

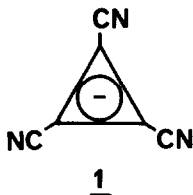
STUDIES ON THE TRICYANOCYCLOPROPENYL SYSTEM

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Abstract: Chlorination of tricyanocyclopropane is observed to lead directly to trichlorotricyanocyclopropane which undergoes a remarkable reductive conversion to hexacyanobenzene. The synthesis of mono- and dichlorotricyanocyclopropane (4 and 5) and their use as potential precursors for tricyanocyclopropenyl anion is described.

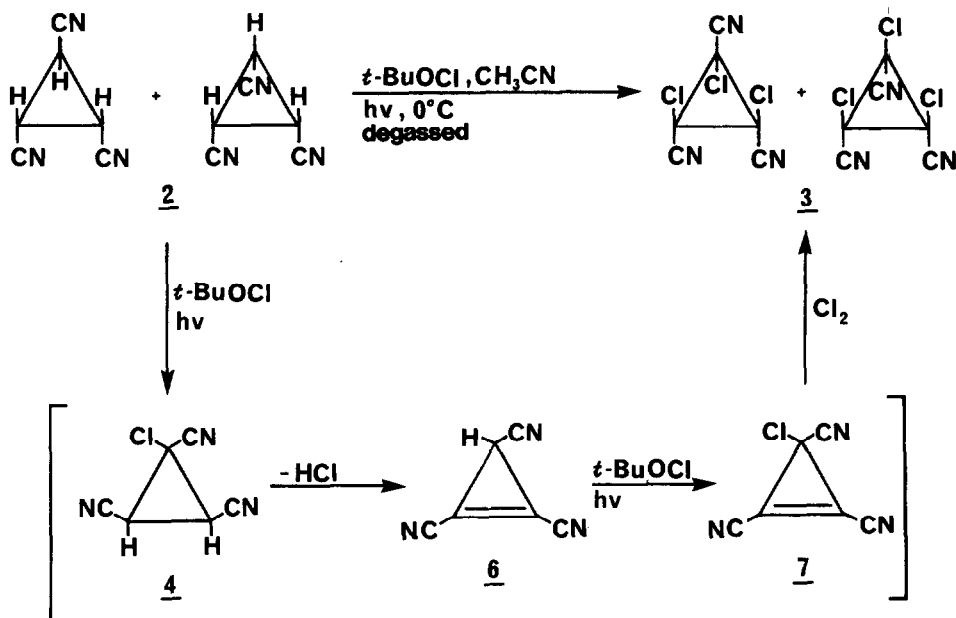
The cyclopropenyl anion is the simplest antiaromatic system. The parent compound is terribly unstable, and trialkyl or triphenyl derivatives are also so unstable that they have only been transient species produced by electrochemical reduction.¹ However, one might hope that with good stabilizing groups the cyclopropenyl anion system could be isolable. For instance, our estimate of the acidity of triphenylcyclopropene indicates that its pK_a is approximately 20 units higher than the pK_a of triphenylmethane.² If this difference were paralleled for cyano substituents, the very low pK_a of tricyanomethane suggests that tricyanopropene could have a pK_a near 20 and thus 1 could be reasonably stable. Similar arguments can be made for other strongly stabilizing substituents.



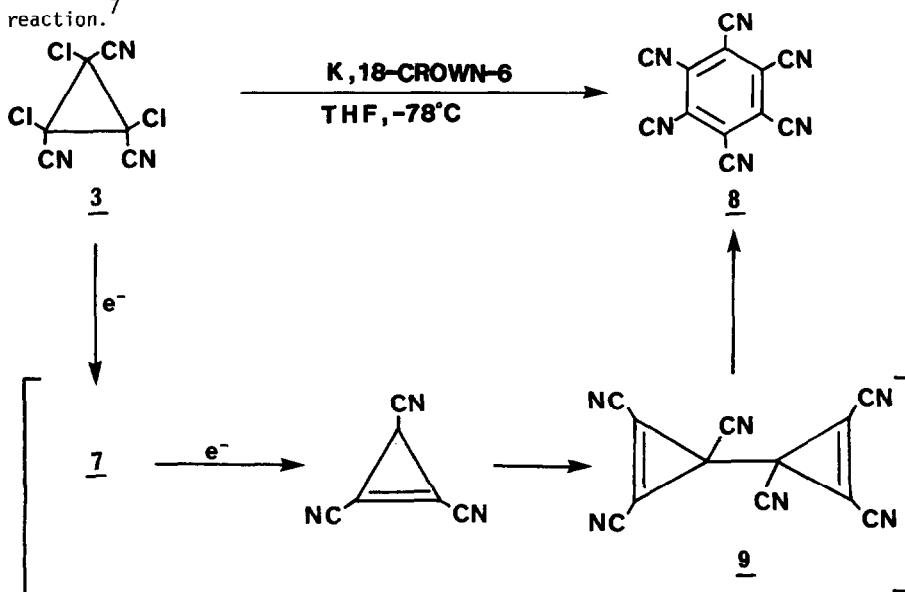
We have reported studies on the tribenzoylcyclopropene system.³ The cyclopropene itself could be generated by HBr elimination from the corresponding bromocyclopropane, but no evidence for the corresponding anion could be obtained since even hindered bases add to the cyclopropene double bond rather than generate the anion. With very hindered bases the tribenzoylcyclopropene rearranged to a furan derivative. Such a path is not open to the linear cyano group, so for this and other reasons we have investigated approaches to the tricyanocyclopropenyl anion (1). We now wish to report our observations which seem to bear on the stability of 1.

