

Figure 1. The structure of the complex [(1-methylcytosine)silver(I)] nitrate. Two dimers in the columnar stack along the c axis are displayed. O(2') is related to O(2) by the transformation $-x, -y, -z$; O(2'') is related to O(2) by $-x, -y, -1 - z$.

chlorate in dilute nitric acid (pH 3). After about 3 days, clear colorless crystals of the complex were harvested. The complex is slightly photosensitive, turning to a light-gray color after several weeks. Crystal data are as follows: $a = 10.474$ (3) Å, $b = 11.141$ (3) Å, $c = 3.642$ (1) Å, $\alpha = 97.33$ (2)°, $\beta = 95.82$ (2)°, $\gamma = 76.76$ (2)°, $V = 409.2$ Å³, $Z = 2$, space group $P\bar{1}$. Intensity data for 1838 symmetry-averaged reflections were collected on a Syntex P-1 automated diffractometer, employing Mo radiation and the θ - 2θ scan technique. The structure was solved by Patterson methods and has been refined by the least-squares technique (anisotropic refinement of the nonhydrogen atoms and isotropic refinement of the hydrogen atoms) to a final R value of 0.033.

Some aspects of the structure of the [(1-methylcytosine)silver(I)] nitrate complex are illustrated in Figure 1. The most pronounced structural feature is the formation of centrosymmetric dimers in which the 1-methylcytosine ligands bridge two Ag ions, see Figure 1. Within these dimers, there are two strong metal-to-ligand bonds: Ag-N(3) = 2.225 (2) Å and Ag-O(2') = 2.367 (2) Å. The N(3)-Ag-O(2') bond angle at 136.2 (2)° is very nonlinear even in comparison to other dimeric systems involving Ag(I) (e.g., the Ag(I) complexes of glycine and the glycinate anion, ref 5, where the Ag-O distances are about 2.2 Å and the O-Ag-O angles are about 160°). The Ag...Ag distance across the crystallographic inversion center is 3.370 (1) Å, and can be compared to the value of 2.9 Å found in the glycine dimers.⁵

The dimers are formed into columnar stacks along the c axis, Figure 1, and connected by Ag-O(2'') bonds (Ag-O(2'') = 2.564 (3) Å). The Ag...Ag (or O(2')...O(2'')) repeat length in this polymeric bridging system is 3.642 Å, the length of the c axis. The O(2')-Ag-O(2'') bond angle is 95.1 (2)°. Within these columnar arrays, there is significant base-base overlap (mean distance = 3.34 Å). The coordination sphere about the silver is completed by a Ag-O(5)[nitrate] bond at 2.469 (3) Å. While the coordination sphere about the Ag(I) does not rigorously correspond to any common coordination polyhedra, it most closely approximates a trigonal pyramid.

The formation of the Ag-N(3) bond was anticipated, but the role that O(2) of the 1-methylcytosine base plays, both within the dimers and in the propagation of the columns along the c axis, suggests a wider scope than has previously been appreciated for this ligating atom. We have recently suggested that the binding of copper(II) to cytosine derivatives⁶ may well be enhanced by the formation of an intramolecular chelate system involving Cu-N(3) and Cu-O(2) bonds. Furthermore, in a study of an octahedral complex of Mn(II) and cytosine

5'-monophosphate,⁷ the Mn(II) forms a strong bond, 2.08 (3) Å, to O(2) of the 5'-CMP ring. It is interesting that Mn(II), which normally prefers hard donors, and Ag(I), which normally prefers soft donors, both form strong bonds to O(2) of a cytosine derivative. This previously unrecognized versatility in the binding of metal ions by the carbonyl group O(2)=C(2) of cytosine contrasts with the lack of evidence that the 6-oxo group of guanine derivatives plays anywhere near such a significant role in direct metal binding. The 6-oxo group can form a weak bond to a metal center in concert with a strong metal-N(7) bond.⁸

The binding mode observed in the dimeric units provides a partial model for the cross-linking of two strands of a DNA helix. The Ag...Ag repeat length (3.642 Å) in the polymeric, columnar stacks is reminiscent of the base-base stacking distance of about 3.5 Å in duplex DNA.⁹ These nearly commensurate spacings suggest that cooperative propagation of base-Ag-base polymers parallel to the helix axis could be induced. In light of the versatility of O(2) of cytosine, both of these features could be readily accommodated in regions of high G-C content.

