Chemistry of Cyclopropanols. VII. Pyrolysis of Cyclopropyl Acetates

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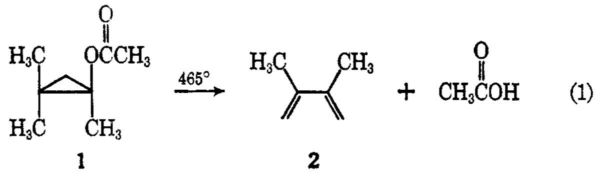
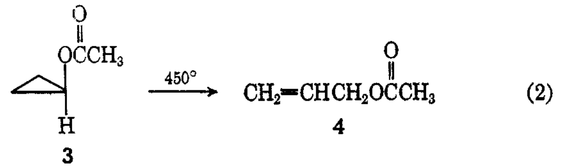
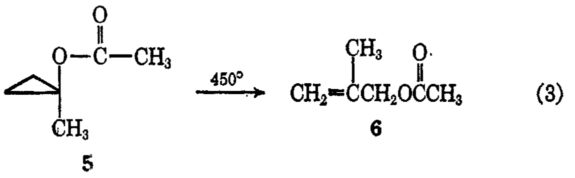
On pyrolysis at 485° cyclopropyl acetate, 1-methylcyclopropyl acetate, and 1,2,2-trimethylcyclopropyl acetate undergo a smooth rearrangement to allylacetates or their pyrolysis products. 1- and 2-arylcyclopropyl acetates, by contrast, give rise to numerous products including methylphenylacetylene, propiophenone, and indene derivatives. The products of both groups of compounds are suggested to arise by cyclopropane-bond homolysis.

In line with our earlier interest in the pyrolysis of cyclic esters,[1] we have subjected a variety of cyclopropyl esters[2] to the normal conditions for these elimination reactions. These studies have uncovered a new cyclopropyl rearrangement and shed some light on the mechanism of the pyrolyses of cyclopropane compounds in general.

We first examined the pyrolysis of the easily obtained[3] 1,2,2-trimethylcyclopropyl acetate. During pyrolysis by dropping through a helices-packed tube at 465° [4] 1 molar equiv of acetic acid was smoothly eliminated, and the cyclopropyl acetate was quantitatively converted into 2,3-dimethylbutadiene (eq 1). Various mechanisms can be written to account for this transformation, but many can be ruled out by our subsequent observation that cyclopropyl and 1-methylcyclopropyl acetate were converted into allyl and 2-methylallyl acetate, respectively, under essentially the same conditions (eq 2 and 3). Obviously a similar rearrangement of the trimethyl acetate would lead to the formation of an allyl acetate which would undergo pyrolytic elimination under the reaction conditions.

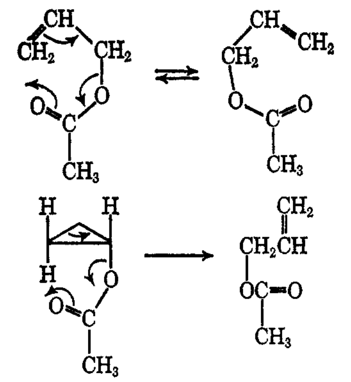






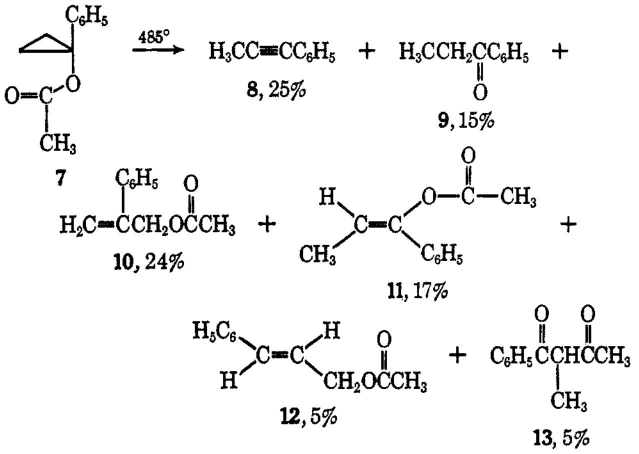
Our initial inclination was to consider this to be a cyclopropyl analog of the well-known Cope rearrangement of allyl esters[5] in which a new C–O bond is formed, the ring opens and the old C–O bond is broken simultaneously (Scheme I). While such a highly concerted reaction might appear attractive, subsequent work has made it unlikely.

