Although the above analysis is certainly not unique, the trigonal-bipyramidal radical structure proposed is consistent with the results of esr studies[3-5] of other phosphoranyl radicals. Furthermore, the proposed stereospecific introduction of the entering alkoxy group into the axial position is in keeping with the rules[9] which appear to apply for the formation of pentacovalent phosphorus intermediates to which **1** and **11-13** probably are related in terms of bonding.

A previous study[1] of the reaction of ^{14}C-labeled *tert*-butoxy radical with tri-*tert*-butyl phosphite gave label distribution consistent with the irreversible formation of an intermediate $(RO)_4P\cdot$ which gives product containing essentially 75% of the available label. Unfortunately, the reactivity ratio $(1.3/1.0)^{10}$ which explains the product distributions encountered in the benzyl diethyl phosphite studies predicts a deviation from statistical label distribution for the tri-*tert*-butyl phosphite system which is so small as to be within the error limits of our radiochemical counting techniques.

Acknowledgment. We gratefully acknowledge support of this work by the National Cancer Institute, Public Health Service Research Grant No. CA-11045.

(9) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968); K. Mislow, *ibid.*, 3, 266 (1970). To the extent that the entrance of the benzyloxy radical into 1 is only stereoselective rather than stereospecific, an increase in the axial/equatorial reactivity ratio would be required to explain the present data. This would also be true if some type of equilibration process, such as pseudorotation, were operative by which axial and equatorial substituents are interchanged. Nonetheless, the primary conclusions of this study, the nonequivalency of alkoxy substituents in 1 and the stereochemically nonrandom introduction of the benzyloxy radical in the formation of 1, remain.

(10) This ratio is likely a function of the C-O bonds undergoing cleavage; thus it may be different for a *tert*-butoxy substituent. It should be made clear that β cleavage of a C-O bond in 1 is not the microscopic reverse of the proposed stereoselective or stereospecific P-O bond formation involved in formation of 1. Violation of microscopic reversibility is not a consideration in the postulated cleavage of both axial and equatorial C-O bonds.

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Ion Radicals. XXIV. Reaction of Thianthrene Perchlorate with Ammonia[1-3]

Sir:

Reactions of cation radicals with amines have been confined in past years to the use of pyridines, which engage in pyridination[4,5] or proton-transfer reactions.[6] Hardly anything at all is known about the reaction of aliphatic amines with cation radicals. *n*-Butylamine is reported to discharge the color of the anthracene cation radical from a silica–alumina surface, *via* displacement of the hydrocarbon from the catalyst surface, rather than by nucleophilic reaction with the ion radical.[7]

(1) Part XXIII: C. V. Ristagno and H. J. Shine, *J. Org. Chem.*, 36, 4050 (1971).

(2) Supported by the National Science Foundation, Grant No. GP-25989X.

(3) In earlier papers we have used incorrectly the name thianthrenium to designate the cation radical in cation–radical salts.

(4) J. Rochlitz, *Tetrahedron*, 23, 3043 (1967).

(5) L. Marcoux, *J. Amer. Chem. Soc.*, 93, 537 (1971).

(6) V. D. Parker and L. Eberson, *Tetrahedron Lett.*, 2839, 2483 (1969); *Acta Chem. Scand.*, 24, 3542 (1970).

(7) R. M. Roberts, C. Barter, and H. Stone, *J. Phys. Chem.* 63, 2077 (1959).

We have now found that when dry ammonia gas is bubbled into a solution of thianthrene perchlorate (**1**)[8] in either nitromethane or acetonitrile, 5,5-dihydro-5-(5-thianthreniumylimino)thianthrene perchlorate (**2**)[9] is formed.

The stoichiometry of the reaction is given in eq 1. The preparation and isolation of **2** are as follows.
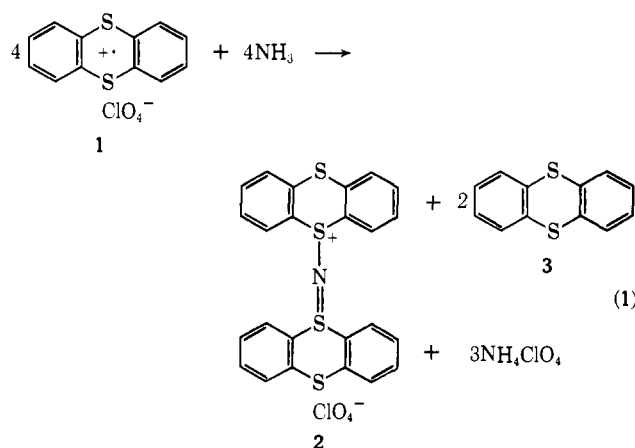
Ammonia gas was bubbled into a solution of 201 mg (0.636 mmol) of **1** in 20 ml of nitromethane. The color of **1** disappeared rapidly. Excess of ammonia was removed with a stream of dry nitrogen. Ammonium perchlorate was filtered off and identified by infrared (Nujol mull).[10] (Ammonium perchlorate was too soluble to precipitate when reaction was carried out in acetonitrile.) Tlc of the solution showed two spots only: thianthrene (**3**), R_f (benzene) = 0.59, and **2**, R_f (all solvents used) = 0. The nitromethane solution was extracted with cyclohexane until tlc no longer showed the presence of **3**. Ultraviolet assay of the cyclohexane solution gave 67.2 mg (0.311 mmol, 98%) of **3**. A similar experiment using 164 mg (0.518 mmol) of **1** gave 54 mg (0.250 mmol, 96%) of **3**. The nitromethane solution was evaporated leaving a white solid, which was washed with water and cyclohexane and dried, giving 42 mg (0.078 mmol, 49%) of **2**. Crystallization from methanol gave mp 240–241° dec. Compound **2** decomposes on heating giving, in part, ammonia and thianthrene. Therefore, the melting point was obtained by plunging a filled capillary into a preheated bath.