Acknowledgments. Support of this research by the National Institutes of Health, Public Health Service Grant No. GM 20544, is gratefully acknowledged.

References and Notes

- (1) G. L. Eichhorn, "Inorganic Biochemistry", Vol. II, G. L. Eichhorn, Ed., Elsevier Press, Amsterdam, 1973, Chapters 33 and 34.
- (2) See the review chapters by L. G. Marzilli and by D. J. Hodgson, *Prog. Inorg. Chem.*, **23**, (1977).
- (3) S. K. Arya and J. T. Yang, *Biopolymers*, **14**, 1847 (1975).
- (4) N. Davidson, J. Widholm, U. S. Nandi, R. Jensen, B. M. Olivera, and J. C. Wang, *Proc. Natl. Acad. Sci. U.S.A.*, **53**, 111 (1965).
- (5) J. K. Mohana Roa and M. A. Viswamitra, *Acta Crystallogr., Sect. B*, **28**, 1484 (1972); C. B. Acland and H. C. Freeman, *Chem. Commun.*, 1016 (1971).
- (6) D. J. Szalda, L. G. Marzilli, and T. J. Kistenmacher, *Biochem. Biophys. Res. Commun.*, **63**, 601 (1975); T. J. Kistenmacher, D. J. Szalda, and L. G. Marzilli, *Acta Crystallogr., Sect. B*, **31**, 2416 (1975); D. J. Szalda, L. G. Marzilli, and T. J. Kistenmacher, *Inorg. Chem.*, **14**, 2076 (1975).
- (7) K. Aoki, *J. Chem. Soc., Chem. Commun.*, 748 (1976).
- (8) D. J. Szalda, T. J. Kistenmacher, and L. G. Marzilli, *J. Am. Chem. Soc.*, **98**, 8371 (1976).
- (9) S. Arnot and D. W. L. Hukins, *J. Mol. Biol.*, **81**, 93 (1973).

Luigi G. Marzilli,* Thomas J. Kistenmacher,* Miriam Rossi

Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Received December 6, 1976

A Novel Substituent Effect in the Intramolecular Cycloaddition Reactions of Nitrile Ylides¹

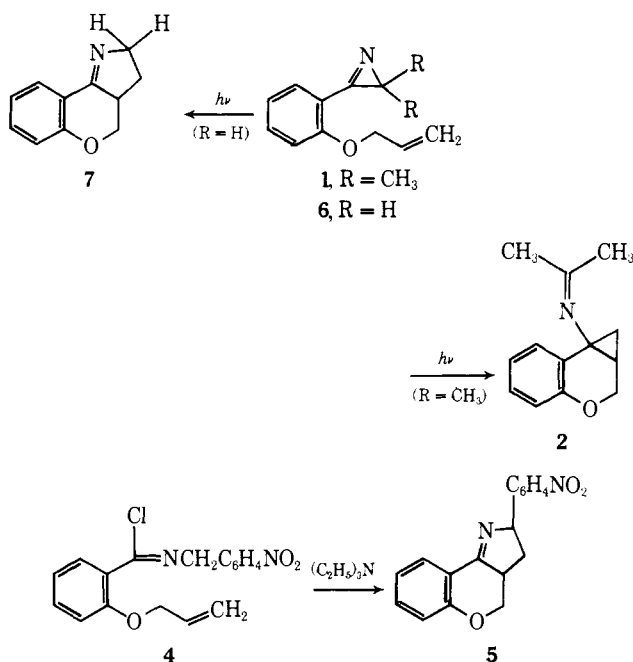
Sir:

Nitrile ylides are members of a class of 1,3-dipoles which contain a central nitrogen atom and a π -bond orthogonal to the 4π -allyl system.² 1,3-Dipolar cycloaddition of this dipole has been widely investigated^{3,4} and in many cases had led to the synthesis of a variety of interesting heterocyclic compounds,⁵ some of which would be tedious to synthesize by other routes. Recent ab initio LCAO-MO-SCF calculations by Houk and Caramella⁶ have suggested that the nonplanar bent nitrile ylide geometry is favored over the linear form. The system still resembles the normal three-orbital, four-electron system present in other 1,3-dipoles so that concerted 1,3-dipolar cycloadditions can still occur. The bent geometry of the ylide⁷ nicely rationalizes the intramolecular 1,1-cycloadditions observed with this 1,3-dipole.⁸ Houk's calculations also indicate that electron-releasing substituents on the 3-carbon of the ylide should increase the preference for the bent geometry while electron-withdrawing groups at C-3 should favor linearization of the dipole. We now wish to report evidence which corrob-

rates Houk's calculations and which also provides an example of a striking substituent effect on the course of the cycloaddition reaction.

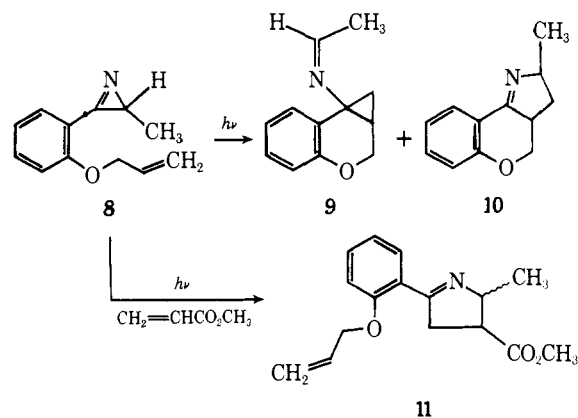
Irradiation of a solution of dimethyl-2*H*-azirine (**1**) ($R = \text{CH}_3$) in benzene with light of wavelength $>250 \text{ nm}$ gave a single photoproduct ($>95\%$) which showed all the properties expected for oxabenzobicyclo[4.1.0]heptane (**2**). This material was readily hydrolyzed to acetone and 1a,2-dihydrobenzo[*b*]cyclopropano[*d*]pyran-7b(1*H*)-amine (**3**) on thick layer chromatography. The NMR spectrum (100 MHz, CDCl_3) of structure **3** (Eu(Fod)₃ added) showed a triplet at τ 8.50 (1 H, $J = 5.0 \text{ Hz}$), a doublet of doublets at 8.30 (1 H, $J = 8.0$ and 5.0 Hz), a multiplet at 7.70 (1 H), doublets at 5.96 (1 H, $J = 10.0 \text{ Hz}$) and 5.65 (1 H, $J = 10.0 \text{ Hz}$), a broad singlet at 4.90 (2 H, exchanged with D_2O), and the aromatic protons at 2.1–3.1 (m, 4 H).

We had previously reported^{8c} that nitrile ylides generated by nonphotochemical techniques also undergo the intramolecular 1,1-cycloaddition reaction. Thus we were rather surprised to find that treatment of *o*-oxyallylimidoyl chloride **4** with triethylamine gave 1,3-dipolar cycloadduct **5**, mp 137–138 °C, as the exclusive product. The identity of **5** was determined by its straightforward spectral properties.⁹



