of pyridine and the picolines in organc solvents.[12] At I_2 concentrations greater than about 10^{-3} M, there is evidence for the formation of a complex of CHA with two iodine molecules.

Infrared spectra of solutions of CHA and I_2 indicate that the N–H stretching frequencies of the amino group in free CHA (at 3425 and 3540 cm^{-1}) decrease to 3410 and 3525 cm^{-1} in the complex; addition of Br_2 to CHA in CCl_4 produces shifts to 3413 and 3529 cm^{-1}. Frequency shifts of these magnitudes are compatible with the assumed formation of a moderately strong CT bond at N(1), adjacent to the C–NH_2 group of CHA.

The present report clearly indicates the ability of adenine to act as an n donor in forming relatively strong molecular complexes with the halogens. Because of the close relation which exists between the charge density or ionization potential of n donors and the stability, bonding, and structure of their CT complexes, results of the type presented here should find application in investigations of biological systems involving the purines and pyrimidines.

Acknowledgment. This research was supported in part by National Science Foundation Grants GP-23278 and GP-33519X.

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[12] Reference 2, pp 276–278; P. V. Huong, N. Platzer, and M. L. Josien, *J. Amer. Chem. Soc.*, **91**, 3669 (1969); W. J. McKinney and A. I. Popov, *ibid.*, **91**, 5215 (1969).

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Multiple Condensations with Methyl β-Vinylacrylate

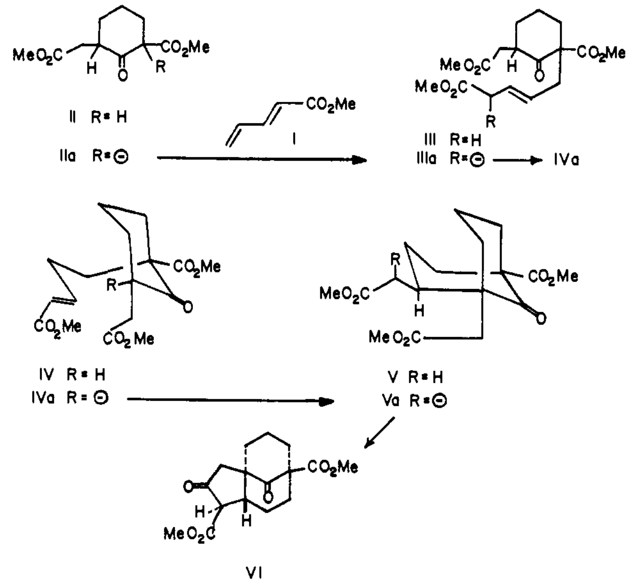
Sir:

Activated butadienes such as I are attacked by nucleophiles in a terminal (1,6-) sense.[1] The multifunctional adducts, so produced, can service subsequent intramolecular processes. Below, we report a *one step* assemblage of the 3a,7-methano-3a*H*-cyclopentacyclooctene system by the condensation of I with II.[2] This process underscores the potentialities of I as a multiple annelating agent.

To a solution of 4.8 g (21.5 mmol) of ketodiester II in 150 ml of DMSO was added 7 ml (2.0 mmol) of a stock solution of dimsylsodium.[3] After 15 min 2.5 g (23 mmol) of I was added. An additional 2.0 mmol of base was added after 8 hr and four additional 2.0 mmol increments introduced at 24 hr intervals.[4] At the end of this period,[5] a final 14 mmol increment of base was added (total base = 26 mmol) and stirring continued for an additional 8 hr (total time = 112 hr). Work-up afforded 2.4 g of VI,[6] mp 145–146° (41% yield), and 0.5 g (11%) of recovered II. The entire operation was conducted at room temperature.

In separate experiments, the products of intermediate levels of condensation were obtained in pure form. Thus, using DMSO as solvent and a 0.2:1:1 ratio of dimsylsodium:I:II for 1.5 hr at room temperature gave an 82% yield of III.[6] When a 1.4:1:1 ratio of the same reagents was employed for 7 hr at 50°, a 12%[4] yield of bicyclic product V[6] was obtained together with 8% of VI. With pure III and V in hand, the course of the multiple condensation of I + II + B^- → VI was monitored.

Scheme I



The intermediacy of anions IIIa and Va was clearly demonstrated by the formation of III and V, respectively, on quenching after shorter reaction times.[4,5] The intermediacy of IVa would appear to be mechanistically reasonable, though its protonated form, IV, was never detected.