Scheme I



Whereas the alkyl-substituted cyclopropyl acetates lead cleanly to a single product upon pyrolysis, aryl cyclopropyl acetates give rise to complex mixtures of products. In the case of 1-phenylcyclopropyl acetate we have attempted a reasonably complete analysis of the compounds formed (Scheme II). The percentages given for the products of this pyrolysis are based on complete conversion of the starting acetate.

Scheme II



The drastic change in products obtained with phenyl substitution is understandable if the pyrolysis is assumed to proceed by homolytic bond cleavage to a 1,3-trimethylene diradical. Such a cleavage is expected to occur at these temperatures, since they are in the region where 1,2-dideuteriocyclopropane undergoes *cis–trans* isomerization.[6] The diradical could be trapped by the carbonyl group of the acetate, leading eventually to rearrangement.

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[1] C. H. DePuy, R. W. King, and D. H. Froemsdorf, *Tetrahedron*, **7**, 123 (1959).

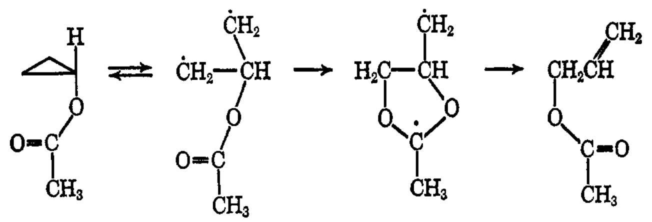
[2] C. H. DePuy, G. M. Dappen, and R. A. Klein, *J. Org. Chem.*, **27**, 3742 (1962).

[3] J. P. Freeman, *ibid.*, **29**, 1379 (1964).

[4] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

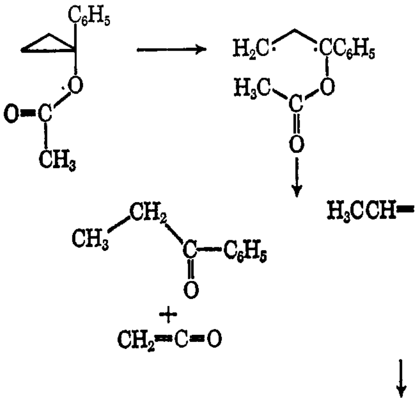
[5] W. J. Bailey and R. Barclay, Jr., *J. Org. Chem.*, **21**, 328 (1956).

[6] B. S. Rabinowitch, E. B. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).



In the case of 1-phenylcyclopropyl acetate pyrolysis, 1,2 cleavage is vastly superior to the 2,3 cleavage needed for this type of rearrangement. As a consequence, a whole new set of products arise and the 2-phenylallyl acetate is only one of a number of products formed (Scheme III). The origin of the methylphenylacetylene is still obscure, and additional experiments are needed to determine its mode of formation. Elimination to phenylcyclopropene and rearrangement of this intermediate is one possibility.

SCHEME III



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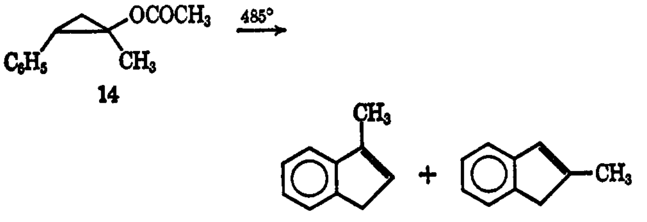
Further evidence for the intermediacy of diradicals is found in the products from the pyrolysis of 1-methyl-2-phenylcyclopropyl acetate. In this case the major products at 450° are the isomeric methylindenes, presumably formed by cyclization of the diradical into the *ortho* position of the benzene ring.