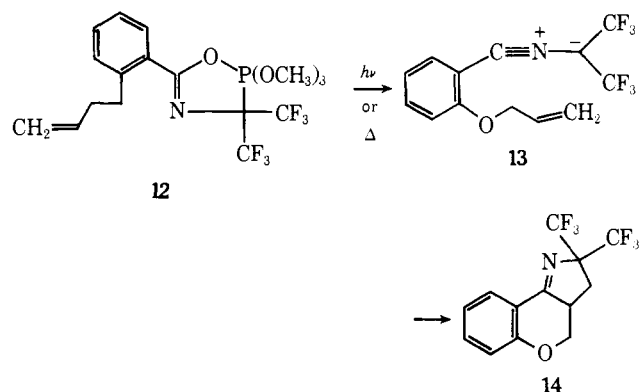
In order to determine whether this striking difference in the course of the intramolecular cycloaddition was related to the manner in which the nitrile ylide was generated, we examined the photochemistry of 2*H*-azirine **6** ($R = \text{H}$). In this case, the only photoproduct obtained was 1,3-cycloadduct **7**, mp 98–99 °C.¹⁰ This observation strongly suggests that the mode of cycloaddition of these *o*-oxyallylphenyl substituted 2*H*-azirines is markedly dependent on the nature of the substituent groups attached to the 3-carbon of the nitrile ylide. Further support for this contention was obtained from a study of the photobehavior of 2*H*-azirine **8**. Irradiation of **8** in benzene produced a 1:1 mixture of the 1,1- and 1,3-cycloadducts **9** and **10** in quantitative yield.

The identity of structure **9** rests on its spectroscopic properties and its facile hydrolysis to acetaldehyde and amine **3**. Structure **10** was assigned on the basis of its characteristic spectral properties.¹¹ Photolysis of **8** in the presence of excess methyl acrylate afforded cycloadduct **11** in high yield. Under these conditions, the formation of both **9** and **10**, which are produced in quantitative yield in the absence of a trapping agent, are completely suppressed. More importantly, when the



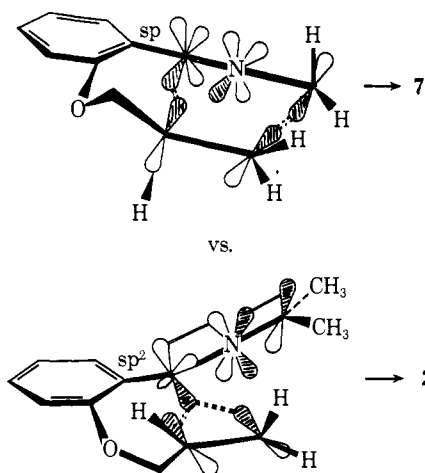
irradiation of **8** was carried out in the presence of limited quantities of methyl acrylate, the ratio of cycloadducts **9/10** did not change. It should also be noted that the ratio of cycloadducts did not vary with changes in temperature or the wavelength of incident light used. These results clearly establish that both the 1,1- and 1,3-cycloaddition reactions of **8** stem from a common intermediate.

In an effort to gain further mechanistic insight into the nature of this novel substituent effect, we studied the photochemistry of oxaphosphole **12**. This material was prepared by a modification of the procedure developed by Burger and co-workers.¹² Thermolysis or photolysis of 4,5-dihydro-1,3,5λ⁵-oxazaphospholes is known to produce bis(trifluoromethyl)benzimidazole ylides in excellent yield.¹³ In this case, the only product obtained from the photolysis or thermolysis of **12** was 1,3-cycloadduct **14**, mp 140–141 °C.¹⁴ The isolation of **14** clearly demonstrates that the substituent effect encountered in these nitrile ylide cycloadditions is electronic rather than steric in nature.¹⁵



The concerted 1,3-dipolar cycloaddition of nitrile ylides proceeds via a "two-plane" orientation approach in which the dipole and dipolarophile approach each other in parallel planes. In the intramolecular 1,1-cycloaddition, however, attack by the alkene is constrained to occur perpendicular to the CNC plane of the bent nitrile ylide. The second LUMO of this dipole, which is perpendicular to the CNC plane, is low-lying and presents a large vacancy at C-1 for attack by the more nucleophilic terminus of the alkene, without the possibility of simultaneous bonding at the C-3 carbon atom. Inspection of molecular models of these *o*-oxyallylphenyl substituted nitrile ylides shows that both approaches are possible depending on the geometry of the nitrile ylide. The energy difference between the nonplanar bent and linear forms is small and the preferred mode of approach depends on the substituent groups present on the nitrile ylide. According to Houk's calculations,⁶ methyl or other electron releasing substituents on the 3-carbon of the ylide will increase the preference for the bent geometry. In other words, the nitrile ylide species becomes more carbene-like