The gross structure and stereochemistry of VI were defined by X-ray diffraction analysis. The compound crystallizes in space group $P2_1/c$ with four molecules per unit cell of the following dimensions: a = 10.907 (13), b = 9.520 (7), c = 15.638 (13) Å; β = 111° 49 (6)′. Intensity data for 2491 independent reflections were measured on a Picker FACS I diffractometer using Cu Kα radiation. Each reflection was scanned 2° in the θ–2θ mode. Lorentz and polarization corrections were made and the data reduced to normalized structure factors (E). The signs of the 450 largest E values were obtained using the computer program, MULTAN.[7] A fourier synthesis with the phased E values as coefficients revealed the 22 nonhydrogen atoms. Hydrogen positions were found in a difference map. The struc-

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[1] (a) E. P. Kohler and F. R. Butler, *J. Amer. Chem. Soc.*, **48**, 1036 (1926); (b) J. W. Ralls, *Chem. Rev.*, **59**, 329 (1959); (c) G. A. Berchtold, J. Ciabattoni, and A. A. Tunick, *J. Org. Chem.*, **30**, 3679 (1965); (d) S. Danishefsky and R. Cunningham, *ibid.*, **30**, 3676 (1965); (e) S. Danishefsky and R. Cavanaugh, *ibid.*, **33**, 2959 (1968); (f) S. Danishefsky, G. Koppel, and R. Levine, *Tetrahedron Lett.* 2257 (1968); (g) S. Danishefsky, J. Eggler, and G. Koppel, *ibid.*, 4333 (1969); (h) E. J. Corey, C. U. Kim, R. H. K. Chien, and M. Taked, *J. Amer. Chem. Soc.*, **94**, 4395 (1972); (i) F. Näf, P. Degen, and G. Ohloff, *Helv. Chim. Acta*, **55**, 82 (1972).

[2] See F. Ramirez and J. W. Sargent, *J. Amer. Chem. Soc.*, 77, 6297 (1955), for diethyl ester.

[3] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

[4] Due to sensitivity of compound I toward base and due to the tendency of III (*via* IIIa) to undergo reversion to I and II with destruction of the former, it is necessary to maintain a low base concentration until III has been transformed to V. At this time,[5] the stoichiometric complement of base, required for the Dieckmann step, may be safely introduced.

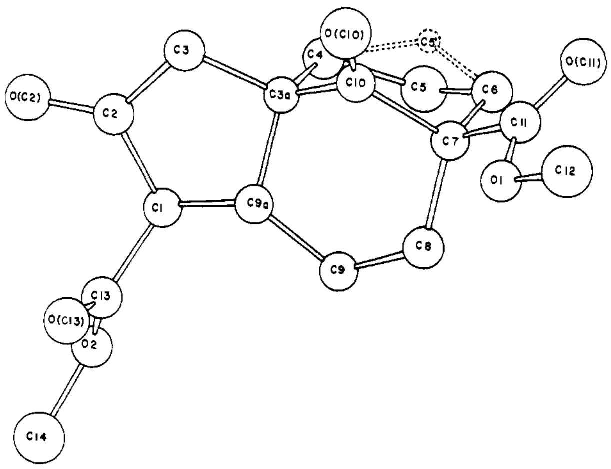
[5] At this stage, work-up of an aliquot shows the predominance of V with small amounts of VI and II present. Compound III is no longer observed.

[6] C and H combustion analysis within 0.3% of theory, as well as infrared, nmr, and mass spectra consistent with the proposed structure, were obtained for this compound.

[7] P. Main, *Acta Crystallogr., Sect. A*, 27, 368 (1971).

ture has thus far been refined to a reliability index,[8] R, of 0.050 for the 2491 reflections. The crucial configurational relationships to be noted are the trans fusion of the perhydroindane system and the trans relationship of the carbomethoxyl at C, and the C_4-methylene group attached to C_{3a}.

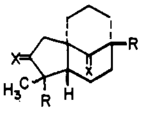
The X-ray study also revealed an interesting conformational feature which is reflected in a disordering of the position of C_5. The high occupancy site (~80%) corresponds to the chair–chair form with a C_5–C_9 separation of 3.11 Å. The low occupancy site (~20%) corresponds to a chair–boat arrangement with a C_5–C_9 separation of 3.66 Å. The chair–chair is the only one observed in previous crystallographic studies of derivatives of the bicyclo[3.3.1]nonane system.[9] These data are summarized in the structure of VI where the broken lines correspond to the low occupancy conformer.

