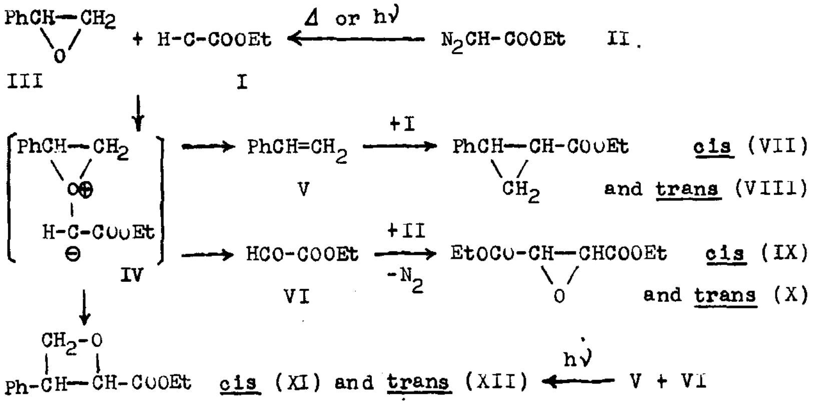
Tetrahedron Letters No.30, pp.2563-2567, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE REACTION OF ETHYL DIAZOACETATE WITH STYRENE OXIDE

Hitosi Nozaki, Hidemasa Takaya and Ryôzi Noyori
Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

(Received 1 June 1965)

The entitled reaction has been examined in hopes of observing the behaviour of carbethoxycarbene towards an epoxide. Following scheme accounts for the products which have been isolated in yields as summarized in Table I.



Oxygen-abstraction from III gives styrene (V) and ethyl glyoxylate (VI) (1), both affording on further reaction ethyl 2-phenylcyclopropanecarboxylate (VII and VIII) (2) and diethyl epoxysuccinate (IX and X) (3), respectively. Insertion of I at the C_α-O bond of III produces 2-carbethoxy-3-phenyloxetane (XI and XII).

Table I. The Effect of Reaction Variables on Product Composition

Mole Ratio	Reaction		Yield (%)[a] of Products Based on II Added					
III/II	Temp.°	hr.	V[b]	VI[b]	VII[c]	VIII[d]	IX + X	XI + XII
10	130-140	4[e]	7.4	< 0.5	4.5	9.0	< 1.0	7.3
2	130-140	4[e]	1.4	< 0.5	5.3	10.2	< 1.0	3.4
1	130-140	4[e]	0.9	< 0.5	5.0	12.3	< 1.0	2.6
2	20-25	150[f]	8.3	< 0.5	5.2	9.8	2.2	6.1
Relative Retention Time:[g]			0.35	0.09	4.73	5.64	2.50[h]	8.64[i]

a. The yields were calculated based on the peak area in the gas chromatogram (high-vacuum silicone grease, He). Besides the products listed, traces of ethyl maleate and fumarate were obtained in each run, the relative retention time being 1.36 and 1.64, respectively.

b. The yields of these products were variable probably due to the ready polymerizability.

c. Alkaline hydrolysis gave cis-2-phenylcyclopropanecarboxylic acid, m.p. 107-108° (lit. (2) 107-108°).

d. Hydrolysis afforded trans-2-phenylcyclopropanecarboxylic acid, m.p. and mixed m.p. 90-91° (lit. (4) 93°).

e. The mixture was pyrolyzed under nitrogen atmosphere.

f. The mixture was placed in a Pyrex test tube under nitrogen and irradiated externally with a 200 w high pressure mercury vapour lamp.

g. With III as the reference.

h. A doublet with an approximate intensity ratio of 2:1 and a separation of 0.28 in relative retention time.

A broad singlet.

All new compounds gave correct C, H analyses and each product was characterized by comparing its retention time and IR spectrum with the ones of the authentic sample. The cis trans mixture of diethyl epoxysuccinate (IX, X), b.p. 76-77° at 1 mm., was independently obtained by the reaction of VI with II at 70° (3). The NMR spectrum (Fig. 1) indicated the abundance ratio of 2:1 in each specimen. The other cis trans mixture of 2-carbethoxy-3-phenyloxetane (XI, XII), b.p. 115-118° at 2 mm., was also prepared by the photochemical cycloaddition (5) of VI to V in benzene solution. The addition proceeded so slowly that 150 hr irradiation resulted in only 15% conversion. The NMR spectrum (Fig. 2) indicated the abundance ratio of 1:1 in the insertion product, while the cycloaddition product contained the trans isomer twice as much as the cis isomer. The indicated structure of the oxetanes is supported by analogous examples previously recorded (5) as well as by the following fact. The photochemical cycloaddition of VI to 1,1-diphenylethylene afforded 2-carbethoxy-3,3-diphenyloxetane, b.p. 134-140° at 0.06 mm., in 25% yield. The NMR spectrum (Fig. 3), particularly the typical AB quartet at τ 4.95 (oxetane methylene), established the structure given. The methyl triplets of the ester ethyl group of XI (Fig. 2) and of the diphenyloxetane (Fig. 3) appeared at remarkably high fields. This should be ascribed to the long-range shielding of the neighbouring phenyl group.

