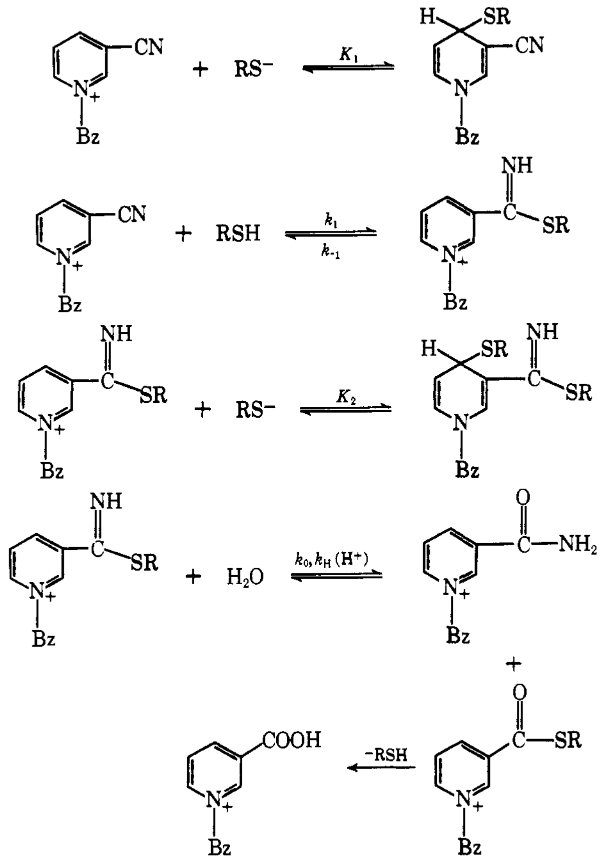
We believe that the data pertinent to this catalytic process are best understood in terms of the sequence of processes outlined in Scheme I. In terms of this scheme

Scheme I



the saturation kinetics can be understood on the basis of the addition of the anion of mercaptoethanol to the substrate to form a 1,4 adduct, which may be detected directly spectrophotometrically and which is unreactive toward attack of the nucleophilic reagent on the nitrile function. Furthermore, the inhibition of the reaction under basic conditions by excess mercaptoethanol may be understood in terms of the addition of this nucleophilic reagent to the thioimidate intermediate yielding a second nonproductive complex. The pH-rate maximum is interpreted as reflecting rate-determining formation of the thioimidate intermediate under acidic conditions and rate-determining hydrolysis of this intermediate, through both pH-independent and acid-catalyzed reaction pathways, under basic conditions. Relative amounts of amide and acid as product depend on the mode of partitioning of the tetrahedral intermediate formed from addition of water to the thioimidate intermediate. The observations that amide is the predominant product under neutral conditions but that acid is formed in increasing amounts as the reaction medium becomes more acidic are entirely consistent with the results of Schmir and his coworkers who have specifically investigated the mode of decomposition of such tetrahedral intermediates.[4]

That the suggested reaction scheme is in fact correct is supported by studies of the course of this reaction in water employing infrared spectroscopy. On the alkaline side of the pH-rate maximum, in which decomposition of the thioimidate is thought to be rate determining, one observes the immediate appearance of a new band at 1662 cm^{-1} which then continues to increase in intensity with time. Presumably this band reflects absorption due both to the thioimidate intermediate and to the amide product. In addition, one observes the immediate appearance of a new band at 1578 cm^{-1} whose intensity decreases with time. Presumably this band is due to the thioimidate intermediate only. In contrast, on the acid side of the pH-rate maximum one observes only the gradual development of a band near 1667 cm^{-1} which presumably reflects the appearance of amide. Clearly, these observations provide support for the transition in rate-determining step outlined above. Finally, the indicated reaction scheme is consistent with the transient appearance of a material, presumably the thiol ester, which is reactive toward neutral hydroxylamine.

