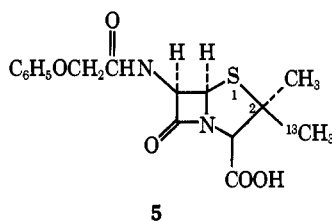


understanding of the formation of this unique class of secondary metabolites; e.g., derivation of cephalosporin C from a common α,β -dehydro valine derivative of tripeptide^{3,4} and/or the biological importance of a "three-point combination" between the symmetrical substrate and the enzyme.^{10,11}

Acknowledgments. We gratefully acknowledge the invaluable help of Mr. R. L. Pieper (fermentation and labeling experiment) and Mr. L. L. Huckstep and Mrs. N. De La Higuera (isolation of crystalline cephalosporin C sodium salt).

(10) A. G. Ogston, *Nature (London)*, **162**, 963 (1948). In this case for instance, one could postulate the existence of a stereochemically fixed complex involving an enzyme and only one of the methyl groups with the other available for transformation necessary for the ring closure.

(11) Since submission of this paper we have also completed labeling experiment of penicillin V (5) in a submerged culture of *P. chrysogenum*



(P. A. Lemke, C. H. Nash, and S. W. Pieper, *J. Gen. Microbiol.*, in press) with (2*RS*,3*S*)-[4-¹³C]valine. Penicillin V was purified and crystallized as the potassium salt. Comparison of the cmr spectrum of this material with that of unlabeled penicillin V (R. A. Archer, R. D. G. Cooper, P. V. Demarco, and L. R. F. Johnson, *Chem. Commun.*, 1291 (1970)) showed a (1.7 ± 0.2)-fold enhanced intensity of the β -CH₃ resonance at C-2 without any other detectable changes in the spectrum. This corresponds to 1.6% of incorporation if one assumes that only L-valine is being utilized.

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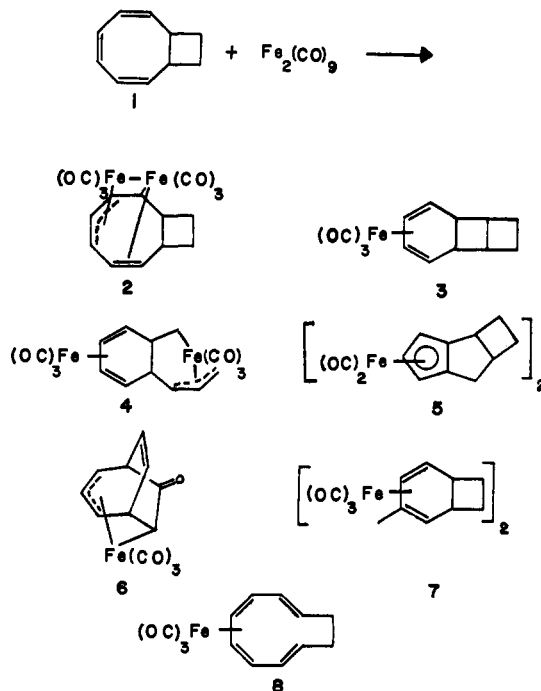
Further Exotic Products from the Reaction of Diiron Nonacarbonyl with Bicyclo[6.2.0]deca-2,4,6-triene. X-Ray Crystallography as a Practical Means of Cheap, Rapid, and Definitive Analysis

Sir:

We wish to report here a study which merits this mode of communication for two reasons. First because at least some of the new compounds described are intrinsically of considerable interest. Second, because in separate, detailed, conventional reports on the different compounds, which will appear in due course, probably in specialist journals, it would not be possible to present to a broad spectrum of readership an overview of the tactical approach employed which, we think, is both novel and uniquely powerful. While no single logical step or technique used is in itself new,

the systematic and consistent way in which we proceeded is demonstrably powerful and is, to our knowledge, unprecedented.