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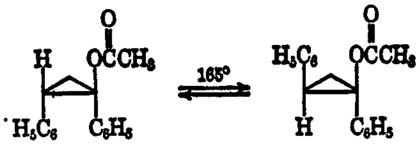
Taken together, the data are best accommodated by the view that a 1,3 diradical is formed reversibly, and that subsequent reactions determine the particular product ratios formed. This is consistent with an earlier observation that 1,2-diphenylcyclopropyl acetates undergo *cis–trans* isomerization faster than any other reaction.[7] We cannot rule out completely a competing concerted rearrangement, but, since the results do not demand such a process, and molecular models do not reveal that it would be particularly favorable, we see no compelling need to invoke it.



Experimental Section

All melting points and boiling points are uncorrected. Analytical vapor phase chromatography (vpc) separations were performed on a Model 500 instrument of F & M Scientific Co., and preparative separations were done with an Aerograph Model A90P instrument. The liquid phases employed were Ucon LB550X, LAC 446, or β,β'-oxydipropionitrile (ODPN) as indicated for the individual separations.

Cyclopropyl acetate (3) was prepared from peroxytrifluoroacetic acid and methyl cyclopropyl ketone by the method of Emmons and Lucas.[8]

1-Phenylcyclopropyl acetate (7) was prepared *via* a modification of the procedure of Smith and Bryant.[9] To a mixture of 8.5 g (63 mmol) of 1-phenylcyclopropanol (prepared as described previously[2]), 25 ml of pyridine, and 150 ml of benzene cooled with an ice–salt bath was slowly added 15.4 g of freshly distilled acetyl chloride. The reaction mixture was then allowed to warm to room temperature and stand for 40 hr. Water (100 ml) was then cautiously added and the aqueous layer was separated and extracted with two 50-ml portions of ether. The combined organic extracts were washed several times with dilute sulfuric acid, followed by successive washings with saturated sodium bicarbonate and water, and finally dried over $MgSO_4$. Solvents were removed under reduced pressure; the product (8.7 g, 78%) was distilled through a short Vigreux column, bp 45–48° (0.12 mm).

1-Methylcyclopropyl Acetate (5).—The 1-methylcyclopropanol, prepared as described previously,[10] was acetylated in the manner described for **7**. The product was purified by distillation, bp 111–113° (lit.[10] bp 112.5–113°).

1,2,2-Trimethylcyclopropyl acetate (1) was prepared by the method of Freeman.[3]

***trans*-2-Phenylcyclopropyl acetate** was synthesized as described previously.[10]

***trans*-Cinnamyl Acetate (12).**—Acetylation[9] of *trans*-cinnamyl alcohol gave 91% of the desired acetate, bp 74–75° (0.15 mm) [lit.[11] bp 139–140° (10 mm)].

2-Phenylprop-2-enyl acetate (10) was prepared by selenium dioxide oxidation of 2-phenylpropene in acetic acid solution.[12]

1-Acetoxy-1-phenylpropene (11) was prepared from propiophenone as described previously;[13] the product was distilled at 86–90° (0.8 mm) [lit.[13] bp 133–136° (17 mm)].

1-Phenyl-2-methyl-1,3-butanedione (13).—Treatment of 1-phenyl-1,3-butanedione with sodium methoxide and methyl iodide as described previously[14] afforded the crude product which distilled at 71–73° (0.08 mm) [lit.[14] bp 150–152° (20 mm)].

Pyrolysis of Cyclopropyl Acetate (3).—The pyrolysis apparatus has been described previously.[1] The acetate (0.4 ml) was added dropwise from a syringe to the vertically mounted apparatus maintained at 480°. The pyrolysate was collected in a Dry Ice–acetone cooled trap and then passed through the apparatus a second time. Analysis of the second pyrolysate by vpc indicated that it contained 55% unreacted **3**, 44% a second compound, and less than 1% volatile materials (acetic acid was not present). The 44% component was isolated by preparative vpc and identified as allyl acetate by comparison with an authentic sample.