There exists a number of parallels between the mercaptoethanol-mediated nitrile hydrolysis and the enzyme-mediated nitrile hydrolysis. In the first place, mercaptoethanol is an effective catalyst and increases the rate of nitrile hydrolysis at pH 7 from 10,000- to 100,000-fold.[5] In the second place, both reactions exhibit pH-rate maxima, and these occur at similar values of pH. Finally, both reactions depend on thiol groups. The results of this study support previous suggestions of participation of the thiol groups of nitrilases as nucleophilic reagents toward the nitrile function and suggest, furthermore, that thioimidate intermediates bound covalently to the enzymes exist. Furthermore, if the pH-rate maximum for the enzymatic processes derives from the same considerations as that observed in this case, it suggests that decomposition of this intermediate ought to be the rate-determining step on the basic side of the pH maximum and, therefore, that this intermediate ought to be isolable and capable of characterization by the usual methods.

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(4) R. K. Chaturvedi, A. E. MacMahon, and G. L. Schmir, *J. Am. Chem. Soc.*, **89**, 6984 (1967).

(5) C. Zervos and E. H. Cordes, unpublished observations.

(6) Career Development Awardee of the National Institutes of Health, Grant K3 GM 10-248-02. Research Fellow of the Alfred P. Sloan Foundation.

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trans-Bicyclo[5.1.0]octanes[1]

Sir:

The last 5 years have witnessed a dramatic insurgence of interest in the chemistry of strained-ring compounds. Bicyclo[1.1.0]butane, bicyclo[2.1.0]pentane, bicyclo-[1.1.0]pentane, and numerous tri- and tetracyclic small-ring compounds have been prepared and studied. Of special interest in relation to these compounds has been the nature of the strained carbon–carbon σ bonds, not only in connection with their remarkable chemical activity but also from a theoretical point of view.[2] We

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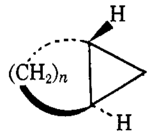
(1) The Chemistry of "Bent" σ Bonds. IX. For the previous paper in this series see P. G. Gassman and G. D. Richmond, *J. Am. Chem. Soc.*, **90**, 5637 (1968).

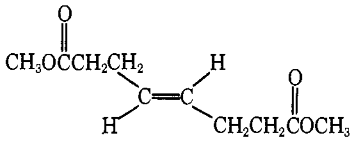
(2) W. Weltner, Jr., *ibid.*, **75**, 4224 (1953); M. Randić and Z. Maksić, *Theor. Chim. Acta*, **3**, 59 (1965); Z. Maksić, L. Klasinc, and M. Randić,

recently indicated[3] that significant carbon–carbon bond strain should exist in systems other than those in which small rings are fused together in a *cis* manner. In particular we noted that *trans*-fused cyclopropanes of the general formula **1** should contain strained carbon–carbon σ bonds which are "bent" in a unique "twisted" manner when *n* is small.[3] We wish to report at this time the synthesis of derivatives of *trans*-bicyclo[5.1.0]octane, the smallest member of this class of compounds to be prepared thus far.[4,5]



