimers of 2-phenyloxirane.

2-Phenyloxetane reacts more selectively with carbethoxycarbene to produce a mixture of *cis* and *trans* isomers of 2-carbethoxy-3-phenyltetrahydrofuran in 72-80% yield.

ALTHOUGH the reactions of carbenes with open chain ethers² have been extensively studied, little has been recorded of the reaction with small ring ethers. Wittig and Schlosser³ have described the copper-catalysed decomposition of diazomethane in 2-phenyloxirane yielding styrene, which may be ascribed to the oxygen abstracting action of intermediary carbene.⁴ We wish to report that the reaction of carbethoxy-carbene with 2-phenyloxirane involves analogous deoxygenation as well as an insertion reaction leading to ring expansion, while a similar reaction with 2-phenyloxetane yields ring-expanded products exclusively.

Thermal decomposition of ethyl diazoacetate (I) in excess 2-phenyloxirane or styrene oxide (III) produced a complex mixture of products (Fig. 1). The dependence of yields on reaction variables is summarized in Table 1.

An oxygen-ylide IV^5 is probably formed by electrophilic attack of the singlet carbene II on the oxygen atom of 2-phenyloxirane (III). This is followed by either (1) decomposition to styrene (V) and ethyl glyoxylate (VI) or (2) isomerization to a *cis trans* mixture of oxetane VII. Secondary attack of each product by carbethoxycarbene or by ethyl diazoacetate ensues subsequently, yielding *cis* and *trans* isomers of ethyl

¹ A part of this article has appeared in a preliminary form: H. Nozaki, H. Takaya and R. Noyori, *Tetrahedron Letters* 2563 (1965).

 ^{*} H. Meerwein, H. Rathjen and H. Werner, Ber. Disch. Chem. Ges. 75, 1610 (1942); * A. W. Johnson, A. Langemann and J. Murray, J. Chem. Soc. 2136 (1953); * C. D. Gutsche and M. Hillmann, J. Amer. Chem. Soc. 76, 2236 (1954); * R. Huisgen, Angew. Chem. 67, 459 (1955);
* V. Franzen and L. Fikentscher, Liebigs Ann. 617, 1 (1958); * W. von E. Doering, L. H. Knox and M. Jones, Jr., J. Org. Chem. 24, 136 (1959); * H. M. Frey, Rec. Trav. Chim. 83, 117 (1964).

⁸ G. Wittig and M. Schlosser, Tetrahedron 18, 1026 (1962).

⁴ For deoxygenation of pyridine N-oxide by dichlorocarbene, see E. E. Schweizer and G. J. O'Neill, J. Org. Chem. 28, 2460 (1963).

^{*} For the possible formation of an oxygen-ylide in the carbene reaction of ethers, see ref. 2d and 2f.



FIG 1. Reaction of carbethoxycarbene with 2-phenyloxirane

2-phenylcyclopropanecarboxylate (VIII) and 2,3-bis(carbethoxy)oxirane (IX). The cis:trans ratio of the products VII, VIII and IX were estimated by NMR to be 1:1, 0.4:1 and 0.5:1, respectively. Stereoisomers of 2,3-bis(carbethoxy)4-phenyltetrahydrofuran (X) was also produced. Other minor products arising solely from each reaction component (I or III) were diethyl maleate and furmarate (0.4:1) and cis-trans isomers (0.2:1) of 2,5-diphenyl-1,4-dioxane (XI). Each product was identified by comparison with the respective authentic sample. The novel oxetane stereomers VII were obtained independently in 11% yield by the photochemical cycloaddition of VI on V. The cis:trans ratio in this photoaddition was 0.5:1. The oxetane structure and the configuration were established by comparison of the NMR spectra with the one of 2-carbethoxy-3,3-diphenyloxetane prepared analogously from VI and 1,1-diphenyl-ethylene in 24% yield.

Figures in Table 1 indicate that higher concentration of I favours the secondary attack producing VIII, IX and X at the expense of the primary products, V, VI and VII as expected. No significant difference was observed between the thermal and photochemical decomposition. The catalytic action of copper and its compounds is remarkable both in the lowered reaction temperature and in the increased yields of the primary products V, VI and VII. The *cis:trans* ratio of VII is roughly 0.3:1 in this case, which means that the catalytic decomposition shows a preference for the *trans*-oxetane three times greater than the non-selective reaction in the absence of such catalysts. Improved yields reflect the decreased formation of polymeric byproducts which form the distillation residue.