The intermediacy of the O-ylide (IV) (6) would presumably be supported by the fact that the typical triplet or diphenylmethylene produced by thermal decomposition of diphenyldiazomethane reacted with III to afford 1,1,2,2-tetraphenylethane and a polymer.

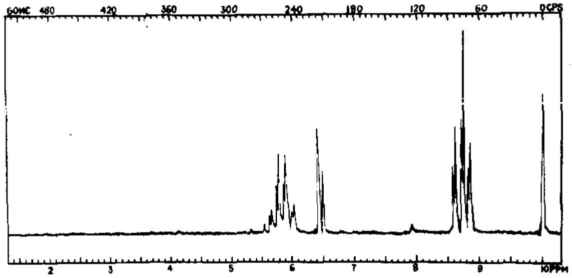


Fig. 1

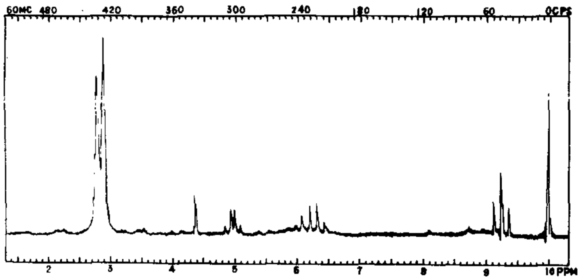


Fig. 3

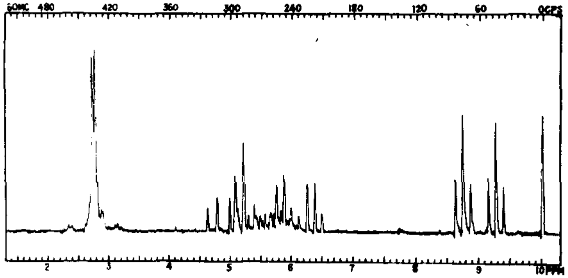


Fig. 2

All NMR spectra were taken in CCl_4 solutions on 60 Mc. machine and are given in τ value.

Fig. 1 cis trans Mixture of diethyl epoxysuccinate (IX, X).

Fig. 2 cis trans Mixture of 2-carbethoxy-3-phenyloxetane (XI, XII).

Fig. 3 2-Carbethoxy-3,3-diphenyloxetane.

neither styrene nor oxetane being produced. In sharp contrast to this, other electrophilic carbenes such as dichlorocarbene showed similar reactions as I. Details will be published in a full paper.

REFERENCES

1. The authentic sample was prepared by applying the method of F. J. Wolf and J. Weijlard (Organic Syntheses Coll. Vol. IV, p. 124, John Wiley, New York (1963)). Phenylhydrazone, m.p. and mixed m.p. 128-129°.
2. A. Burger and W. L. Yost, J. Amer. Chem. Soc. **70**, 2198 (1948).
3. For similar reaction of diazoalkanes with carbonyl compounds, see C. D. Gutsche, Organic Reactions Vol. VIII, p. 364, John Wiley, New York (1954).
4. D. B. Denney and M. J. Boskin, J. Amer. Chem. Soc. **81**, 6330 (1959). See also Ref. 2.
5. For orientation of the photochemical cycloaddition, see (a) J. F. Harris, Jr. and D. D. Coffman, ibid. **84**, 1553 (1962); (b) N. C. Yang, M. Nussim, M. J. Jorgenson and S. Murov, Tetrahedron Letters 3657 (1964) and references cited therein.
6. Analogous betain formation has been assumed in the deoxygenation of amine oxides with carbenes: (a) E. E. Schweizer and G. J. O'Neill, J. Org. Chem. **28**, 2460 (1963); (b) E. E. Schweizer G. J. O'Neill and J. N. Wemple, ibid. **29**, 1744 (1964).

Acknowledgement. The authors are grateful to Mr. H. Konishi, Kao Soap Co., Wakayama, for NMR spectra herein recorded.