1

Starting with 1,4-dibromo-*trans*-2-butene we prepared *trans*-4-octene-1,8-dioic acid (**2**) according to literature procedures.[7] Esterification with diazomethane or with methanol under acid-catalyzed conditions converted **2** into the dimethyl ester **3** in high yield. Reaction of **3** with Simmons–Smith reagent[8] gave the *trans*-disubstituted cyclopropane, **4**, in 70% yield. *Anal.* Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.74; H, 8.44. Acyloin condensation of **4** utilizing sodium in xylene gave the bicyclic acyloin **5**. Direct cupric acetate oxidation of **5**, which existed in diastereomeric forms, gave the dione **6** in 38% over-all yield from **4**. *Anal.* Calcd for $C_9H_{12}O$: C, 71.02; H, 7.95. Found: C, 70.90; H, 7.98. Reaction of **6** with tosylhydrazine gave the monotosylhydrazone **7**, mp 179–180°. *Anal.* Calcd for $C_{16}H_{20}O_3N_2S$: C, 59.97; H, 6.29; N, 8.75. Found: C, 59.77; H, 6.26; N, 8.85. Treatment of **7** with aqueous sodium hydroxide at low temperature gave the desired 5-diazo-*trans*-bicyclo[6.1.0]nonan-4-one (**8**) which, without purification, was dissolved in a dioxane–water solution and irradiated using a bank of eight 15-W Sylvania "Blacklite" fluorescent tubes. Photolysis gave the immediate nitrogen evolution anticipated for the photochemical ring contraction of α-diazo ketones. This reaction gave a 22% yield of *trans*-bicyclo[5.1.0]octane-4-carboxylic acid (**9**), based on the monotosylhydrazone **7**. The white crystalline acid, mp 85–87° (*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.90; H, 9.11), showed an absorption in the near-infrared at 1.643 μ (ϵ 0.408) indicative of a disubstituted cyclopropane.[9] In addition, the nmr spectrum of **9** showed a two-hydrogen multiplet at τ 9.93 characteristic of cyclopropyl hydrogens.[10]



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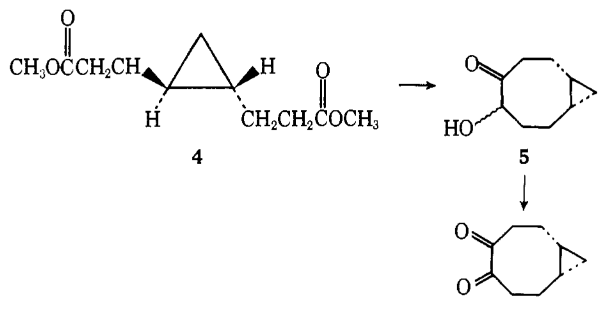

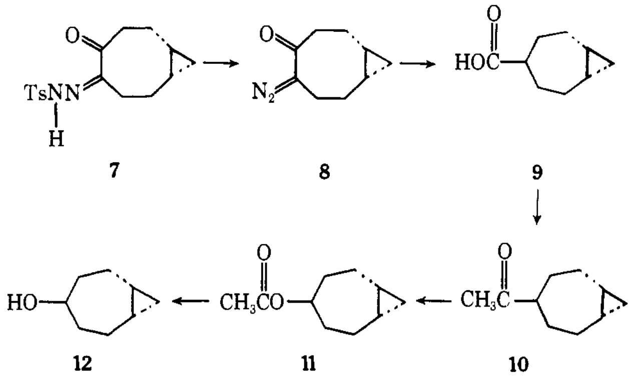

Although both the chemical and spectroscopic data were consistent with the indicated *trans*-fused ring junction in **9**, it was deemed worthwhile to ensure that *trans* to *cis* isomerization of the cyclopropyl substituents had not occurred during the photochemical ring contraction[11] or inadvertently during one of the steps leading to the α-diazo ketone **8**. In order to establish the absence of such isomerization we converted **9** into the methyl ketone **10** in 76% yield using methyllithium (2,4-dinitrophenylhydrazone of **10**, mp 120–121°. *Anal.* Calcd for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.67; H, 5.83; N, 16.68).

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ibid., **4**, 273 (1966); M. Randić, J. M. Jerkunica, and D. Stefanović, *Croat. Chem. Acta*, **38**, 49 (1966); M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3970 (1966); W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967); N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, **89**, 3966 (1967); K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(3) P. G. Gassman, *Chem. Commun.*, 793 (1967).

(4) Only four examples of the next higher member of the series, *trans*-bicyclo[6.1.0]nonane, have been previously prepared. These are the parent hydrocarbon in both optically inactive and optically active forms [A. C. Cope and J. K. Hecht, *J. Am. Chem. Soc.*, **85**, 1780 (1963); E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968)], *trans*-bicyclo[6.1.0]nona-2,4,6-triene [G. Moshuk, G. Petrowski, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 2179 (1968)], and *trans*-bicyclo[6.1.0]nonan-2-one [C. H. DePuy and J. L. Marshall, *J. Org. Chem.*, **33**, 3326 (1968)].