| Mole ratio | Mode of | | Reaction | Reaction | | | Yield in % based | | on I | | |
|------------|------------|-------------------------|----------------|-----------|-----|-----|------------------|------|------|-----|-----|
| III/I | dec. | Catalyst | temp. | time (hr) | V٥ | ٧I٩ | VII | VIII | IX | X۴ | XI4 |
| 10 | thermal | none | 130–140° | 4 | 7.4 | tr | 7.3 | 14 | <1.0 | tr | tr |
| 2 | thermal | none | 130-140° | 4 | 1-4 | tr | 3-4 | 16 | <1.0 | 1.8 | tre |
| 1 | thermal | none | 130-140° | 4 | 0.9 | tr | 2.6 | 17 | <1.0 | tr | tr |
| 2 | photochem. | none | 20–25° | 150 | 8.3 | tr | 6.1 | 15 | 2.2 | tr | tr |
| 10 | thermal | Cu' | 8082° | 3 | 47 | 11 | 18 | 1.5 | tr | tr | tr |
| 10 | thermal | Cu(acac) ₂ " | 70–72° | 3 | 35 | 11 | 16 | 1.2 | 2.5 | tr | tr |
| 2 | thermal | Cu(acac), | 40-42° | 6 | 24 | 17 | 15 | 8∙5 | tr | 2.6 | tr |
| 10 | thermal | Cu(acest), ^A | 45–4 7° | 3 | 30 | 19 | 19 | 1-4 | tr | tr | tr |
| 10 | thermal | CuSO4 | 50–52° | 3 | 61 | 35 | 18 | 1.8 | tr | tr | 2.7 |

TABLE 1. DEPENDENCE OF PRODUCT DISTRIBUTION ON REACTION VARIABLES⁶

• For characterization of the products V-XI, see Experimental. NMR spectra of VII and IX were given in Ref. 1. Yields of V-IX were obtained by GLC analyses.

- * Yields of these products were variable probably due to ready polymerizability.
- * This was a mixture of stereoisomers. For details see Experimental.
- "Yields were calculated based on 2-phenyloxirane used.
- The cis/trans ratio was ca. 0.2:1.
- ¹ Electrolytic copper powder was washed with 4% HNO₃, then with H₃O thoroughly and dried at 110°.
- Bis(acetylacetonato) copper(II).
- * Bis(ethyl acetoacetato) copper(II).
- ⁴ Anhydrous cupric sulphate was used.

¹ This is a mixture of *trans* dimer and a trace of *cis* isomer.

Reaction products of 2-phenyloxirane (III) with other carbenes are tabulated in Table 2. The oxygen-abstraction was observed with dihalo- and phenylcarbenes to a liner extent, while diphenylcarbene, produced from diphenyldiazomethane without either deoxygenation or oxetane formation, yielded 1,1,2,2-tetraphenylethane and benzophenone azine. The bis(benzenesulphonyl)carbene catalysed polymerization of III yielded the crystalline dimers (XI) as the only products in the reaction of this particularly electrophilic carbene.⁶ This may indicate that the dimers XI originate from the electrophilic attack of the oxygen-ylide such as IV on 2-phenyloxirane III similar to the proton-catalysed dimerization of oxirane.⁷

| | | | | Yield in % CH ₂ ° | | | |
|---------------------|-------------------|---|------------------|---|-----|------|--|
| Substituents X Y | | Origin of carbene | Reaction temp | Ph-CH V ⁴ CXY XI ⁹ | | | |
| Cl | Cl | CCl ₂ COONa | 130° | 3.8 | 3.3 | tr | |
| Cl | Cl | CHCl _a + KOBu-t | -10-0° | 6.2 | 1.2 | tr | |
| Cl | Cl | CHCl _a + NaOH | 90-95° | 2.6 | 4.1 | tr | |
| Br | Br | CHBr ₃ + KOBu-t | -10-0° | 5·5 | 2.9 | tr | |
| Ph | н | PhCHN ₃ ^e | 25° (hv) | tr | tr | tr | |
| Ph | Ph | Ph ₂ CN ₂ ⁴ | 160165° | nil | nil | nil | |
| Ph | Ph | Ph ₃ CN ₃ | 25° (hv) | nil | nil | nil | |
| PhSO ₃ | PhSO ₂ | (PhSO ₂) ₂ CN ₂ | 80°1 | nil | nil | 6.7 | |
| PhSO ₂ | PhSO ₂ | $(PhSO_2)_2CN_2$ | 10° (hv) | nil | nil | 7.30 | |

TABLE 2. REACTION OF 2-PHENYLOXIRANE WITH OTHER CARBENES $(X - \ddot{C} - Y)$

• Yields were based on the respective carbene source and determined by GLC.

