experiment since they predict that the most abundant form of $(NO)_2$ is noncentrosymmetric. However, they cannot be taken as the final word on the structure of the dimer. Our calculated geometry does not agree very well with the analysis performed by Dinerman and Ewing[4] on the unresolved P, Q, and R structure of $(NO)_2$. The equilibrium bond lengths in our calculation for structure I are more indicative of N–O single bonds whereas the observed stretching frequencies are characteristic of NO double bonds. Possibly an improved calculation would give better agreement with experiment. We present our work simply to encourage investigators to consider cyclic $(NO)_2$ in their interpretation of future theoretical and experimental work.

Acknowledgment. The author thanks Terry Jacobsen for helping with the preparation of the manuscript and the MUCOM MISD for providing computer facilities. Professor Jules Moskowitz and Dr. Charles Hornback have kindly supplied computer programs. Thanks are also due to Dr. Yvon P. Carignan and Dr. George F. Adams for their interest and encouragement.

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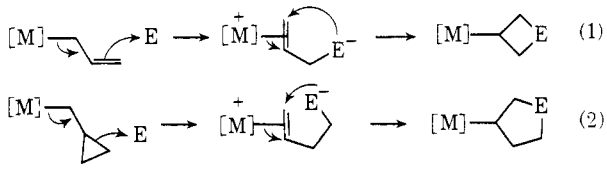
Synthesis of γ-Lactams and Sultams by Metal Assisted Cycloaddition. Stereochemistry of Cycloaddition and of the Deprotonation of Cationic *Pentahaptocyclopentadienyldicarbonyl(olefin)iron* Complexes

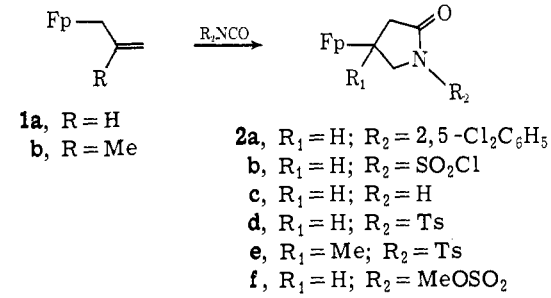
Sir:

We recently showed that the reactions of h^1-allyliron and of cyclopropylmethyliron complexes with electrophilic olefins and with SO_2 gave cycloaddition products whose formation was accounted for in terms of a two-step reaction sequence involving the initial formation of homologous dipolar intermediates and their subsequent closure[1,2] (eq 1 and 2). We now wish to report



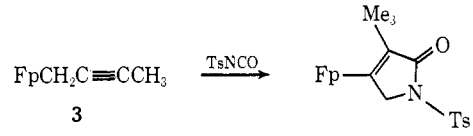
the extension of these cycloaddition reactions to isocyanates, which provides a new and expeditious route to γ-lactams from cyclic and acyclic allyl and propargyliron complexes.[2a]

Although the allyliron complex **1a** does not react with either ethyl or phenyl isocyanate, 2,5-dichlorophenyl isocyanate reacts over a period of several days at room temperature to give the butyrolactam (**2a**),[3] mp 153–155°, in moderate yield. With the highly reactive chlorosulfonyl isocyanate, **1a** reacts instantaneously below 0° affording the chlorosulfonyl lactam (**2b**): ir (CH_2Cl_2) 1767 (C=O), 1967, 2014 cm^{-1} (C≡O). This substance may be converted in 72% overall yield to the unsubstituted lactam **2c**,[3] dec 180–181° (ir (KBr) 1675 (C=O), 1940, 1995 cm^{-1} (C≡O)), by treatment with thiophenol in the presence of sodium methoxide.[4] Toluenesulfonyl and methoxysulfonyl[5] isocyanates react similarly, within 30 min at room temperature, with **1a** and the methallyl complex **1b** to give the butyrolactams (**2d–f**)[3] in 40–70% yield. The butynyl complex **3** also



1a, R = H
b, R = Me

2a, R_1 = H; R_2 = 2,5-$Cl_2C_6H_5$
b, R_1 = H; R_2 = SO_2Cl
c, R_1 = H; R_2 = H
d, R_1 = H; R_2 = Ts
e, R_1 = Me; R_2 = Ts
f, R_1 = H; R_2 = $MeOSO_2$

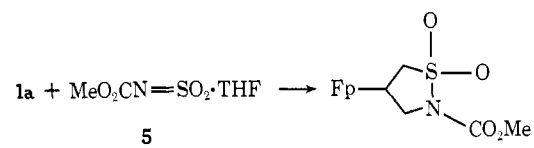


3 4

Fp≡h^5-$C_5H_5Fe(CO_2)$

reacts with toluenesulfonyl isocyanate affording the butenolactam (**4**[3]: ir (KBr) 1695 (C=O) 1960, 2020 cm^{-1} (C≡O); nmr (CD_3NO_2) τ 4.88 (s, 5, Cp), 5.59 (q, 2, J = 1.5 Hz, CH_2), 7.58 (s, 3, $ArCH_3$), 8.20 (t, 3, J = 1.5 Hz, CH_3C=).

