

II, and other 1,3-cyclobutanediones will be the subject of a future publication.

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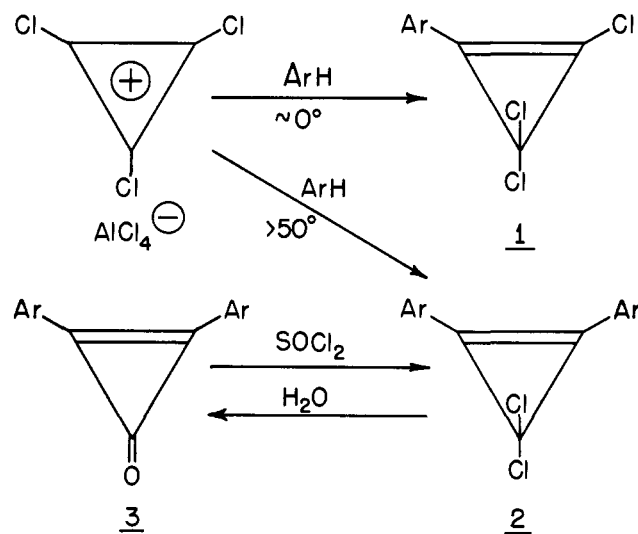
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Diarylcyclopropenones via the Trichlorocyclopropenium Ion

Sir:

We have found that the trichlorocyclopropenium ion¹ reacts smoothly with benzene derivatives to provide either aryltrichlorocyclopropenes (1) or *gem*-dichlorodiarylcyclopropenes (2) depending on reaction conditions, and that the *gem*-dichlorodiarylcyclopropenes obtained can be readily interconverted with the corresponding diarylcyclopropenones (3). These reactions



provide additional evidence for the existence of halo- and mixed arylhalocyclopropenium ions and demonstrate the ability of these species to effect electrophilic aromatic substitution. Moreover, they provide an exceptionally convenient route to compounds of the types 1, 2, and 3.

The following experiments using trichlorocyclopropenium tetrachloroaluminate and fluorobenzene illustrate the synthetic methods employed and the properties of the products obtained. Momentary local warming of 12.1 g. (0.039 mole) of C₃Cl₃⁺AlCl₄⁻ in 10 ml. of fluorobenzene at 0° started a vigorous exothermic reaction which evolved much HCl. The solution

turned deep red. Immediate recooling caused the reaction to subside after 30 sec. On quenching the reaction mixture in ice-water the red color was discharged and 6.2 g. of a clear oil was obtained. This oil showed a single sharp v.p.c. peak at 135° on a silicone oil column and had an analysis corresponding to 1 (Ar = *p*-F-C₆H₄-) (0.026 mole, 67% yield). *Anal.* Calcd. for C₉H₄Cl₃F: C, 45.52; H, 1.70; Cl, 44.78; F, 8.00. Found: C, 45.34; H, 1.65; Cl, 44.76; F, 8.04. The F¹⁹ n.m.r. spectrum (10% v./v. in CCl₄) shows the triplet of triplets diagnostic of a *para*-substituted fluorobenzene.² The position of the central resonance at 10.0 p.p.m. downfield from fluorobenzene suggests the structure 1.³ The infrared spectrum (liquid film) shows strong bands at 1603, 1505, 1254, 1239, 1155, 1009, 841, 728, and 710 cm.⁻¹ in the NaCl region. On standing in air the oil hydrolyzes to give a *p*-fluorophenylchloroacrylic acid.

If the reaction between C₃Cl₃⁺AlCl₄⁻ and fluorobenzene is carried out at higher temperatures two phenyl groups can be attached to the cyclopropene nucleus. Thus when 3.9 g. (0.0125 mole) of C₃Cl₃⁺AlCl₄⁻ and 5.0 ml. of fluorobenzene were treated as above, and then warmed to 50°, HCl evolution began again and continued for 10 min. The solution gradually turned from red to brown. Quenching this material in ice-water produced a tan solid which was dried and repeatedly extracted with hot CCl₄. The solid obtained by evaporation of the combined extracts was treated with a small amount of 95% ethanol (see below) and then sublimed at 50 μ and 135° to provide 1.45 g. of colorless bis-*p*-fluorophenylcyclopropenone (3, Ar = *p*-F-C₆H₄-) (0.006 mole, 48% yield), m.p. 184–185°. *Anal.* Calcd. for C₁₅H₈F₂O: C, 74.38; H, 3.33; F, 15.69; O, 6.61. Found: C, 74.26; H, 3.44; F, 15.52; O, 6.78 (by difference). The F¹⁹ n.m.r. pattern of this compound also indicates *para*-fluoro substitution. The infrared spectrum (Nujol mull) of this compound shows strong bands at 1842 (C=O), 1632 (C=C), 1592, 1500, 1409, 1299, 1240, 1152, 1101, 834, and 759 cm.⁻¹ in the NaCl region.