(5) Various *trans*-fused bicyclo[4.2.0]octanes and bicyclo[3.2.0]heptanes have been prepared.[6] Due to the conformational flexibility of the cyclobutane ring, these systems would be expected to be considerably less strained than the corresponding *trans*-fused bicyclo[5.1.0]octanes and bicyclo[4.1.0]heptanes.

(6) M. P. Cava and E. Moroz, *J. Am. Chem. Soc.*, **84**, 115 (1962); J. Meinwald, G. C. Curtis, and P. G. Gassman, *ibid.*, **84**, 116 (1962); J. L. Mateos, O. Chao, and H. Flores R., *Tetrahedron*, **19**, 1051 (1963); G. Muller, Ch. Huynh, and J. Mathieu, *Bull. Soc. Chim. France*, 296 (1962); A. Hassner, A. W. Coulter, and W. S. Seese, *Tetrahedron Lett.*, 759 (1962); P. de Mayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963); E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **85**, 362 (1963); N. L. Allinger, M. Nakazaki, and V. Zalkow, *ibid.*, **81**, 4074 (1959); E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964); O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, **90**, 1657 (1968); J. Meinwald, J. J. Tufariello, and J. J. Hurst, *J. Org. Chem.*, **29**, 2914 (1964); J. Meinwald, P. Anderson, and J. J. Tufariello, *J. Am. Chem. Soc.*, **88**, 1301 (1966).

(7) K. Sisido, K. Sei, and H. Nozaki, *J. Org. Chem.*, **27**, 2681 (1962).

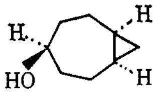
(8) For a leading reference to the method used see E. LeGoff, *ibid.*, **29**, 2048 (1964).

(9) For a detailed discussion of the near-infrared spectra of cyclopropanes and of the effect of substituents on the position and intensity of the absorption see P. G. Gassman and F. V. Zalar, *ibid.*, **31**, 166 (1966).

(10) For a recent discussion of cyclopropyl hydrogen absorptions of *cis*-fused bicyclo[*n*.1.0]alkanes see J. G. Traynham, J. S. Dehn, and E. E. Green, *ibid.*, **33**, 2587 (1968).

(11) The *cis* to *trans* photochemical isomerization of 1,2-diphenylcyclopropane has been reported [G. S. Hammond and R. S. Cole, *J. Am. Chem. Soc.*, **87**, 3256 (1965)]. However, **9** does not have substituents which would be conducive to such photochemical isomerization.

Baeyer–Villiger oxidation of **10** utilizing trifluoroperacetic acid gave the acetate **11** which reacted with methyllithium to give 4-hydroxy-*trans*-bicyclo[5.1.0]-octane (**12**) in 64% yield based on **10**. *Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.53; H, 11.32. The continued presence of the cyclopropyl moiety was demonstrated by near-infrared (1.643 μ (ϵ 0.276)) and nmr spectroscopy (two-proton multiplet at τ 9.88). A comparison of **12** with **13** and **14** showed that these compounds had different ir and nmr spectra and different vpc retention times, indicating that these compounds were distinct entities. However, the mass spectra of **12**, **13**, and **14** were virtually identical, thus demonstrating the structural similarity between these three isomers. The nonidentity of **12** with both **13** and **14** required that the cyclopropyl ring of **12** be *trans* fused,[12] and completed the structure proof.



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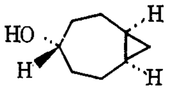

14

The availability of this new class of strained *trans*-fused bicyclo[*n*.1.0]alkanes will permit a wide variety of theoretically interesting studies. We are currently investigating those aspects of *trans*-bicyclo[5.1.0]octane chemistry related to the unique nature of the strain incorporated into this molecule.