^b Yields were based on 2-phenyloxirane used.

^c The major products were trans-stilbene (53% yield) and banzal azine (15% yield).

The major products were 1,1,2,2-tetraphenylethane (18%) and benzophenone azine (34%).

• Tetraphenylethane (32%) and benzophenone azine (60%) were obtained.

^t Cu(AcAc)_a was used as a catalyst. Decomposition at 90° in the absence of the catalyst resulted in polymerization.

• This is a mixture of trans dimer and a trace of cis isomer.

As anticipated, the more basic oxygen atom of 2-phenyl-oxetane (XII)⁸ is more susceptible to the attack by electrophilic carbene or carbenoids to form O-ylide XIII than was found in the case of oxirane. The results are listed in Table 3.

Copper-catalysed decomposition of I in the oxetane XII yielded a product with a single peak on GLC but the NMR spectrum as well as hydrolysis indicated that this was a 0.3:1 mixture of *cis* and *trans* isomers of 2-carbethoxy-3-phenyltetrahydrofuran (XIV). The *trans* carboxylic acid (XVb) formed a solid monohydrate, while the *cis* acid (XVa) was isolated as anhydrous crystals. The configurational assignment was based on the coupling constants of C_2 and C_3 protons as well as on the shielding effect of phenyl substituents.⁹ Photochemical decomposition of I in XII gave inferior yields of the tetrahydrofuran derivative XIV in this case.

⁶ J. Diekmann, J. Org. Chem. 30, 2272 (1965).

- ⁷ D. J. Cram. and G. S. Hammond, Organic Chemistry, p. 209. McGraw-Hill, New York (1959). See also Ref. 18.
- ⁸ For the basicity of cyclic ethers, see S. Searles and M. Jamres, J. Amer. Chem. Soc. 73, 3704 (1951). The authors are grateful to Prof. T. Saegusa for valuable suggestions.
- Details are given in the Experimental.

Decomposition of diphenyldiazomethane in 2-phenyloxetane yielded 1,1,2,2tetraphenylethane and benzohenone azine as in the reaction with 2-phenyloxirane. Photolysis of bis(benzene-sulphonyl)diazomethane in XII resulted in polymerization of the oxetane, but no single substance was isolated.

The reactions mentioned failed to occur with small ring ethers such as methyloxirane which have no phenyl substituent on the α -carbon.



TABLE 3. REACTION OF 2-PHENYLOXETANE WITH CARBENES (X - C - Y)

| Substituents | | Molar ratio | Reaction | Reaction | Yield in % | |
|-------------------|-------------------|-------------|----------|-----------|------------------|--|
| х | Y | XII/XYCN2 | temp | time (hr) | XIV | |
| н | COOEt | 10 | 80° (Cu) | 6 | 80 | |
| н | COOEt | 10 | 130–135° | 5 | 72 | |
| н | COOEt | 10 | 5° (hν) | 50 | 35 | |
| PhSO ₁ | PhSO ₂ | 23 | 5° (hv) | 15 | nil ^o | |
| Ph | Ph | 10 | 5° (hv) | 24 | nilª | |

* These values were based on the diazoalkanes used.

Polymerization of XII was the only reaction observed in this case.

• The major products were 1,1,2,2-tetraphenylethane (37%) and benzophenone azine (56%).

EXPERIMENTAL

All temps were uncorrected. Microanalyses were performed at the Elemental Analyses Centre of Kyôto University.

Starting materials. Ethyl diazoacetate (I) was prepared by the method of Womack and Nelson.¹⁰ Commercial 2-phenyloxirane (III) was distilled under vacuum through a Vigreux column before use and was ascertained sufficiently pure by UV, IR spectra and GLC. 2-Phenyloxetane (XII) was prepared from 3-chloro-1-phenylpropyl acetate by the method of Bartok and Gilde in 71 % yield.¹¹ IR spectrum was identical with one of the authentic sample.¹³ B.p. 90-91°/12 mm, n_D^{ss} 1.5332. (Found: C, 80.8; H, 7.6. Calc. for B₂H₁₀O: C, 80.6; H, 7.5%.)