Neither triarylcyclopropenium ion salts⁴ nor triarylcyclopropenes⁵ have been observed in any of the reactions we have carried out. Prolonged heating of solutions of C₃Cl₃⁺AlCl₄⁻ in benzene derivatives leads to extensive tarring.

If the treatment with aqueous ethanol in the work-up of the diphenylcyclopropenones is omitted, the corresponding *gem*-dichlorodiphenylcyclopropene (2) is a major side product. This suggests that 2 is actually the initial reaction product, and 3 arises by hydrolysis.⁶ Since separation of 2 and 3 is difficult, we have found it convenient to convert everything to the ketone 3 as outlined above, work up the ketone, and then convert the ketone back to the *gem*-dihalide 2 if it is desired. This can be done quickly and quantitatively merely by warming the ketone with thionyl chloride.

For example, treatment of bis-*p*-fluorophenylcyclopropenone with SOCl₂ followed by recrystallization from cyclohexane containing a small amount of SOCl₂

(2) B. Bak, J. N. Shoolery, and G. A. Williams, III, *J. Mol. Spectry.*, **2**, 525 (1958).

(3) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(4) R. Breslow, *ibid.*, **79**, 5318 (1957).

(5) R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958).

(6) See also R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959).

(1) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964).

provides 1,2-bis-*p*-fluorophenyl-3,3-dichlorocyclopropane (2, Ar = *p*-F-C₆H₄-), m.p. 169–170°. *Anal.* Calcd. for C₁₅H₈Cl₂F₂: C, 60.63; H, 2.71; Cl, 23.86; F, 12.79. Found: C, 60.81; H, 2.95; Cl, 23.66; F, 12.91. This material shows strong infrared bands (Nujol mull) at 1600, 1515, 1360, 1351, 1232, 1150, 1120, 839, 689, and 660 cm.⁻¹ in the NaCl region. On standing in air this compound rapidly reverts to bis-*p*-fluorophenylcyclopropanone. It is remarkable that compounds of the type 2 hydrolyze exclusively to the cyclopropanone, whereas the monoaryl compounds 1, like tetrachlorocyclopropane, hydrolyze to give ring-opened products.⁷

Using the methods outlined herein we have also obtained examples of compounds 1, 2, and 3 in which Ar is phenyl, *p*-chlorophenyl, *p*-tolyl, and mesityl. Work on other functionally substituted benzene and polynuclear aromatic derivatives, and on the properties of the diarylcyclopropanones, is in progress.

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(7) S. W. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963).

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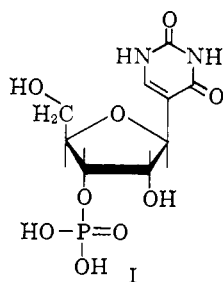
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ROBERT WEST

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Photolysis of Pseudouridine 3'-Phosphate and sRNA

Sir:

In the course of our studies on periodate oxidation of pseudouridine 3'-phosphate¹ (I, Ψ3'P), we routinely looked for 5-formyluracil (FoU) by spraying paper



chromatograms with the aldehyde reagent *o*-dianisidine.² We noticed that when the chromatogram was inspected over an ultraviolet light prior to spraying with *o*-dianisidine, Ψ3'P, applied as a standard, gave the yellow color characteristic of an aldehyde. Investigation of this peculiar observation led to the discovery of a new photolytic reaction which we wish to record in this communication.

An aqueous solution (10 ml.) of Ψ3'P³ (1 *A*₂₆₀ unit/ml.)⁴ was placed in a 1-l. quartz erlenmeyer flask and

(1) M. Tomasz and R. W. Chambers, *Abstr. Sixth Intern. Congr. Biochem.*, **1**, 90 (1964).