Finally, the *N*-sulfonylurethane (**5**), derived by treatment of carbomethoxysulfamoyl chloride with sodium hydride following the recently reported procedure of Burgess and Williams,[6] has also been found to enter into a (2 + 3) cycloaddition reaction to give the γ-sultam (**6**): (KBr) 1940, 1995 (C≡O), 1695 (C=O), 1300, 1145 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 4.96 (s, 5, Cp), 6.06 (s, 3, Me), 6.0–7.2 (m, 5, CH,CH_2).

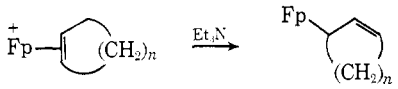


5 6

Extension of these reactions to cycloalkenyliron complexes provides a means for examining the stereospecificity of the cycloaddition process. The requisite 3-cyclopentenyl- and 3-cyclohexenyliron complexes (**7**) may be prepared by deprotonation of the related

(1) W. P. Giering and M. Rosemblum, *J. Amer. Chem. Soc.*, **93**, 5299 (1971).
(2) Similar reactions of **1** and of the related molybdenum complex with tetracyanoethylene have recently been reported by S. R. Su and A. Wojcicki, *J. Organometal. Chem.*, **31**, C34 (1971). We have also found that h^1-allyl derivatives of cyclopentadienyltungsten tricarbonyl, cyclopentadienylchromium dinitrosyl, and cobaloxime also give cycloaddition products with TCNE, and that β,β-dicyano-*o*-chlorostyrene likewise enters into cycloaddition reactions with h^1-allylmetal complexes.
(2a) NOTE ADDED IN PROOF. Since submitting this paper, a paper by Y. Yamamoto and A. Wojcicki, *Inorg. Nucl. Chem. Lett.*, 883 (1972), has appeared reporting similar results.
(3) An acceptable elemental analysis was obtained for this substance and its ir and nmr spectra were compatible with the structure assigned.
(4) R. Graf, *Justus Liebigs Ann. Chem.*, 661, 111 (1963); *Org. Syn.*, **46**, 51 (1966).
(5) R. Graf, *Chem. Ber.*, **96**, 56 (1963); R. Lattrell and G. Lohaus, German Patent No. 1,300,556 (1969); *Chem. Abstr.*, **71**, 101292 (1969).
(6) E. M. Burgess and W. M. Williams, *J. Amer. Chem. Soc.*, **94**, 4386 (1972).

cationic metal–olefin complex **8**[7] with triethylamine.[11]



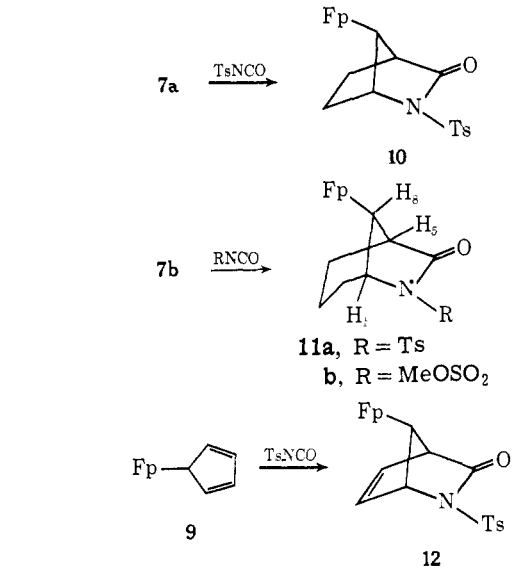
8a, $n = 2$
b, $n = 3$
c, $n = 4$

7a, $n = 2$
b, $n = 3$

Significantly, the deprotonation reaction, which proceeds quantitatively with the cyclopentene and cyclohexene cations (**8a,b**), fails with the cycloheptene cation (**8c**). An examination of models shows that, in the preferred conformation of the latter complex in which the pendent Fp group lies exo to the ring,[14] no allylic protons trans to the Fp–olefin bond are available. This is in sharp contrast to the situation prevailing in the cyclopentene and cyclohexene complexes. The inference that deprotonation of these complexes is highly stereospecific is supported by subsequent observations.