as methyl groups are added and is more prone to undergo the 1,1-cycloaddition reaction. This is exactly what is observed. Placing electron withdrawing groups at C-3 (i.e., CF_3 , H, etc.) will favor linearization of the nitrile ylide. As the dipole becomes less bent, the C_1N bond shortens and the NC_3 lengthens and the system prefers to undergo 1,3-dipolar cycloaddition. More recent calculations by Houk and Gandour¹⁷ show that



introduction of a phenyl or vinyl group at C_1 flattens the dipole considerably so that it is much more sensitive to C-3 substitution than the unsubstituted case. Thus, when the energy difference between the nonplanar bent and linear forms is small, substituent effects can play an extremely important role in determining the course of the intramolecular cycloaddition reactions of nitrile ylides.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation and the National Institutes of Health. We should also like to express our appreciation to Professor K. N. Houk for informing us of his substituted nitrile ylide computational results and for some helpful discussions.

References and Notes

- (1) Photochemical Transformations of Small Ring Heterocyclic Compounds. 87. For part 86, see A. Padwa, T. J. Blacklock, D. Getman, and N. Hatanaka, *J. Am. Chem. Soc.*, **99**, 2344 (1977).
- (2) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).
- (3) A. Padwa and J. Smolanoff, *J. Am. Chem. Soc.*, **93**, 548 (1971); A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *ibid.*, **94**, 1395 (1972); **95**, 1945, 1954 (1973).
- (4) N. Gatis, M. Marky, J. H. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 748 (1972); H. Giezendanner, M. Marky, B. Jackson, H. J. Hansen, and H. Schmid, *ibid.*, **55**, 745, 919 (1972).
- (5) See A. Padwa, *Acc. Chem. Res.*, **9**, 371 (1976), for some leading references.
- (6) P. Caramella and K. Houk, *J. Am. Chem. Soc.*, **98**, 6397 (1976); P. Caramella, R. W. Gandour, J. A. Hall, C. G. Deville, and K. N. Houk, *J. Am. Chem. Soc.*, **99**, 385 (1977).
- (7) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963), previously postulated that the bent form of a nitrile ylide would be less stable than the planar form, because allyl resonance would be more important for the planar geometry.
- (8) A. Padwa and P. H. J. Carlsen, *J. Am. Chem. Soc.*, **97**, 3862 (1975); **98**, 2006 (1976); A. Padwa, A. Ku, A. Mazzu, and S. I. Wetmore, Jr., *ibid.*, **98**, 1048 (1976).
- (9) Compound 5: IR (neat) 6.05 μ ; UV (methanol) 260 nm (ϵ 35 200); NMR (100 MHz, CDCl_3) τ 8.60 (ddd, 1 H, $J = 12.0, 10.0,$ and 10.0 Hz), 7.20 (ddd, 1 H, $J = 12.0, 6.0,$ and 6.0 Hz), 6.60 (m, 1 H), 6.08 (dd, 1 H, $J = 12.0$ and 10.5 Hz), 5.28 (dd, 1 H, $J = 10.5$ and 6.0 Hz), 4.80 (ddd, 1 H, $J = 10.0, 6.0,$ and 2.0 Hz), 1.68–3.02 (m, 8 H).
- (10) Compound 7: IR (neat) 6.05 μ ; m/e 173 (M^+), 145, 119, 91, and 77; NMR (100 MHz, CDCl_3) τ 8.48 (dddd, 1 H, $J = 12.0, 10.0, 10.0,$ and 9.0 Hz), 7.78 (ddd, 1 H, $J = 12.0, 8.0,$ and 7.0 Hz), 6.80 (m, 1 H), 6.24 (dddd, 1 H, $J = 16.0, 10.0, 8.0,$ and 2.0 Hz), 6.19 (dd, 1 H, $J = 13.0$ and 10.0 Hz), 5.80 (ddd, 1 H, $J = 16.0, 9.0,$ and 2.0 Hz), 5.38 (dd, 1 H, $J = 10.0$ and 6.0 Hz), 2.08–3.16 (m, 4 H).
- (11) Compound 10, mp 60–61 °C; NMR (100 MHz, CDCl_3) τ 8.62 (d, 3 H, $J = 7.0$ Hz), 8.30 (m, 1 H), 7.76 (pent., 1 H, 6.0 Hz), 6.80 (m, 1 H), 6.26 (dd, 1 H, $J = 12.0$ and 10.0 Hz), 6.0 (1 H, m), 5.40 (dd, 1 H, $J = 10.0$ and 6.0 Hz), and 2.1–3.3 (m, 4 H).