cis- and trans-Tricyanocyclopropane (2) were prepared as reported.⁴ The cis isomer could be chlorinated with t-butyl hypochlorite in benzonitrile, or the cis and trans mixture could be chlorinated in acetonitrile with an excess of t-butyl hypochlorite to produce some chlorinated solvent along with the cis, trans mixture of trichlorotricyanocyclopropane (3).⁵ Depending on the excess of chlorinating agent used various amounts of recovered starting material (2) were also obtained, but remarkably no monochlorotricyanocyclopropane 4 or dichloro derivative 5 were detectable. The most likely explanation of this is that 4 is indeed formed, but readily loses HCl to generate tricyanocyclopropene 6. This should rapidly chlorinate to generate the chlorocyclopropene 7, which could add chlorine (from

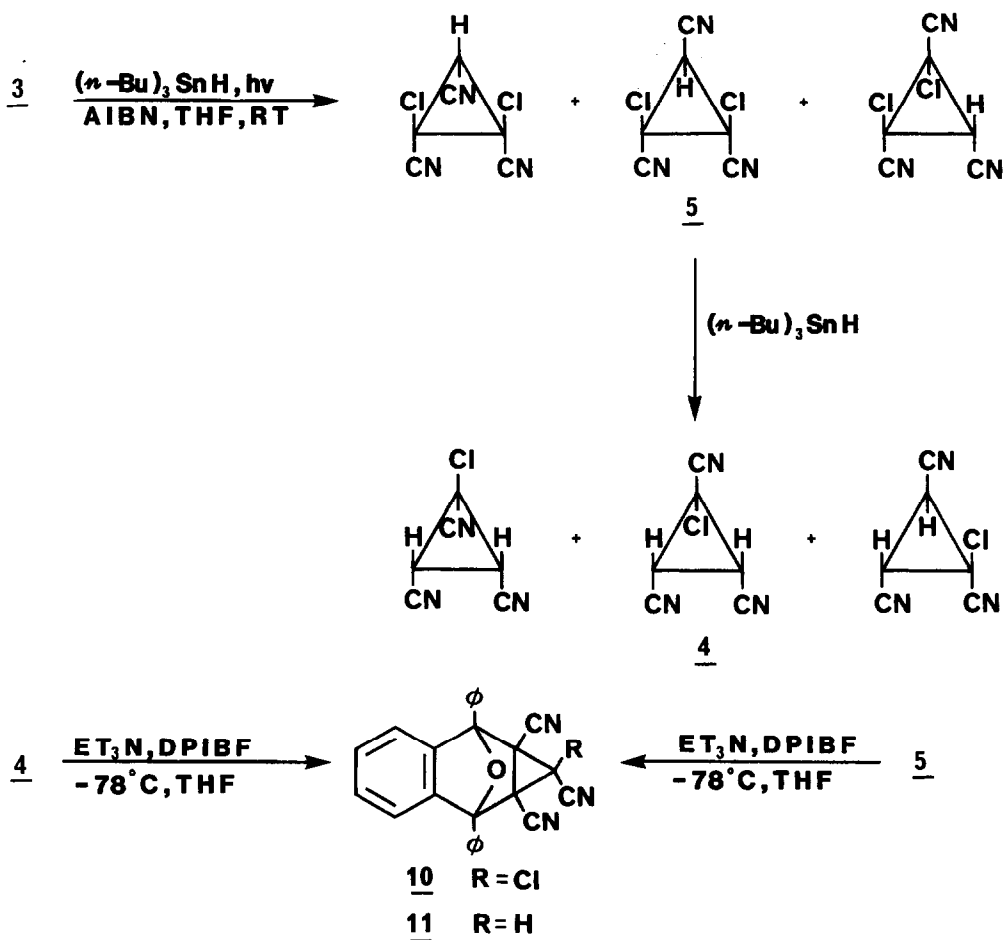
reaction of the *t*-butyl hypochlorite with HCl) to form 3. This mechanism, which depends on the very easy loss of HCl from a chlorocyclopropane, is supported by the properties of authentic 4 and 5 which are reported below.