The cycloalkenyl complexes **7a,b** and the h^1-cyclopentadienyl complex **9** react readily with toluenesulfonyl isocyanate to give the bicyclic γ-lactams **10**, **11**, and **12**.[3] Methoxysulfonyl isocyanate similarly reacts with **7b** to give the adduct **11b**,[3] but no well-defined product could be isolated from the reaction with **7a**. The stereochemistry assigned to each of these products corresponds to that resulting from sterically preferred cycloaddition trans to the bulky organometallic group. The stereochemical assignment is confirmed for **11a** by an examination of its nmr spectrum which exhibits triplet absorption for H_8 at τ 6.83 ($J_{1,8} = J_{5,8} = 5$ Hz).[15]

The reactions of **7a,b** with chlorosulfonyl isocyanate proceed otherwise. No well-defined product could be obtained from the reaction of **7b** with this reagent, but the cyclopentene complex **7a** reacts rapidly below room temperature to give the cyanoolefin cation **14a**[3] which separates spontaneously from solution, and is evidently derived by loss of $ClSO_3^-$ from the intermediate dipolar ion **13a** in a process which competes favorably with the cyclization step.[16,17] The stereochemistry assigned to this substance, in conformity with that of the cycloaddition products **10**, **11**, and **12**, places the Fp–olefin bond trans to the cyano group. The cyclopentene complex **7a** reacts similarly with **5** to give an inner sulfonic acid salt **14b**[3] derived by loss of methyl cyanate from the dipolar intermediate **13b**. Consistent with these formulations and with the failure of the cycloheptene complex **8c** to deprotonate, treatment of **14a** and **14b** with triethylamine yields **15a** and **15b**, respectively, notwithstanding the presence of the activating function: **15a**, nmr ($CDCl_3$) τ 4.0 (m, 1, CH═), 4.55 (m, 1, CH═), 5.08 (s, 5, Cp), 6.10 (m, 1, CHFp), 7.18 (m, 3, CH_2,CHCN); **15b**, ($CDCl_3$) τ 3.84 (m, 1, CH═), 4.36 (m, 1, CH═), 5.16 (s, 5, Cp), 6.16 (m, 1, CHFp), 7.66 (m, 3, CH_2,$CHSO_3H$).[18]

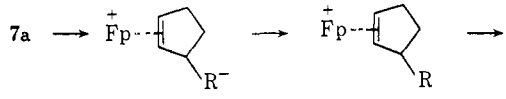


10

11a, R = Ts
b, R = $MeOSO_2$

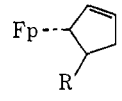
9

12



13a, R = $CONSO_2Cl$
b, R = SO_2NCO_2Me

14a, R = CN
b, R = SO_3^-



15a, R = CN
b, R = SO_3H

Thus, base-assisted proton abstraction from h^2-(olefin)iron complexes occurs preferentially exo to the metal–ligand bond in contrast to cationic h^3-allyliron complexes in which endo proton exchange with the solvent is apparently preferred.[19]

Acknowledgment. This work was supported by grants from the National Science Foundation (GP-

(7) These cationic metal complexes are readily available either through hydride abstraction from cycloalkyl complexes,[8] by an exchange reaction of an olefin with the related isobutylene–Fp cation,[9] or through treatment of epoxides with the Fp anion, followed by acid.[10] The cyclopentenyl complex **7a** may also be prepared from the complex iron anion (Fp^-) and 3-chlorocyclopentene, but the metallation reaction fails with the tosylate of cyclohexenol.

(8) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, 1, 58 (1963).

(9) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 414 (1971).

(10) W. P. Giering, M. Rosenblum, and J. Tancrede, *J. Amer. Chem. Soc.*, **94**, 7170 (1972).

(11) While a number of cationic h^3-allyl- and h^5-pentadienylmetal complexes have been deprotonated with tertiary amines,[12] an early attempt by Green and Nagy[13] to deprotonate simple cationic iron–olefin complexes was unsuccessful.

(12) F. M. Chaudhari and P. L. Pauson, *J. Organometal. Chem.*, **5**, 73 (1960); G. T. Rodeheaver, G. C. Farrant, and D. F. Hunt, *ibid.*, **30**, C22 (1971); J. Evans, B. F. G. Johnson, and J. Lewis, *Chem. Commun.*, 1252 (1971); E. O. Greaves, G. R. Knox, and P. L. Pauson, *ibid.*, 1124 (1969); B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *ibid.*, 177 (1971).