Pyrolysis of 1-Methylcyclopropyl Acetate (5).—A 1.0-ml sample of the acetate was pyrolyzed in the manner described for **3**. The pyrolysate contained 48% unreacted starting material, *ca.* 52% of a single product, and trace amounts of volatile materials. The major component was separated by preparative vpc on a UCON column and identified as 2-methylallyl acetate by comparison with an authentic sample.

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[7] C. H. DePuy and L. B. Rodewald, *Tetrahedron Lett.*, 2951 (1964).

[8] W. D. Emmons and G. B. Lucas, *J. Amer. Chem. Soc.*, **77**, 2287 (1955).

[9] D. M. Smith and W. M. D. Bryant, *ibid.*, **57**, 61 (1935).

[10] C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, **29**, 2813 (1964).

[11] M. Bouis, *Ann. Chim.* (Paris), **9**, 402 (1928).

[12] L. F. Hatch and T. L. Patton, *J. Amer. Chem. Soc.*, **76**, 2705 (1954).

[13] P. Z. Bedoukian, *ibid.*, **67**, 1430 (1945).

[14] W. Dieckmann, *Chem. Ber.*, **45**, 2685 (1912).

Pyrolysis of 1,2,2-Trimethylcyclopropyl Acetate (1).—The pyrolysis of 20.0 g of this acetate was accomplished at 515° in the usual manner. Analysis of the pyrolysate by vpc indicated complete conversion of the ester; the mixture was washed with saturated sodium bicarbonate solution and dried over Na_2SO_4. Distillation of the organic material afforded a hydrocarbon which was identified as 2,3-dimethyl-1,3-butadiene (**2**) by comparison with an authentic sample.

Pyrolysis of **1** at several different temperatures indicated little conversion into product at 350°, about 50% conversion at 395°, and essentially complete reaction above 465°.

Pyrolysis of 1-Phenylcyclopropyl Acetate (7).—A 3.0-ml sample of this compound was pyrolyzed at 485° as described for **3**. Analysis of the pyrolysate by vpc on an LAC column indicated the presence of 11 compounds in addition to unreacted starting material. The components of the mixture were separated by preparative vpc and six were identified by comparison with authentic samples in each case. These compounds and their relative percentages are as follows: 1-phenylpropyne (**8**), 12.4%; propiophenone (**9**), 7.6%; phenallyl acetate (**10**), 11.4%; 1-acetoxy-1-phenylpropene (**11**), 8.7%; *trans*-cinnamyl acetate (**12**), *ca.* 2%; and 1-phenyl-2-methyl-1,3-butanedione (**13**), *ca.* 2–4%. Unreacted **7** accounted for 52% of the pyrolysate; the five unidentified components accounted for the remaining *ca.* 6%.

Pyrolysis of *trans*-2-Phenylcyclopropyl Acetate.—Reaction of a 1.0-ml sample of this compound in the usual manner at 465° produced a complex mixture as indicated by vpc analysis on a UCON column. The major product, comprising 50% of the mixture, was identified as *trans*-cinnamyl acetate by comparison with an authentic sample. Unreacted starting material accounted for a further 18% of the mixture and the remaining 32% contained a mixture of at least 13 additional compounds, none of which has been identified.

Pyrolysis of *cis*-2-Phenylcyclopropyl Acetate.—At 450°, 0.25 ml of this compound was pyrolyzed as described previously. Analysis of the pyrolysate by vpc on a UCON column indicated a mixture as complex as that produced from the corresponding *trans* compound; the major component again was shown to be *trans*-cinnamyl acetate.