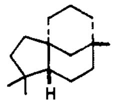


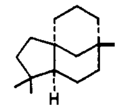
VI

The definition of the stereochemistry of VI allows for the indicated assignment to its precursor Va and, hence to the bicyclic product, V. The transformation of IVa to Va is decisive in defining the stereochemistry at C_{9a} in the subsequent products. The extended prechair conformation postulated for IVa is well disposed to give rise to the equatorially oriented enolate in Va which is probably also thermodynamically preferred.[10]

Before the crystal structure of VI was in hand, it was converted to what can now be formulated as *dl*-epiclovane (XI). Methylation (1-TlOEt; 2-CH_3I)[11] gave the crystalline (mp 103–110°) but epimeric mixture, VII.[6] Double thioketalization gave epimers VIII, mp 145–150,[12] which upon desulfurization (Raney Nickel) provided the epimeric diesters, IX.[12] The latter were transformed ((i) $LiAlH_4$–ether, (ii) Collins oxidation,[13] (iii) ethanedithiol-BF_3) into the bis(thioketal) epimers, X.[12] Desulfurization (Raney nickel) of X gave a single hydrocarbon, XI,[12] whose infrared, nmr (τ (CCl_4) 250 MHz, 9.03 (6 H, s), 9.15 (3 H s)) and mass spectra all differed in detail from those of authenic clovane XII (τ (CCl_4) 250 MHz, 9.02 (3 H, S), 9.13 (3 H, s), 9.15 (3 H, s)) whose cis fusion is well established.[14]







VII X=O, R=CO_2Me

VIII X= $S(CH_2)_2S$; R=CO_2Me

IX X=H_2, R=CO_2Me

X X=H_2, R=$CHS_2(CH_2)_2$

XI Epiclovane

XII Clovane

Further chemical and crystallographic studies of this new ring system are in progress.

Acknowledgments. This research was supported by Public Health Service Grants CA-12107-08, N.S.-09178, and RR-00292-07.

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[8] $R = \Sigma F_o - KF_c/\Sigma F_o$ where F_o and F_c are observed and calculated structure factors, respectively, and K is the overall scale factor.

[9] *Cf.* (a) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); (b) N. C. Webb and M. R. Becker, *ibid.*, 1317 (1967).

(10) For an analysis of conformations of bicyclo[3.3.1]nonanes, see J. M. McEuen, R. B. Nelson, and R. G. Lawton, *J. Org. Chem.*, **35**, 690 (1970).

(11) *Cf.* E. C. Taylor, G. H. Hawkes, and A. McKillop, *J. Amer. Chem. Soc.*, **90**, 2421 (1968). The use of conventional alkylating bases led to extensive amounts of *O*-methylated product,[6] mp 132–135°. Under the Taylor conditions this was reduced to 8% yield.

(12) The structure of this product is consistant with its infrared, nmr, and mass spectra.

(13) J. C. Collins, W. W. Hess, and F. S. Frank, *Tetrahedron Lett.*, 3363 (1968).

(14) *Cf.*, *inter alia*, A. Abei, D. H. R. Barton, A. W. Burgstahler, and A. S. Lindsay, *J. Chem. Soc.*, 4659 (1954); D. Becker and H. J. E. Lowenthal, *ibid.*, 1338 (1965); P. Doyle, I. R. McLean, R. D. H. Murray, W. Parker, and R. Raphael, *ibid.*, 2749 (1965).

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Book Reviews

Catalysis in Chemistry. By A. J. B. ROBERTSON (University of London). Methuen Educational Ltd., London. 1972. v + 56 pp. $2.75.

This book is one of about a dozen introductory surveys of science topics in the Methuen Studies in Science series. Ably written by Professor Robertson, it is composed of five chapters: (1) Historical Introduction, (2) The Adsorption of Gases by Solids, (3) The Rate of Heterogeneous Catalytic Reactions and the Adsorption Theory, (4) Catalysis and Solid State Chemistry, and (5) The Probable Importance of Active Catalytic Centres at the Catalytic Surface. The discussion emphasizes heterogeneous catalysis in general and the gas–solid interface, in particular. An historical approach has been used in developing the topics, and the text has been occasionally enlivened with brief accounts of controversies which occurred during the formulation of some of the basic concepts such as the nature of physical adsorption.

The material in this, as well as the other science topics in the series, is at the college preparatory or entering college level. The mathematical treatments do not go beyond simple algebra and are not extensive. The subject is covered in much more detail than is