(13) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

(14) This is true for either the boat or chair conformation of the ring, the latter of which is apparently preferred: N. Neto and C. DiLaurro, *Spectrochim. Acta, Part A*, **26**, 1489 (1970).

(15) For similar assignments in bicyclo[3.2.1]octane and in 6-azobicyclo[3.2.1]-7-octanone systems see E. Munck, C. S. Sodano, R. L. McLean, and T. H. Haskell, *J. Amer. Chem. Soc.*, **89**, 4158 (1967); C. W. Jefford, B. Waegell, and K. Ramey, *ibid.*, **87**, 2191 (1965); A. C. Ochlschlager and L. H. Zalkow, *J. Org. Chem.*, **30**, 4205 (1965); T. N. Margulis, L. Schiff, and M. Rosenblum, *J. Amer. Chem. Soc.*, **87**, 3269 (1965).

(16) A small amount of dicarbonyl(cyclopentadienyl)(*cis*-1-cyanoallyl)iron may also be isolated from the reaction of **1a** with chlorosulfonyl isocyanate, but cyclization of the intermediate dipolar ion competes favorably with its loss of $ClSO_3^-$ in this reaction.

(17) For the conversion of *N*-chlorosulfonylamides to nitriles see G. Lohaus, *Chem. Ber.*, **100**, 2719 (1967), G. Lohaus, *Org. Syn.*, **50**, 18, 52 (1970).

(18) This may be compared with the nmr spectrum of **7a**: ($CDCl_3$) τ 3.92 (m, 1, CH═), 4.48 (m, 1, CH═), 5.26 (s, 5, Cp), 6.22 (m, 1, CHFp), 7.9 (m, 4, CH_2).

(19) T. H. Whitesides and R. W. Arkart, *J. Amer. Chem. Soc.*, **93**, 5296 (1971).

27991-X), by the National Institutes of Health (GM-16395), and by the U. S. Army Research Office—Durham.

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Synthesis of Benzyl 6-Oxopenicillanate[1] and Derivatives. I

Sir:

We wish to report the synthesis of benzyl 6-oxopenicillanate (II) and illustrate the potential of this type of substance as a source of new antibacterial agents, for example by transformation to 6β-(phenoxyacetoxy)penicillanic acid (VI)—an oxygen analog, including stereochemistry, of penicillin V.

Benzyl 6-α-hydroxypenicillanate (I) was prepared from 6-aminopenicillanic acid by the method of Hauser and Sigg.[2] Oxidation of I by diisopropylcarbodiimide in methyl sulfoxide[3] gave benzyl 6-oxopenicillanate[4] (II) which was purified by column chromatography: ir (film) 1830, 1780, 1735 cm^{-1}; nmr ($DCCl_3$) δ 7.4 (s, 5 H), 5.85 (s, 1 H), 5.3 (s, 2 H), 4.87 (s, 1 H), 1.55–1.62 (d, 6 H). The contaminant originating from diisopropylcarbodiimide was removed with difficulty. Water-soluble carbodiimides such as 1-ethyl-3-(dimethylamino)carbodiimide hydrochloride and methiodide are not promising for this oxidation. Under these conditions no benzyl 6-oxopenicillanate (II) could be isolated. Only the starting hydroxy compound I was recovered.