Thermal decomposition of ethyl diazoacetate (I) in 2-phenyloxirane (III)

Over a period of 3 to 4 hr, I (20.0 g, 0.18 mole) was added dropwise to III (40.0 g, 0.33 mole) heated at 130-140° with vigorous stirring under N. After N evoln was complete, the mixture was distilled *in vacuo* to give 5 fractions: fraction A, 4.2 g, b.p. up to 93°/45 mm; fraction B (mainly III), 26.0 g, b.p. 90-94°/26 mm; fraction C, 6.6 g, b.p. 60-103°/1 mm; fraction D, ca. 0.5 g, b.p. 90-100°/ 0.06 mm; fraction E, ca. 1.5 g, b.p. 120-130°/0.05 mm and ca. 15 g non volatile polymeric products. The volatile fractions were analysed (GLC) with high vacuum silicon grease-Celite (30:70) column. Each component except ethyl maleate and fumarate was separated by distillation or preparative GLC and characterized as follows.

- ¹⁰ E. B. Womack and A. B. Nelson, Organic Syntheses Coll. Vol. 3; p. 392. J. Wiley New York (1955).
- ¹¹ M. Bartok and A. S. Gilde, Acta Univ. Szeged., Acta Phys. Chem. 9, 25 (1963); Chem. Abstr. 60, 4093 (1964).
- ¹³ G. M. Barrow and S. Searles, J. Amer. Chem. Soc. 75, 1175 (1959).

Both styrene (V) and unchanged III were identified by comparison of retention time on GLC and IR spectra with those of authentic samples. Although ethyl maleate and fumarate were not isolated pure due to small amounts, they had retention times on GLC similar to standard specimens.

Authentic ethyl glyoxylate (VI) was synthesized by the application of the Wolf and Weijlard method.¹⁸ To a well stirred soln of diethyl tartarate (50.0 g, 0.24 mole) in benzene (250 ml) maintained below 30°, lead tetraacetate (111.0 g, 0.25 mole) was added in 5 g portions during 2 hr, and the mixture stirred for an additional 1 hr. The resulting ppt was filtered off, and the filtrate distilled *in vacuo* to afford colourless VI (19.5 g. ca. 28%), b.p. 78–81°/140 mm, containing ca. 30% AcOH which was azeotropically distilled. Phenylhydrazone melted at 128–129° (from benzene) (lit.¹⁴ 130°). Identity of the sample isolated from the decomposition mixture with authentic glyoxylate was established by IR spectrum and GLC. On admixture of samples of phenylhydrazone no depression of m.p. was observed. Details of identification of other products are given below.

(a) cis- and trans-2-carbethoxy-3-phenyloxetane (VII). Fractional distillation of the fraction C (preferably from the Cu-catalysed reaction) yielded an isomeric mixture of VII as a colourless oil, b.p. 115-118°/2 mm, n_D^{30} 1.5143. (Found: C, 69.6; H, 6.9. $C_{13}H_{14}O_3$ requires; C, 69.9; H, 6.8%.) No parent peak was observed in the mass spectrum, but fragment peaks at m/e 131, 104, 103, 77, 51, 44 and 29 supported the structure assigned. UV absorption showed the presence of benzenoid chromophore only. Attempted hydrogenation of 10% Pd-C under ordinary press resulted in recovery of the starting material. IR spectrum (neat); 1755, 1280, 1200 (ester group), characteristic bands in 2000–1650 region, 750, 700 (phenyl group), 1065, 1030, 1000, 990, 940 and 860 cm⁻¹. NMR spectrum (60 Mc, CCl₄)¹ showed the existence of two kinds of Et group in the oxetane fraction indicating that this consisted of *cis* and *trans* isomers (almost 1:1 mole ratio); the Et group of the *cis* comp appeared at τ 9.27 (3H, triplet, J = 7.5 c/s, methyl) and 6.31 (2H, quartet, J = 7.5 c/s, methylene) and that of the *trans* isomer at τ 8.75 (3H, triplet, J = 7.5 c/s, methyl) and 5.82 (2H, quartet, J = 7.5 c/s, methylene), respectively. This assignment is based on the photochemical prep of VII and 2-carbethoxy-3,3-diphenyloxetane as described below.

Treatment of the mixture with mineral acids gave a complicated mixture together with some formaldehyde which was identified as the 2,4-dinitrophenylhydrazone.¹⁵

(b) Ethyl cis- and trans-2-phenylcyclopropanecarboxylate (VIII). Both cis- and trans-VIII could be isolated pure by GLC of fraction C. Hydrolysis of cis-VIII with 10% NaOHaq afforded cis-2-phenylcyclopropanecarboxylic acid, m.p. 107-108° (from aq EtOH) (lit.¹⁶ 106-107°) as prisms. The trans-VIII gave trans-2-phenylcyclopropanecarboxylic acid as needles, m.p. 90-91° (lit.¹⁶ 93°). No m.p. depression was observed upon admixture with the authentic acid.