Anal. Calcd for $C_{24}H_{16}S_4NClO_4$: C, 52.8; H, 2.93; S, 23.5; N, 2.56; Cl, 6.49. Found:[11] C, 52.6; H, 3.00; S, 23.2; N, 2.99; Cl, 6.94.

The nmr spectrum in DMSO had δ_H 7.6 (m, 12 H) and 8.0 (m, 4 H) consistent with the 1,1',2,2',3,3',-7,7',8,8',9,9' protons and the 4,4',6,6' protons of **2**. The ultraviolet spectrum in acetonitrile had maxima at 335, 291, and 227 nm, $\epsilon = 5 \times 10^2$, 1.1×10^3, and 4.3×10^3, respectively.

The structure of **2** was deduced from hydrolysis experiments which are summarized in Scheme I.

A mixture of 133 mg (0.243 mmol) of **2** in 40 ml of methanol and 15 ml of 15% aqueous sodium hydroxide was boiled for 5 hr. Tlc showed only two products, **4**, R_f (ether) = 0.10, and **5**, R_f (ether) = 0.59. Both prod-
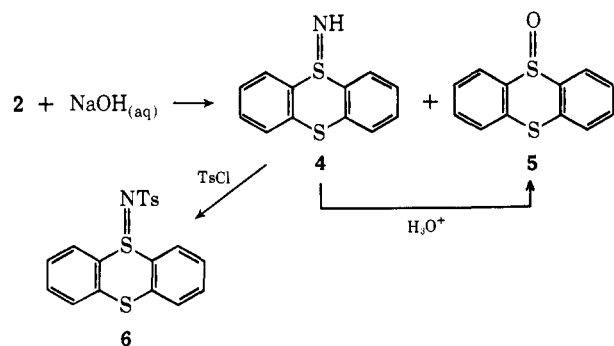
(8) Y. Murata and H. J. Shine, *J. Org. Chem.*, 34, 3368 (1969).

(9) We wish to thank Dr. K. L. Loening, Nomenclature Division, Chemical Abstracts Service, for naming this compound.

(10) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, 24, 1253 (1952).

(11) Schwarzkopf Laboratories, Woodside, N. Y.

Scheme I

6

ucts were extracted into benzene from the aqueous methanol solution, and separated on a column of silica gel, giving 51.3 mg (0.221 mmol, 99%) of **5** and 30 mg (0.129 mmol, 53%) of **4** (5,5-dihydro-5-imino-thianthrene[9]), mp 130–143° dec. A sample of **4** was taken up in methanol and hydrolyzed by stirring with 30% hydrochloric acid for 2 hr. Tlc showed the presence of **5** only. Extraction of **5** into benzene and assay (ultraviolet spectrum) gave 90% of the anticipated **5**. The acidic methanol solution was made alkaline with sodium hydroxide and heated. Ammonia was evolved (silver nitrate–manganese nitrate paper test).

The tosylate **6** of **4** was obtained without isolating **4** because **4** was found to be unstable to too much handling in the light. A sample (52 mg, 0.095 mmol) of **2** was hydrolyzed by base as described. The products were extracted into benzene, the benzene was evaporated, and the residue was dissolved in dry ether. To the ether solution was added the calculated amounts of pyridine (0.1 ml, 0.12 mmol), and, dropwise, p-toluene-sulfonyl chloride (18 mg, 0.1 mmol). The solid residue from the evaporated ether solution was washed with water and was shown to contain only two compounds by tlc: **5**, R_f (benzene) = 0.30, and the tosylate **6**, R_f (benzene) = 0.11. The two compounds were separated on a column of silica gel. Elution with benzene–ether (10:1) gave 21 mg (0.090 mmol, 95%) of **5**, while elution with ether gave 11 mg (0.026 mmol, 27%) of 5,5-dihydro-5-(N-p-toluenesulfonyl)imino-thianthrene (**6**), mp 172–173° (methanol); lit. mp 168–169° (reaction of thianthrene with chloramine-T).[12]

Anal. Calcd for $C_{19}H_{15}S_3NO_2$: C, 59.2; H, 3.89; S, 24.9; N, 3.63. Found:[11] C, 59.3; H, 3.88; S, 24.8; N, 3.75.