Acknowledgment. This research was supported by Grant GP7063 from the National Science Foundation.

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[12] Compounds **13** and **14** were prepared by a modification of the published procedure: A. C. Cope, S. Moon, and C. H. Park, *J. Am. Chem. Soc.*, **84**, 4843 (1962).

[13] Alfred P. Sloan Research Fellow, 1967–1969.

[14] On leave from the Israel Ministry of Defense Scientific Department.

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Received September 3, 1968

Additions and Corrections

Linkage Isomerism in Phenylmercuric Benzenesulfinate [*J. Am. Chem. Soc.*, **90**, 493 (1968)]. By G. B. Deacon and P. W. Felder, Chemistry Department, Monash University, Clayton, Victoria, Australia.

The values for the sulfur–oxygen stretching frequencies of isomer A of phenylmercuric benzenesulfinate (the O-sulfinate) in chloroform (p 494) are incorrect. It has now been found that isomer A in chloroform reacts with sodium chloride plates, and the reported sulfur–oxygen stretching frequencies correspond closely to those of sodium benzenesulfinate. When silver chloride plates are used, the values for the chloroform solution (1053 and 850 cm^{-1}) are close to those (p 494) for solid isomer A (Nujol mull). This observation invalidates the conclusion (p 494) that isomer A is polymeric or dimeric (structure IV) in the solid state. It now appears probable that this isomer is a monomeric O-sulfinate complex (structure II or III) in the solid state, as in chloroform. It follows that the other $RHg(SO_2R')$ derivatives (Table I, p 495) with sulfur–oxygen stretching frequencies similar to those of isomer A are likely to have a similar structure.

The Dimerization of Styrene [*J. Am. Chem. Soc.*, **90**, 1289 (1968)]. By Frank R. Mayo, Stanford Research Institute, Menlo Park, California 94025.

Reference 2 was inadvertently omitted. It should read: (2) F. R. Mayo, *J. Am. Chem. Soc.*, **75**, 6133 (1953).

A Revised Structure for Ceanothine-B [*J. Am. Chem. Soc.*, **90**, 4179 (1968)]. By Robert E. Servis and Alvin I. Kosak, Department of Chemistry, New York University, New York, New York 10003.

The second to last sentence should read: We have found that ceanothamine-A[4] is identical with frangulanine[8] (obtained from *Rhamnus frangula*) and that ceanothamine-B[4] is identical with adouetine-X[2,8] (isolated from *Waltheria americana*).

Charge Distribution and Nucleophilic Reactivity in Sulfur Ligand Chelates. Dialkyl Derivatives of Nickel(II), Palladium(II), and Platinum(II) Bis(*cis*)ethylenedithiolates [*J. Am. Chem. Soc.*, **90**, 4297 (1968)]. By G. N. Schrauzer and H. N. Rabinowitz, Department of Chemistry, University of California at San Diego, Revelle College, La Jolla, California.

There is an error in Table VI. The corrected table is

Table VI. Observed and Calculated Bond Lengths (Å) in the Complexes $NiS_4C_4R_4^{0,-,2-}$ [a]

Ni–S		C–S		C–C			
Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Compound	Ref
2.101 (0.002)	*c*	1.71 (0.01)	1.70	1.37 (0.014)	1.39	$NiS_4C_4Ph_4$	25
2.146 (0.001)	*c*	1.71 (0.004)	1.72	1.35 (0.007)	1.37	$Ni(MNT)_2^-$	*b*
2.165 (0.005)	*c*	1.75 (0.01)	1.73	1.33 (0.02)	1.37	$Ni(MNT)_2^{2-}$	24

[a] Standard deviations in parentheses. [b] C. J. Fritchie, *Acta Cryst.*, **20**, 107 (1966). [c] Ni–S distances were not varied in this calculation.