A mixture of *cis*- and *trans*-VIII was obtained from the reaction of styrene with I at 130°.¹⁴ GLC analysis indicated *cis*: *trans* ratio of 0.4:1, which is similar to the value obtained from the decomposition reaction of I in III. *trans*-VIII was independently synthesized from 2-phenyloxirane and ethyl phosphonoacetate.¹⁷

(c) cis- and trans Isomers of 2,3-bis (carbethoxy)oxirane (IX). The isomers appeared as a closely separated doublet on GLC of fraction C and were isolated as a cis-trans mixture, b.p. 76-77°/1 mm. (Found: C, 51·0; H, 6·7. C₈H₁₈O₈ requires: C, 51·0; H, 6·4%.) IR spectrum (neat); 1760-1730, 1300, 1200 (ester), 900 (epoxy group), 1095, 1060, 1030, 960 and 860 cm⁻¹. Mass spectrum consisted of the parent peak at m/e 188 and eminent fragment peaks at m/e 166, 144, 87, 45 and 29. NMR spectrum¹ showed the two kinds of methine as well as Et signals in a ratio which indicated that the mixture consisted of cis and trans-epoxy esters in 0·5:1 ratio. Signals due to the major trans isomer appeared at τ 8·74 (6H, triplet, J = 7·0 c/s, 2 methyls), 6·42 (2H, singlet, 2 methines) and 5·85 (4H, quartet, J = 7·0 c/s, 2 methyls), 6·49 (2H, singlet, 2 methines), and 5·81 (4H, quartet, J = 7·0 c/s 2 methyls), 6·49 (2H, singlet, 2 methines), and 5·81 (4H, quartet, J = 7·0 c/s 2 methyls), 6·49 (2H, singlet, 2 methines), and 5·81 (4H, quartet, J = 7·0 c/s 2 methyls), 6·49 (2H, singlet, 2 methines), and 5·81 (4H, quartet, J = 7·0 c/s 2 methyls), 6·49 (2H, singlet, 2 methines), and 5·81 (4H, quartet, J = 7·0 c/s 2 methyls), 6·49 (2H, singlet, 2 methines), and 5·81 (4H, quartet, J = 7·0 c/s 2 methyls), 6·49 (2H, singlet, 2 methines), and 5·81 (4H, quartet, J = 7·0 c/s 2 methyls), 6·49 (2H, singlet, 2 methines), and 5·81 (4H, quartet, J = 7·0 c/s 2 methylenes). IR spectrum and retention time on GLC were quite identical with those of the sample

¹⁹ F. J. Wolf and J. Weijlard, Organic Syntheses Coll. Vol. 4; p. 124, J. Wiley, New York (1963).
¹⁴ W. Traube, Ber. Dtsch. Chem. Ges. 40, 4953 (1907).

- ¹⁶ For acid catalyzed cleavage of oxetane rings, see. G. Büchi, C. G. Inman and E. S. Lipingsky, J. Amer. Chem. Soc. 76, 4327 (1954).
- ¹⁶ A. Burger and W. L. Yost, J. Amer. Chem. Soc. 70, 2198 (1948).
- ¹⁷ D. B. Denney and M. L. Boskin, J. Amer. Chem. Soc. 81, 6330 (1959); ^b D. B. Denney, J. J. Vill and M. J. Boskin, *Ibid.* 84, 3944 (1962).

independently obtained from the reaction of ethyl glyoxylate and ethyl diazoacetate at 70° in ca. 20% yield.

(d) cis- and trans-2,5-Diphenyldioxane (XI). Fraction D crystallized on standing. Fractional recrystallizations from acetone and then EtOH gave cis-XI as needles, m.p. 119-120° (lit.¹⁸ 121-122°) (60 mg) and trans-XI as platelets, m.p. 173-174° (lit.¹⁸ 173-174°) (300 mg), resp. IR spectra (Nujol) of cis isomer: 1110, 1070, 1030, 970, 890, 750 and 700 cm⁻¹; trans isomer: 1110, 1070, 1020, 900, 750 and 700 cm⁻¹. Mass spectrum: parent peak at m/e 240 and large fragment peaks at m/e 104, 91 and 77.

