

REACTION OF TRANSITION METAL CARBONYL WITH HETEROCYCLIC SYSTEMS I.

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The interaction of N-Phenyl-2-oxa-3-azabicyclo-[2.2.2]-octen-5 with $\text{Fe}_2(\text{CO})_9$ results in the series of products (2)-(5). The reaction between the two components occurs under surprisingly mild conditions. Thus, when equimolar quantities of the above reactants in dry benzene were heated at 40° under nitrogen for 20 minutes all starting material (1) disappeared (tlc analysis). The products (2)-(5) were separated by column chromatography and the purified compounds accounted for 47% of the starting material.

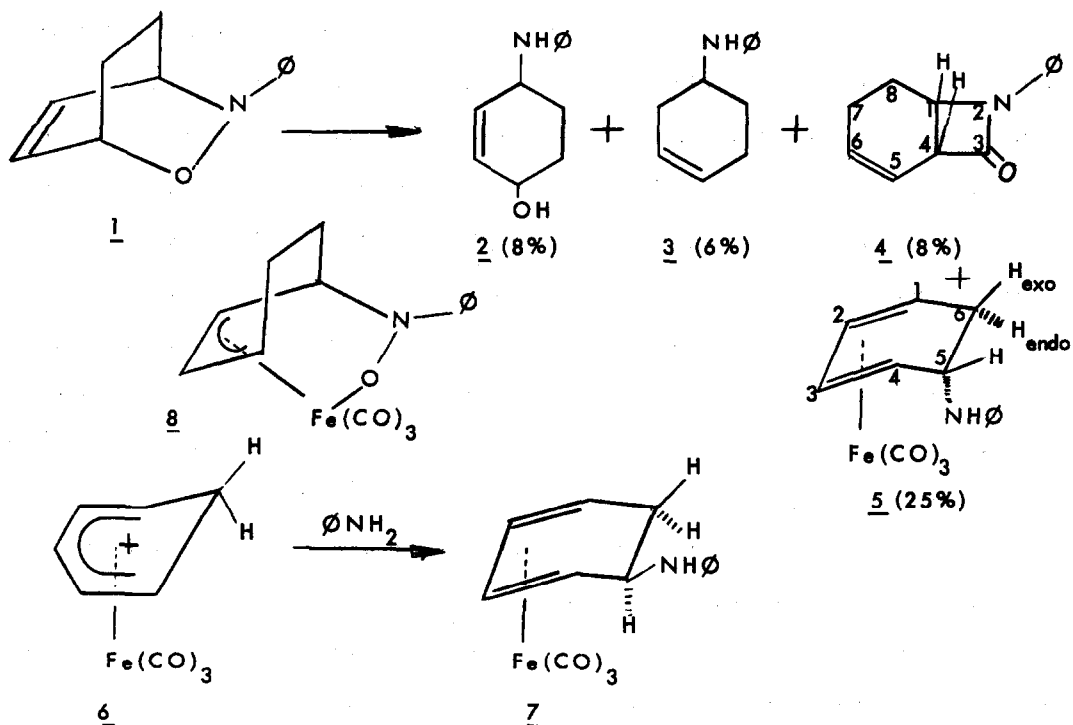


Table I. Physical Data.

Compd.	m.p.(°C)	Infra Red (cm ⁻¹)	M ⁺ , m/e
4*	76.5-77	1735 (C=O) in CHCl ₃	199
5*	104.5(dec)	3420 (NH) in CHCl ₃ 2040, 1980 (C=O) in hexane	311
7	84-5	3410 (NH) in CHCl ₃ 2040, 1985 (C=O) in hexane	311

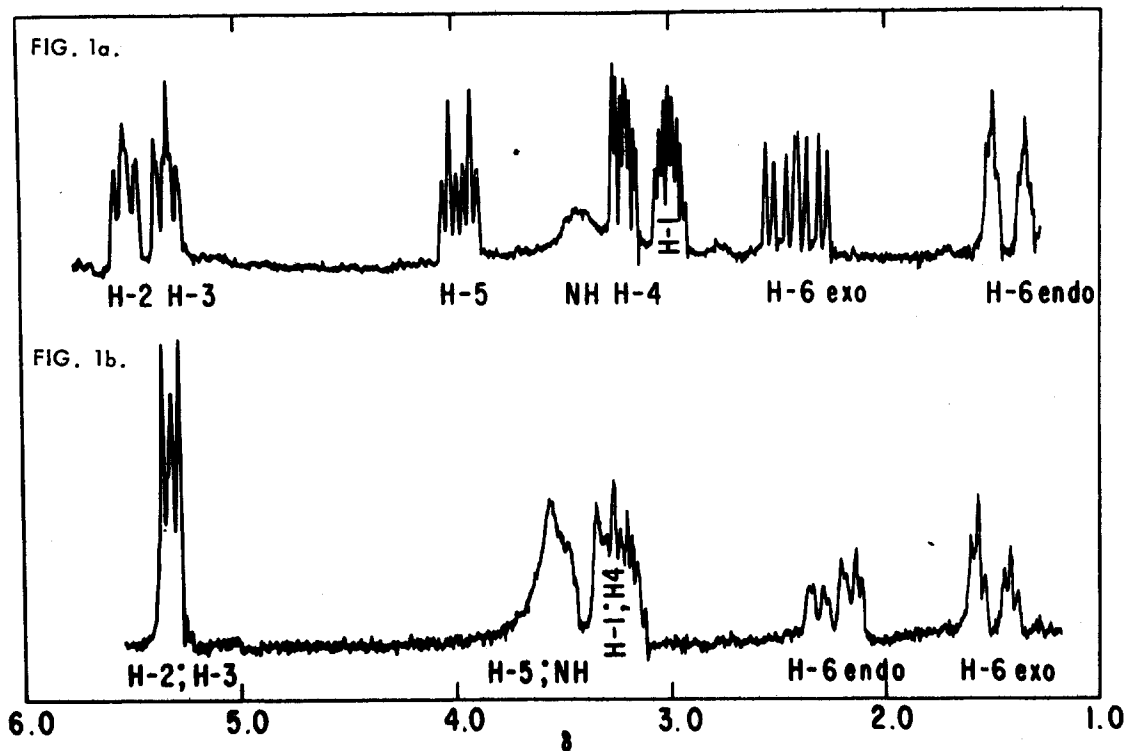
* Elemental analysis is in agreement with the proposed molecular formula.