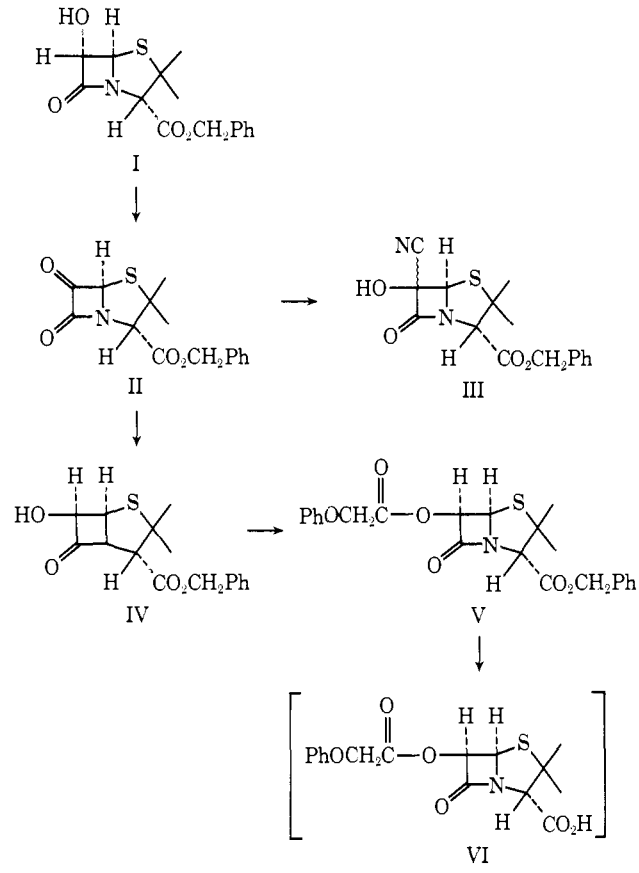
Treatment of benzyl 6-oxopenicillanate (II) with liquid hydrogen cyanide immediately gave a solid. After washing with benzene and recrystallization from methylene chloride, a colorless, crystalline cyanohydrin[4] (III) of II was obtained [mp 148–162° dec; ir (KBr) 3300, 1790, 1730 cm^{-1}; nmr (acetone-d_6) δ 7.5 (s, 5 H), 5.9 (s, 1 H), 5.35 (s, 2 H), 4.7 (s, 1 H), 3.1 (s, 1.5 H), 1.63 (s, 3 H), 1.50 (s, 3 H)].

Reduction of II by potassium borohydride in aqueous alcohol gave only one hydroxy isomer, namely, benzyl 6-β-hydroxypenicillanate (IV). The product was isolated by column chromatography and purified by recrystallization [ir (KBr) 3420, 1775, 1725 cm^{-1}]. Table I compares some of the physical properties of the 6-α- and 6-β-hydroxy isomers I and IV.

Table I. Physical Properties of I and IV

	I (lit.)[2]	IV
Mp, °C	157–160	97.5–98.5
$[\alpha]^{25}D$, deg	191 (*c* 0.53, methanol)	222 (*c* 0.87 methanol)
Nmr		
C_5	δ 5.3, d, J = 1.5 Hz	δ 5.65, d, J = 4.0 Hz
C_6	δ 4.83, m	δ 5.1–5.3, q, J = 4.0, 11.0 Hz
OH	δ 4.3, s, br	δ 3.2–3.5, d, br, J = 11.0 Hz

(1) See J. C. Sheehan, K. R. Henery-Logan, and D. A. Johnson, *J. Amer. Chem. Soc.*, 75, 3292 (1953) for naming system.
(2) D. Hauser and H. P. Sigg, *Helv. Chim. Acta*, 50, 1327 (1967).
(3) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, 85, 3027 (1963).
(4) All new compounds gave satisfactory analytical data.



Benzyl 6-β-hydroxypenicillanate (IV) was phenoxyacetylated to give benzyl 6-β-(phenoxyacetoxy)penicillanate[4] (V). The compound was purified by column chromatography and isolated as an oil [ir (film) 1790, 1740, 1600, 1500 cm^{-1}; nmr ($DCCl_3$) δ 7.35 (s, 5 H), 7.4–6.7 (m, 5 H), 5.8–5.6 (q, 2 H, J = 4 Hz), 5.25 (s, 2 H), 4.7 (s, 2 H), 4.55 (s, 1 H), 1.6 (s, 3 H), 1.45 (s, 3 H)].[5]

Compounds IV and VI[6] were submitted for bioassay and showed little or no bioactivity against a variety of organisms.[8]

(5) This work was assisted financially by the Sloan Basic Research Fund.
(6) Hydrogenolysis of V over 5% Pd/$BaCO_3$ in ethyl acetate for 8 hr^2 gave a pale yellow syrup containing 6-β-(phenoxyacetoxy)penicillanic acid (VI) based on spectroscopic data (ir, nmr). Attempts to remove all contaminants from this material by column chromatography were unsuccessful due to strong adsorption of the acid on the support. The acid does not readily form a crystalline *N*-ethylpiperidine salt[7] analogous to penicillin G and V.
(7) J. C. Sheehan, W. J. Mader, and D. J. Cram, *J. Amer. Chem. Soc.*, 68, 2407 (1946).
(8) Bristol Laboratories, Division of Bristol-Myers Co., Syracuse, N. Y.

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Negatively Charged Electrophiles. Acylation of Strong Nucleophiles by Enolate Salts of β-Keto Esters

Sir:

Poly-β-carbonyl compounds are presently of interest because their reactions bear a relationship to the biosynthesis of phenolic natural products.[1] We have de-

(1) For a review, see T. Money, *Chem. Rev.*, 70, 553 (1970).