(e) 2,3-Bis(carbethoxy)4-phenyltetrahydrofuran (X). Fraction E formed a yellow viscous oil. (Found: C, 65.6; H, 7.1. $C_{16}H_{20}O_{5}$ requires: C, 65.7; H, 6.9%.) IR spectrum (neat): 1760–1740, 1270, 1200 (ester), characteristic bands in 2000–1650 region, 755, 700 (phenyl), 1100 (tetrahydrofuran ring), 1030, 945 and 860 cm⁻¹. NMR spectrum (CDCl₂) was consistent with the tetrahydrofuran structure assigned, showing the existence of at least four kinds of Et ester group at τ 9.16, 8.95, 8.74 and 8.72 (triplet, J = 7.0 c/s,) resp. The absence of signals at τ 5.1–4.6 (characteristic to oxetane methine¹) and ones at 8.2–7.5 (C₂ methylene in tetrahydrofuran ring) ruled out the other possible structures. An identical mixture was obtained from the reaction of VII and I in the presence of Cu powder. Ethyl diazoacetate (1.4 g, 0.012 mole) was added to a well stirred mixture of Cu powder (1.0 g) in VII (2.5 g, 0.012 mole) and benzene (20 ml) at 80°. Distillation *in vacuo* yielded a colourless oil (1.2 g, 34%), b.p. 120–125°/0.05 mm, whose IR peaks all appeared at the same positions as the mixture obtained above.

Photochemical preparation of oxetanes VII and 2-carbethoxy-3,3-diphenyloxetane

A soln of styrene (15.5 g, 0.15 mole), ethyl glyoxylate (13.6 g, 0.093 mole) ca. 70% purity contaminated with AcOH and hydroquinone (0.2 g) in benzene (65 ml) was irradiated with a 200W high press Hg-arc with a Pyrex glass filter in N atm at room temp. After 140 hr irradiation, the mixture was concentrated *in vacuo* and distillation of the residue yielded a mixture of oxetanes VII (2.1 g, 11%), b.p. 116–119°/2 mm. About 85% styrene was recovered and the non-volatile residue was formed in small amount. This photochemical method afforded a *trans*-rich mixture; the *cis:trans* ratio was ca. 0.5:1.

In a similar manner the photochemical addition of ethyl glyoxylate to 1,1-diphenylethylene afforded 2-carbethoxy-3,3-diphenyloxetane as a viscous pale yellow oil, b.p. 134–140°/0.06 mm, in 25% yield. (Found: C, 76.5; H, 6.6. $C_{19}H_{18}O_3$ requires: C, 76.6; H, 6.4%.) IR absorptions (neat): 2970, 1735, 1600, 1495, 1450, 1370, 1280, 1210, 1095, 1075, 1030, 965, 860, 755 and 699 cm⁻¹. NMR spectrum (CCl₄)¹ consisted of signals at τ 9.22 (3H, triplet, J = 7.5 c/s, methyl), 6.25 (2H, quartet, J = 7.5 c/s, methylene of ethyl group), 4.95 (2H, AB quartet, methylene of oxetane ring), 4.36 (1H, singlet, methine) and 2.88 (10 H, multiplet, aromatics). The chemical shifts of strongly shielded carbethoxy ethyl group were comparable to those of cis-VII.

Photochemical decomposition of ethyl diazoacetate (I) in 2-phenyloxirane (III)

A mixture of I (8.0 g, 0.37 mole) and III (17.0 g, 0.14 mole) in a Pyrex tube was irradiated with a 200W high press Hg. arc for 150 hr under N atm at 20–25°. After photolysis was complete, the mixture was distilled *in vacuo* to give fraction A, 14.1 g, boiling up to $78^{\circ}/15$ mm, and fraction B, 3.7 g, b.p. $65-120/2^{\circ}$ mm, which were analysed by GLC. Non-distillable polymer weighed ca. 3 g. Further results were summarized in Table 1.

Copper-catalyzed decomposition of ethyl diazoacetate (I) in 2-phenyloxirane (III)

The following experiment illustrates this type of reaction. To a well stirred mixture of III (21.6 g, 0.18 mole) and a catalytic amount of CuSO₄ freshly prepared I (2.1 g, 0.018 mole) was added dropwise in the course of 3-4 hr in N atm. When the N evoln had ceased, the catalyst was filtered off, and the filtrate distilled *in vacuo* to yield an oily mixture, which was subjected to GLC analysis. Further results were given in Table 1.

¹⁸ M. J. Kland-English, R. K. Summerbell and I. M. Klotz, Ibid. 75, 3709 (1953).

Reaction of dihalocarbenes with 2-phenyloxirane (III)

Sodium trichloroacetate (7.0 g, 0.038 mole) was added in 0.5 g portions to III (30.0 g, 0.25 mole) at 130° under vigorous stirring in N atm. After gas evoln was completed, the mixture was worked up as above. Styrene and 1,1-dichloro-2-phenylcyclopropane¹⁹ were identified by comparison of the retention times on GLC and IR spectra with those of authentic specimens. Formation of phosgene was confirmed qualitatively by *p*-dimethylaminobenzaldehydediphenylamine test. A trace amount of XI was also isolated from the distillation residue on column chromatography (silica gel, benzene).