The mass spectrum[13] of **6** showed the parent peak, mass 385. The ratio of the intensities of peaks 387/385 (16.3%) was consistent with the formula for **6**.[14]

Reaction of **1** with water leads to **3** and **5**, and the reaction has been interpreted from kinetic data as going through the thianthrene dication **7**.[8] Reaction of **1** with ammonia can be interpreted similarly, in which case compound **4**, formed in the reaction of **7** with ammonia (eq 2), would have to react rapidly with another molecule of **7** to give **2** (eq 3). Kinetic data are needed to settle this point.

Compound **2** is a member of an only recently discovered class of compounds containing the group

(12) D. Hellwinkel and G. Fahrbach, *Justus Liebigs Ann. Chem.*, **715**, 68 (1969).

(13) Morgan-Schaffer Laboratories, Montreal, Canada.

(14) J. H. Beynon, "Mass Spectrometry and Applications to Organic Chemistry," Elsevier, Amsterdam, 1960, p 301.

$$7 + 4 \longrightarrow 2 + H^+ \qquad (3)$$
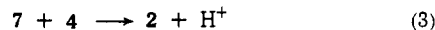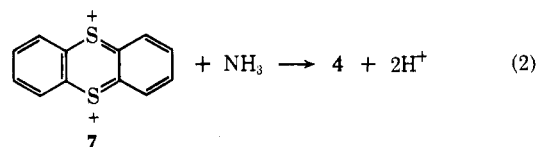
$R_2S^+N{=}SR_2$, analogous in form to the allyl cation. The first known example (R = Me; anion Cl⁻) was made by the reaction of DMSO with trithiazyl chloride,[15] while an aromatic analog (R = phenyl; anion Cl_3^-) was made by reaction of phenyl sulfide with nitrogen trichloride.[16] The present reaction (leading to **2**) may be general for organosulfur cation radicals. This and the reaction of organosulfur cation radicals with alkylamines are being explored.

(15) M. Becke-Goehring and H. P. Latscha, *Angew. Chem.*, **74**, 695 (1962).

(16) G. Appel and G. Buchler, *Justus Liebigs Ann. Chem.*, **684**, 112 (1965).

(17) Predoctoral student.

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Cycloaddition of tert-Butylcyanoketene to 1,2-Cyclononadiene and cis- and trans-Cyclooctene

Sir:

Reported here is the first stereochemical investigation of the cycloaddition of a ketene to an allene, specifically tert-butylcyanoketene[1] (**1**) to racemic and optically active 1,2-cyclononadiene (**2**). These cumulenes react to give a mixture of the diastereomeric cyclobutanones **5** and **6** in a ratio of 3:2. When partially resolved 1,2-cyclononadiene is used both epimers show appreciable optical activity. It is also established that tert-butylcyanoketene behaves as a "normal" ketene in its cycloadditions to simple alkenes, i.e., it reacts stereospecifically with cis- and trans-cyclooctene to give, respectively, the cyclobutanones **7** and **8**.[2]

The cycloaddition of tert-butylcyanoketene (**1**) to 1,2-cyclononadiene (**2**) was accomplished by adding the allene to a benzene solution of the ketene. The reaction was complete within a few minutes at room temperature to give a mixture of the cyclobutanones **5** and **6** in a ratio of 3:2 as evidenced by gas chromatography and nmr analysis of the crude reaction mixture. Compounds **5** and **6** were separated by preparative gas chromatography.[3] The nmr spectra of **5** and **6** are consistent with their proposed formulations, i.e., the tert-butyl is cis to the adjacent CH_2 group in the major isomer **5** and trans to it in **6**. The pertinent

(1) H. W. Moore and W. Weyler, Jr., *J. Amer. Chem. Soc.*, **92**, 4132 (1970); H. W. Moore and W. Weyler, Jr., *ibid.*, **93**, 2812 (1971).

(2) The cycloadditions of ketenes to alkenes have received marked attention. These highly regio- and stereoselective reactions are best interpreted as concerted $[_\pi2_a + _\pi2_a]$ cycloadditions in which the ketene functions as the antarafacial component: (a) T. DoMinh and O. P. Strausz, *ibid.*, **92**, 1766 (1970); (b) W. T. Brady, E. F. Hoff, R. Row, Jr., and F. H. Parry, *ibid.*, **91**, 5679 (1969); (c) J. E. Baldwin and J. A. Kapecki, *ibid.*, **92**, 4874 (1970); (d) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970); (e) R. Montaigne and L. Ghosey, *Angew. Chem., Int. Ed. Engl.*, **80**, 194 (1968); (f) R. Huisgen, L. A. Feiler, and P. Oho, *Tetrahedron Lett.*, 4485 (1968); (g) N. S. Isaacs and P. F. Stanbury, *Chem. Commun.*, 1061 (1970).

(3) 10 ft × ¼ in. 15% SE-30 Chromosorb W 60–80 acid-washed dimethyldichlorosilane-treated columns, 85°.