- (12) K. Burger, W. Steglich, M. Durr, and E. Burgig, *Chem. Ber.*, **107**, 1488 (1974).
- (13) K. Burger and J. Fehn, *Chem. Ber.*, **105**, 3814 (1972).
- (14) Compound 14; NMR (100 MHz, CDCl_3) τ 8.12 (dd, 1 H, $J = 14.0$ and 9.0 Hz), 7.36 (dd, 1 H, $J = 14.0$ and 8.0 Hz), 6.52 (dddd, 1 H, $J = 12.5, 9.0, 8.0,$ and 5.5 Hz), 6.08 (dd, 1 H, $J = 12.5$ and 9.5 Hz), 5.37 (dd, 1 H, $J = 9.5$ and 5.5 Hz), 2.6–3.28 (m, 3 H), and 2.0–2.20 (m, 1 H).
- (15) A steric effect would have been expected to result in the formation of a 1,1-cycloadduct since the trifluoromethyl group is larger than a methyl group.¹⁶
- (16) E. W. Della, *Tetrahedron Lett.*, 3347 (1966).
- (17) Private communication, K. Houk and R. Gandour.

Albert Padwa,* Per H. J. Carlsen, Audrey Ku

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Received December 6, 1976

Carbanions. 19. Reactions of Cesium or Cesium–Potassium–Sodium Alloy with Benzene and Toluene

Sir:

1,1,1-Triphenylethane has been recently reported¹ to react with Cs–K–Na alloy of eutectic composition² at -70 °C in tetrahydrofuran (THF) to give an insoluble red organoalkali compound (2) which upon protonation gives 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene (3). The reaction may be explained by Scheme I. The alloy has been now analyzed³ before and after reaction⁴ at -50 °C; the change in composition of the alloy and the number of hydrogen atoms added to the starting 1,1,1-triphenylethane are in agreement with 2 being formulated as a dicesium compound. This reaction of 1,1,1-triphenylethane caused us to wonder if benzene would give a similar reaction.

Hackspill⁵ in 1912 reported that benzene reacts with cesium at 28 °C to give a black solid containing cesium in an amount near that expected for phenylcesium. He accordingly suggested that the substance was phenylcesium although it was said to be formed without evolution of hydrogen and gave biphenyl and hydrogen⁶ upon hydrolysis. Hackspill⁶ later questioned his assigned structure and noted that the product merited further study. Subsequently de Postis⁷ came to the conclusion that the black compound had the empirical formula of $\text{C}_6\text{H}_6\text{Cs}_6$ and was a loose addition compound of benzene with cesium since it was attacked by water with evolution of hydrogen, did not react with gaseous CO_2 , and failed to give "normal" alkylation products with alkyl halides. Clusius and Mollet⁸ found that cesium reacts with benzene at 50–60 °C with steady evolution of hydrogen and that the black product reacts with water to give biphenyl and phenol.

We wish to report that reaction of excess benzene with finely divided cesium in THF at -70 °C gives a black precipitate which has a broad-line ESR spectrum indicative of a high yield of a radical anion in a doublet state. Quenching of the fine

Scheme I