Dichlorocarbene was also produced from chf and potassium t-butoxide¹⁰ or NaOH⁸⁰ under standard conditions.

The reaction of III with dibromocarbene produced from bromoform and potassium t-butoxide gave 1,1-dibromo-2-phenylcyclopropane, b.p. 86°/1 mm, in low yield. The identification was performed by comparison of the IR spectrum with an authentic sample.³¹

Decomposition of phenyldiazomethane in 2-phenyloxirane (III)

A mixture of phenyldiazomethane $(3.0 \text{ g}, 0.025 \text{ mole})^{22}$ and III (30.0 g, 0.25 mole) in a Pyrex tube was well degassed and irradiated with a 200W Hg-lamp at 20–25°. Distillation followed by GLC and TLC (silica gel, AcOEt-n-hexane mixture (1:6)) indicated the formation of styrene and *trans*-1,2diphenylcyclopropane,²² each in trace amounts. The main products were *trans*-stilbene (1.2 g, 53% yield), m.p. and m.m.p. 123–124°, and benzal azine (0.4 g, 15% yield), m.p. and m.m.p. 92–93°, which were produced from phenyldiazomethane only. Small amounts of XI was also obtained on column chromatography (silica gel, benzene).

Decomposition of bis(benzenesulphonyl)diazomethane in 2-phenyloxirane (III)

A mixture of bis(benzenesulphonyl)diazomethane (1·1 g, 0·0034 mole)³⁴ in III (16·8 g, 0·14 mole) was placed in a Pyrex tube, degassed *in vacuo* and then irradiated externally with a 200W high press Hg-lamp for 45 hr at 10°. As the reaction proceeded, III polymerized to a resinous solid. At the end of the reaction, monomeric oxirane III was no longer detected by GLC. An isomeric mixture of XI was obtained when the mixture was chromatographed on a silica gel column. Similar results, were obtained by thermal decomposition at 80°.

Decomposition of diphenyldiazomethane in 2-phenyloxirane (III)

Diphenyldiazomethane (2.5 g, 0.013 mole)²⁵ dissolved in III (2.0 g) was added dropwise to well stirred III (14.0 g, total 0.13 mole) at 160–165°, in N atm and the mixture kept at this temp for 3 hr. 1,1,2,2-Tetraphenylethane³⁶ (0.4 g, 18%), m.p. and m.m.p. 209–210° and benzophenone azine³⁸ (0.8 g, 34%), m.p. and m.m.p. 162–163° together with polymeric materials were produced. Photolysis of a mixture of diphenyldiazomethane (2.5 g, 0.013 mole) and III (16.0 g, 0.13 mole) with a 200W high press Hg-lamp gave 1,1,2,2-tetraphenylethane (0.7 g, 32%) and benzophenone azine (1.4 g, 60%).

Copper catalysed decomposition of ethyl diazoacetate (I) in 2-phenyloxetane (XII)

To a well stirred suspension of Cu powder $(1 \cdot 0 \text{ g})$ in XII (35 \cdot 0 \text{ g}, 0.26 mole) I (3 \cdot 0 \text{ g}, 0.026 mole) was added at 80° during 6 hr. After N evoln ceased, the reaction mixture was concentrated and distilled *in vacuo* to yield 4 \cdot 6 g (80% yield) of a colourless oil, b.p. 93–97°/0·07 mm, n_{D}^{50} 1·5147, which was a *cis-trans* mixture of 2-*carbethoxy*-3-*phenyltetrahydrofuran* (XIV). (Found: C, 70 \cdot 6; H, 7 \cdot 5. C₁₈H₁₆O₈ requires: C, 70 · 9; H, 7 \cdot 3%) GLC gave a single peak. IR spectrum (neat): 1740, 1270, 1190

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(ester), characteristic bands in 2000-1650 region, 760, 700 (phenyl) and 1100-1080 cm⁻¹ (tetrahydrofuran ring). NMR spectrum (CCl₄) showed the existence of two kinds of methyl group (0·3:1) at τ 9·29 (relative integrated area 3H, triplet, J = 7.5 c/s, methyl) and at 8·84 (9H, triplet, J = 7.5 c/s, methyl). Other signals appeared at 8·3-7·5 (8H, multiplet, methylene in tetrahydrofuran ring), a complex multiplet at 6·7-5·8 (20H, C₄ methine, C₄ methylene and methylene in Et group), 5·70 (3H, doublet, J = 6.0 c/s) C₄ methine), 5·49 (1H, doublet, J = 8.0 c/s, C₄ methine), 2·82 (5H, singlet, aromatics) and 2·78 (15H, singlet, aromatics). The major component is *trans*-XIV and the minor one *cis*-XIV, this assignment being based on the following findings.