(2) F. Feigl, "Spot Tests," Vol. II, Elsevier Publishing Co., New York, N. Y., 1954, pp. 148–151.

(3) W. E. Cohn, *Biochem. Prep.*, **8**, 116 (1961).

(4) *A*₂₆₀ = absorbance in a 1-cm. quartz cuvette at 260 mμ.

irradiated from below with a low pressure mercury lamp equipped with a filter passing mainly 253.7-mμ light.⁵ The solution was stirred magnetically and cooled with a fan during the reaction (~27°). After 1.5 hr. the reaction mixture was analyzed by paper chromatography, paper electrophoresis, and ion-exchange chromatography. In addition to starting material (29%), inorganic phosphate (P_i, 0.65 equiv.)⁶ and 5-formyluracil⁷ (FoU, 0.37 equiv.)⁸ were found. A product of unknown structure (13% of the original *A*₂₆₀) was also detected. This compound does not contain phosphate; it has a spectrum at pH 6 similar to that of Ψ3'P; at pH 2 or 12 the spectrum is similar to, but not identical with, that of FoU.

Irradiation of pseudouridine 3',5'-diphosphate⁹ also gave FoU and P_i. However, neither of these products was produced by irradiation of pseudouridine 2'-phosphate, pseudouridine 2',3'-cyclic phosphate, or pseudouridine itself.¹⁰

Irradiation of yeast uridylic acid under the same conditions resulted in a 79% loss in *A*₂₆₀ which was restored by treatment with acid as expected.¹¹ No P_i was produced by this reaction nor by irradiation of a mixture of yeast adenylic, guanylic, cytidylic, and uridylic acids. However, when the mixture included Ψ3'P, 0.33 equiv. (based on Ψ3'P) of P_i was formed in 1.5 hr.

These results suggested that it might be possible to cleave transfer RNA (sRNA) specifically at its pseudouridine residues. Accordingly, partially purified phenylalanine sRNA (40 *A*₂₆₀ units in 10 ml. of water) was irradiated for 3.5 hr. The ability to load phenylalanine was completely destroyed. The sedimentation coefficient, *S*_{20,w}, of the irradiated product was 1.93 while that of the starting material was 3.01. This information plus some preliminary light-scattering measurements indicate that a decrease in molecular weight occurred during irradiation.¹²

Treatment of the irradiated product with crystalline *Escherichia coli* phosphatase¹³ liberated 0.26 μmole of P_i as compared to 0.12 μmole released from the un-irradiated control. Alkaline hydrolysis of the irradiated product and analysis of the nucleotides by ion-exchange chromatography indicated that 23% of the pseudouridine had been destroyed.¹⁴

The sum of the evidence strongly suggests that cleavage of the sRNA molecule occurred during irradiation. We have been unable to separate any fragments on columns of Sephadex or methylated albumin-

(5) Mineralite, Model SL 2537, Ultraviolet Products, South Pasadena, Calif.

(6) Determined directly on an aliquot from the reaction mixture by the Lowry-Lopez method [O. H. Lowry and J. A. Lopez, *J. Biol. Chem.*, **162**, 421 (1946)]. No evidence of any phosphate containing intermediate could be found by chromatography or electrophoresis.

(7) R. E. Cline, R. M. Fink, and K. Fink, *J. Am. Chem. Soc.*, **81**, 2521 (1959).

(8) In a separate experiment it was established that a 27% loss of *A*₂₆₀ occurs when FoU is irradiated under these conditions.

(9) M. Tomasz and R. W. Chambers, to be published.

(10) An 11–13% loss of *A*₂₆₀ occurred with these three compounds. Similar results were obtained with pseudouridine by Lis and Allen [A. W. Lis and F. W. Allen, *Biochim. Biophys. Acta*, **49**, 190 (1961)].

(11) R. L. Sinsheimer, *Radiation Res.*, **1**, 505 (1954).

(12) We are grateful to Dr. Robert C. Warner and Mr. Frank Zaboretzky for the ultracentrifuge data and to Dr. David B. Ludlum and Mr. Robert Pollet for the light-scattering measurements.

(13) We are indebted to Dr. Michael Malamy for a sample of this enzyme.

(14) This is in contrast to the findings of Lis and Allen,¹⁰ who reported that "all but a trace" of the pseudouridine was destroyed by irradiation of "1 M NaCl soluble" RNA from wheat germ.