Pyrolysis of 1-Methyl-*trans*-2-phenylcyclopropyl Acetate (14).—The acetate, 4.0 g, was pyrolyzed in the usual manner at 515°. The pyrolysate was diluted with pentane and extracted with saturated sodium bicarbonate. After drying over $MgSO_4$ and removal of pentane, the mixture was distilled at reduced pressure. In addition to starting material and a number of lesser components which have not been identified, distillation provided 0.8 g of a mixture of 2- and 3-methylindene (two-thirds and one-third, respectively, by analysis on an ODPN column). The latter compound was identified by comparison with a sample prepared by an independent route;[15] the 2-methyl derivative was identified by comparison of its nmr spectral properties with those previously reported.[16]

Registry No.—**1**, 16526-20-8; **3**, 4606-06-8; **5**, 16526-22-0; **7**, 16031-49-5; **14**, 16526-24-2; *cis*-2-phenylcyclopropyl acetate, 16526-25-3; *trans*-2-phenylcyclopropyl acetate, 16526-26-4.

Acknowledgment.—The authors are indebted to the National Science Foundation for support of this work.

[15] Prepared by reaction of indanone with methylmagnesium iodide and subsequent acid-catalyzed dehydration of the indanol derivative.

[16] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 590 (1963).

Substituent Effects on the Photoaddition of Diphenylacetylene to 1,4-Naphthoquinones

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The photoaddition of diphenylacetylene to 1,4-naphthoquinone and the corresponding 2-methoxyl and acetoxyl derivatives was investigated. In all cases, cyclobutene formation occurred to varying extents depending on the 2 substituent, thereby establishing this process as a useful synthetic method. In addition, the work provides the first examples of simultaneous C_4 and C_3O cycloaddition of alkynes to quinones and, in the case of 1,4-naphthoquinone, a particularly attractive system for studying the effects of reaction variables on the competing modes of addition.

Relative to the number of olefin and 1,3-diene photoadditions to *p*-quinones,[1] few reports on alkyne addition have appeared. Of these, only methoxy-*p*-benzoquinone undergoes C_4 cycloaddition[2] and affords 1-methoxybicyclo[4.2.0]octa-3,7-diene-2,5-diones of general structure I.[3] Both *p*-benzoquinone[4] and the tetrachloro derivative[5] photoadd diphenylacetylene to afford compounds II (X = H and Cl, respectively), presumably, by C_3O cycloaddition[2] *via* the unstable oxetenes III.[4] In contrast to olefins,[6] alkynes have not been observed to undergo concurrent C_4 and C_3O cycloaddition to quinones, a potentially attractive situation for determining the effects of solvent, temperature, and concentration changes on the competing modes of addition. The findings that tetrachloro-*p*-benzoquinone undergoes different modes of addition with cyclooctene[7] and diphenylacetylene[5] indicate clearly that ene and yne additions are not necessarily analogous and merit independent study. In addition, the varying extents to which energy transfer may occur between excited quinones and unsaturated compounds must be considered.

The photoaddition of alkynes to *p*-quinones has been of interest to us, primarily, as a synthetic route to the new class of compounds, represented by I, which are desirable for chemical studies and also as potential precursors of the cyclobutadiene derivatives IV. Consequently, our short-range objective was to extend the scope of this process with particular emphasis on varying the bridgehead substituents. For the long run, we hoped to uncover a system which provides both C_4 and C_3O cycloaddition products for mechanistic studies.

[1] For a current review, see J. M. Bruce, *Quart. Rev.* (London), **21**, 405 (1967).

[2] The terms C_4 and C_3O cycloadditions are adopted from C. H. Krauch, W. Metzner, and G. O. Schenck, *Ber.*, **99**, 1723 (1966).

[3] S. P. Pappas and B. C. Pappas, *Tetrahedron Lett.*, 1597 (1967).

[4] H. E. Zimmerman and L. Craft, *ibid.*, 2131 (1964); D. Bryce-Smith, G. I. Fray, and A. Gilbert, *ibid.*, 2137 (1964).

[5] J. A. Barltrop and B. Hesp, *J. Chem. Soc.*, *Sect. C*, 1625 (1967).

[6] For example, see C. H. Krauch and S. Farid, *Tetrahedron Lett.*, 4783 (1966).

[7] D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.* (London), 87 (1964); *Tetrahedron Lett.*, 3417 (1964).