Hydrolysis of this mixture with NaOH aq (5.0 g in EtOH (20 ml), and H₂O (20 ml)) gave cis and trans acids (XVa and XVb). cis-2-Carboxy-3-phenyltetrahydrofuran (XVa) melted at 149-150° (from benzene). (Found: C, 68.7; H, 6.1. C₁₁H₁₂O₃ requires: C, 68.7; H 6.3%.) IR spectrum (Nujol): 1735-1720, 1235, 1100, 970, 935-900, 770 and 700 cm⁻¹. NMR spectrum (CDCl₂) consisted of peaks at τ 7.8–7.4 (2H, multiplet, C₄ methylene), guartet centred at 6.24 (1H, C₄ methine), 6.0–5.5 (2H, multiplet, C_s methylene), 5.33 (1H, doublet, J = 8.0 c/s, C_s methine) and 2.71 (5H, singlet, aromatics). The methyl ester or cis-2-carbomethoxy-3-phenyltetrahydrofuran (XVIa) formed an oil, b.p. 90-92°/0.09 mm, n³⁰ 1.5217. (Found: C, 69.7; H, 6.8. C₁₂H₁₄O₂ requires: C, 69.9; H, 6.8%.) IR spectrum (neat); 1750, 1300, 1210 (ester), characteristic bands in 2000-1650 region, 750, 700 (phenyl), and 1100-1080 cm⁻¹ (tetrahydrofuran ring). NMR spectrum (CDCl₂) consisted of peaks at τ 7.8-7.4 (2H, multiplet, C₄ methylene), 6.72 (3H, singlet, methyl), quartet centred at 6.24 (1H, C₄ methine), 6.0-5.5 (2H, multiplet, C₄ methylene), 5.33 (1H, doublet, J = 8.0 c/s, C₂ methine) and 2.77 (5H, singlet, aromatics). The monohydrate of trans-2-carboxy-3-phenyltetrahydrofuran (XVb) melted at 74-75° (from benzene). (Found: C, 63.1; H, 6.5. C₁₁H₁₄O₄ requires: C, 62.8; H, 6.7%.) IR spectrum (Nujol): 3370 (OH group), 1730-1690, 1290, 1230-1210, 1100-1070, 980-960, 930, 920, 870, 850, 760 and 700 cm⁻¹. NMR spectrum (CDCl₁) consisted of signals at τ 8·2–7·3 (2H, multiplet, C₄ methylene), quartet centred at 6.38 (1H, C₄ methine), quartet centred at 5.80 (2H, C₅ methylene), 5.45 (1H, doublet, J = 6.0 c/s, C₂ methine), 2.65 (5H, singlet, aromatics) and 2.28 (2H, broad singlet, crystal water). When XVb was dried at $50^{\circ}/2$ mm for 10 hr, a colourless liquid was obtained and the absorption at 3370 cm⁻¹ disappeared. These facts indicated that XVb was a monohydrate. The methyl ester, or trans-2-carbomethoxy-3-phenyltetrahydrofuran (XVIb) formed an oil, b.p. 93-95°/ 0.09 mm, n⁵⁰ 1.5215. (Found: C, 69.6 H, 7.1. C₁₃H₁₄O₃ requires: C, 69.9; H, 6.8%.) IR spectrum (neat); 1750, 1275, 1210 (ester group), characteristic bands in 2000-1650 region, 760, 700 (phenyl group), and 1100-1080 cm¹ (tetrahydrofuran ring). NMR spectrum (CDCl₂) consisted of peaks at 7 8.2-7.3 (2H, multiplet, C4 methylene), quartet centred at 6.42 (1H, C2 methine), 6.25 (3H, singlet, methyl), quartet centred at 5.80 (2H, C_s methylene), 5.48 (1H doublet, J = 6.0 c/s, C_s methine) and 2.69 (5H, singlet, aromatics).

Further results were listed in Table 3.

Acknowledgement—The authors are grateful to Prof. K. Sisido for help and encouragement. They are indebted to Dr. T. Singû, Faculty of Pharmaceutical Sciences, Kyôto University, to Mr. H. Konisi, Kaô Soap Co., Wakayama, for NMR measurements, and also to Dr. S. Yuguti, Central Research Institute of Tôyô Rayon Co. for mass spectra.