The isolation of four products from the reaction of bicyclo[6.2.0]deca-2,4,6-triene (1) with Fe₂(CO)₉ has been reported.¹ The identities of two (2 and 3) of them were inferred from analytical and spectroscopic data¹ and these structures have since been confirmed crystallographically.²⁻⁴ The structure of 4 was not deduced¹ from the analytical and spectroscopic data; it has since been found by crystallography to be as shown. The yields of 5 are minute but highly



reproducible; the quantity from any single reaction is too small for analysis for adequate spectroscopic characterization.⁵ Thus, recourse to X-ray crystallographic characterization⁶ was mandatory. Using a sample with an approximate mass of 50 μ g the structure was solved in an elapsed time of ca. 60 hr at a computing cost of \$157 (see Table I).

In the meantime, we had reinvestigated the reaction under varied conditions, and it was found that still

(1) F. A. Cotton and G. Deganello, *J. Organometal. Chem.*, **38**, 147 (1972).

(2) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, **50**, 227 (1973) (compound 2).

(3) F. A. Cotton, B. A. Frenz, and J. M. Troup, manuscripts in preparation (compounds 3 and 4).

(4) Actually, the correct structure of 2 was not obtained from the spectroscopic data prior to the X-ray work, because the molecule is fluxional and has a surprisingly low coalescence temperature. However, further low-temperature nmr work subsequent to the X-ray work did provide spectroscopic evidence sufficient to yield the correct structure. Of course, the spectroscopically inferred structure of 3 was incomplete in that the stereochemistry of ring fusion was not elucidated.

(5) It is unlikely that even with a full set of the conventional spectroscopic data the actual structure, including ring fusion geometry, of 5 could have been deduced anyway.

(6) In this and all subsequent structures, the crystals were examined and data collected on a Syntex PI computer-controlled diffractometer equipped with a graphite crystal monochromator. The structures were solved using a three-dimensional Patterson function to locate the metal atom(s). A subsequent least-squares cycle and difference Fourier synthesis generally revealed all of the remaining nonhydrogen atoms. The refinement to convergence was always achieved after three full-matrix least-squares cycles on all positional and isotropic thermal parameters.

Table I. Data for Compounds Characterized Solely by Crystallography

Compound	Unit cell; space group ^f (no. of nonzero reflections used)	Discrepancy	Working time, man hr	Elapsed time, ^c hr	Computing cost, ^e dollars
		indices ^{a,b} R_1, R_2			
5 ^d	$a = 9.252, b = 9.146, c = 12.153 \text{ \AA}, \beta = 106.25^\circ;$ $P2_1/n (790)$	0.083 0.094	9	60	157
6 ^e	$a = 7.476, b = 11.912, c = 6.606 \text{ \AA}, \alpha = 94.55,$ $\beta = 110.17, \gamma = 92.38^\circ; P\bar{1} (1283)$	0.072 0.101	9	96	138
7	$a = 8.178, b = 6.800, c = 9.729 \text{ \AA}, \alpha = 101.98,$ $\beta = 106.99, \gamma = 95.83^\circ; P\bar{1} (1433)$	0.082 0.102	6	60	134
8	$a = 10.401, b = 9.779, c = 6.554 \text{ \AA}, \alpha = 98.69,$ $\beta = 111.76, \gamma = 82.65^\circ; P\bar{1} (1091)$	0.076 0.105	6	120	127
Mean			7.5	84	139

^a After convergence of isotropic refinement, omitting hydrogen atoms. ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$. ^c From first observation that crystals had formed to termination of crystallographic study. ^d Collaboration of Dr. B. A. Frenz is acknowledged. ^e Computing was done on an IBM 360-65 machine at a cost of \$325 per hr. ^f Delauney reduction indicates that there is no higher space group symmetry for the triclinic compounds. ^g This compound also crystallizes in space group $Pna2_1$ and the structure in this form has been independently determined (A. H.-J. Wang, I. C. Paul, and R. Aumann, private communication).

other products could be isolated, some in very small quantities, but all in crystalline form. In view of our previous experience, especially with compounds 4 and 5, we decided to adopt the following strategy. No attempt whatever would be made to identify or characterize products by classical (*i.e.*, analysis or ir, nmr, or mass spectra) methods; instead, the structure would immediately be determined and refined isotropically to convergence. In this way compounds 6, 7, and 8 were quickly, cheaply and completely identified and characterized. The working time, total elapsed time, and direct cost are all as good as or better⁷ than they would be in a classical approach. Moreover, the structures, especially of 6 and 8, would probably have been indeterminate from spectroscopic data, anyhow.