Reduction of 3 with metals should generate 7, and further reduction might be expected to form the anion 1. Thus this was examined under a variety of conditions, using electrochemical reduction and electron solutions. In no case was there any evidence for the formation of a stable anion 1, but strikingly, the reduction of 3 with potassium metal and 18-crown-6 in tetrahydrofuran led to the formation of a 25% yield of hexacyanobenzene (8).⁶ Apparently the chlorocyclopropene (7) is formed but it reductively dimerizes to the bis-cyclopropenyl (9), probably by generating the tricyanocyclopropenyl radical. The rearrangement of such bis-cyclopropenyls to benzene derivatives is a well preceded reaction.⁷



Treatment of the trichloro compound (3) with tributyltin hydride indeed generates a stereoisomeric mixture of the dichlorocyclopropanes (5)⁸, and further reaction with more of the hydride reagent generates a mixture of the stereoisomers of the monochlorocyclopropane (4)⁹. In both cases some of the original tricyanocyclopropane (2) is also produced. The dichloro compound (5) readily loses HCl even on standing, and on treatment with various bases at room and low temperatures. When the elimination is performed in the presence of diphenylisobenzofuran, the adduct 10 of the chlorocyclopropene 7¹⁰ is formed, but in the absence of the trapping reagent polymeric material is produced and stable solutions do not survive. Similarly the monochlorocyclopropane (4) eliminates HCl with base, and in the presence of DPIBF it also generates an adduct 11 of the corresponding cyclopropene 6.¹⁰ However, when the monochlorocyclopropane 4 is treated with two equivalents of such hindered bases as lithium tetramethylpiperidide, a brown solution is formed. Quenching of this solution with deuteriomethanol in the presence of DPIBF gives adduct 11 with no deuterium incorporation. Thus the generation of tricyanocyclopropene 4 in the presence of strong base is apparently not forming a stable solution of the anion 1, whose quenching should have led to deuterated 11 (R=D).



These studies illustrate synthetic methods which make some highly substituted cyclopropane derivatives available, and they also provide examples of two interesting and unusual reactions in the chlorination sequence by which 2 is converted directly to 3 and in the reductive conversion of 3 to the benzene derivative 8. However, perhaps most importantly they indicate again how elusive the antiaromatic cyclopropenyl anion derivatives are, even when substituted by strongly stabilizing groups.^{11,12}

References

References

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2. Breslow, R.; Chu, W. J. Am. Chem. Soc. 1973, 95, 411-418.
3. Breslow, R.; Erlich, K; Higgs, T.; Pecoraro, J.; Zanker, F. Tetrahedron Lett. 1974, 1123-1126.
4. Griffin, G.W.; Peterson, L.I. J. Org. Chem. 1963, 28, 3219-3220.
5. The two isomers in approximately equal amount, as judged by gas chromatography. CMR: 111.5, 110.2, 109.2, 44.7, 43.5 ppm. Anal. C,H(none), Cl, N. MS 220, 222, 224 (M+1, three chlorine pattern). Tlc (silica) r.f. = 0.50 with 80% EtOAc/ 20% hexane.
6. Identical with an authentic sample.
7. Davis, J.H.; Shea, K.J.; Bergman, R.G. J. Amer. Chem. Soc. 1977, 99, 1499-1501.
8. Characterized by PMR (singlets at 4.3 and 4.0 ppm in the mixture of isomers) and MS. It had an r.f. of 0.45 on silica with CH₂Cl₂.
9. The three isomers were separated by medium pressure liquid chromatography on silica with CH₂Cl₂ (ref. 11). The unsymmetrical isomer had an AB quartet in the PMR at 3.65 and 3.34 ppm (J 7 Hz), with an r.f. of 0.20 on silica with CH₂Cl₂. The two symmetrical isomers had r.f. 0.15, and showed singlets at 3.46 and 3.33 ppm in the PMR. CMR and MS were also consistent with these structures.
10. Adduct 10 was characterized by MS. Adduct 11 showed an M+1 of 386, and PMR of 7.60 and 7.42 multiplets (14 H) and 3.60 singlet ppm (1H). It had r.f. 0.45 on silica with CH₂Cl₂.
11. Taken in part from the Ph.D. thesis of D.A. Cortes, Columbia University, (1981), which may be consulted for experimental details.
12. Support of this work by the National Science Foundation is gratefully acknowledged.

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