We note also that two other products were quickly, conclusively, and without direct cost shown to be known compounds, namely *trans*- $C_8H_8[Fe(CO)_3]_2$ and $C_8H_8Fe_2(CO)_8$,⁸ which presumably arise from traces of cyclooctatetraene present (*vide infra*) as an impurity in the $C_{10}H_{12}$.

Compound 6 can be considered as a derivative of barbaralone¹⁰ derived from it by opening of the three-membered ring and insertion of $Fe(CO)_3$. We do not mean to suggest that the compound necessarily arises in that way, although it might, in view of the known reaction of semibullvalene with iron carbonyl.¹¹ The question of how the barbaralone itself might form would then have to be answered. The origin of compound 7 is also quite mystifying. Perhaps a part of the answer is that the bicyclodecatriene used was slightly con-

taminated with some 1,3,5-cyclooctatriene as well as with C_8H_8 , although vpc of the ligand showed approximately 95% $C_{10}H_{12}$ and 5% C_8H_8 , and no other significant component.

Compounds 4, 5, and 8 can be reasonably assigned parentage in the bicyclodecatriene, but it is certainly not obvious how and why they are formed.

Even today one frequently sees or reads the assertion that spectroscopic structure methods must be accorded great reverence because of the relatively immense difficulty, time requirement, and expense of crystallography. As a *generalization*, this notion is a kind of *recherche du temps perdu*, and we offer the foregoing report in evidence of this judgment.

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An Experimental Method for the Determination of the Structure of Complex Negative Ions in Solution

Sir:

A nematic ternary middle soap phase¹ of decanol, sodium decyl sulfate, and water has been used as an orienting environment for certain small polar solute molecules.²⁻⁶ The nuclear magnetic resonance (nmr) spectra of these solutes can be used for structural studies by determining the partially averaged dipole-dipole

(1) G. H. Brown, J. W. Doane, and V. D. Neff, "A Review of the Structure and Physical Properties of Liquid Crystals," Chemical Rubber Publishing Co., Cleveland, Ohio, 1971.

(2) K. D. Lawson and T. J. Flautt, *J. Amer. Chem. Soc.*, **89**, 5489 (1967).

(3) P. J. Black, K. D. Lawson, and T. J. Flautt, *Mol. Cryst. Liquid Cryst.*, **7**, 201 (1969).

(4) R. C. Long, Jr., S. L. Baughcum, and J. H. Goldstein, *J. Magn. Resonance*, **7**, 253 (1972).

(5) L. W. Reeves, J. M. Riveros, R. A. Spragg, and J. A. Vanin, *Mol. Phys.*, **20**, 9 (1973).

(6) S. A. Barton, M. A. Raza, and L. W. Reeves, *J. Magn. Resonance*, **9**, 45 (1973).

(7) Clearly, the working times to record and interpret various spectra would be comparable to those listed in the Table I. Elapsed times for obtaining elemental analyses commercially normally exceed those in the table by a factor of 2 or 3. Aggregate costs of instrument use for ir, nmr, and mass spectra, plus the cost of microanalyses for three elements, and the cost of duplicate molecular weight determinations usually exceed \$100 at a typical American university.

(8) In the case of $C_8H_8Fe_2(CO)_8$ we were slightly delayed because our crystallographic parameters, *viz.*, $Pnma$, $a = 7.304 \text{ \AA}$, $b = 15.451 \text{ \AA}$, $c = 11.065 \text{ \AA}$, disagreed with those in the literature⁹ with respect to a , which was reported as 7.71 \AA . Professor E. B. Fleischer has informed us that the published value is a misprint.

(9) E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 3158 (1966).

(10) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 2155 (1972).

(11) R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, **93**, 6709 (1971). Subsequent to submitting this manuscript we learned that direct reaction of $Fe_2(CO)_9$ with barbaralone does in fact give compound 6 (A. H.-J. Wang, I. C. Paul, and R. Aumann, private communication).