Of the four products only 2 and 3 were previously reported¹, and their mps were compared with the literature data². Also, their spectral properties (infra red and nmr) unambiguously confirm the structures assigned to these two compounds. For the third product we propose the bicyclic β -lactam structure (4).

The mass spectral molecular peak and the elemental analysis of 4 (Table I)

indicate a formal insertion of one carbon with respect to the starting material (1). The fact that this compound contains a non-basic nitrogen atom and exhibits a carbonyl stretching band at relatively high frequency (1735 cm⁻¹)³ lends a strong support to a β -lactam structure. Its nmr spectrum exhibit, among others, an apparent triplet of one proton at δ 3.80 (H-4), a one proton multiplet centered at δ 4.46 (H-1) and two protons multiplet at δ 5.98 (H-5 and H-6). Spin decoupling experiments reveal that the olefinic protons are coupled to H-4 and the latter is coupled to H-1 (5.0 cps). This coupling pattern clearly demonstrates that the protons α to the carbonyl and α' to the nitrogen atom are vicinal, substantiating the 4.2.0 nature of the bicyclic system. Furthermore, from the magnitude (5.0 cps)⁴ of J (H-1, 4) a cis configuration is proposed for the bicyclic juncture.

To the major product of this reaction we propose the structure of endo-5-anilino-clohexa-1,3-diene-irontricarbonyl (5). The mass spectral and elemental analysis data (Table I) yield the corresponding molecular formula. A structure of secondary amine was revealed by the infra red spectrum of 5 (Table I) and by detection of a signal of an exchangeable proton (NH) in the nmr spectrum of 5 (Fig 1b). The complexed 1,3-conjugated diene system can be detected in the nmr spectrum (Fig.1b). The multiplet at δ 3.25 (2H) is assigned to the two protons H-1 and



NMR spectra (100 Mc) in CDCl_3 with TMS as zero reference: 1a) Compd.7. 1b) Compd.5. Aromatic signals are not shown.

H-4 of 5 which are appropriately shielded⁵ with respect to the normal resonance frequency of H-2 and H-3 (δ 5.35; 2H). The coupled AB system of the two C-6 protons is clearly visible at highest field. Spin decoupling experiments reveal that these protons are coupled both to H-5 and H-1. The stereochemistry of this complex is unique inasmuch as the anilino and the metal groups occupy the same side of the six-member ring (endo configuration). To our knowledge no synthetic route to this endo complex is presently feasible. We have, therefore, prepared the hitherto unknown exo isomer (7) by quenching the cyclohexadienyl irontricarbonyl complex (6) with aniline. The reactions of 6 with nucleophiles are known to produce the exo products⁶. Indeed, 5 and 7 were found to be isomeric (Table I). Although their nmr spectra are grossly similar, the differences are clearly noticeable (Figs. 1a,b). Appropriately, in the exo isomer, H-5 is magnetically deshielded⁷ by the metal and its signal is being shifted downfield (ca 0.5 ppm) with respect to H-5 in the endo isomer (Figs. 1a,b). At present, insufficient experimental data pre-

clude the understanding of the mechanistic details of this interesting reaction. However, we did establish that the amino alcohol (2), which is the formal reduction product of 1 is unreactive under the original reaction conditions. Furthermore, the products distribution was not altered when the reaction was carried out under CO atmosphere. It is noted that in three out of the four products, formal de-oxygenation occurred. To rationalize the formation of 3, 4 and 5, intermediate (8) is tentatively postulated and its possible intervention is presently being investigated. It is noted that 8 may account for the stereospecific formation of the endo isomer (5). Furthermore since the bicyclic lactam (4) has a rearranged skeleton and a cis configuration at the juncture, the π delocalized allylic system of 8 may constitute a logical precursor to its formation.

We are further pursuing the mode of interaction of transition metal complexes with related compounds and other heterocyclic systems.

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References.

1. Yu.A. Arbuzov and T.A. Maatyukova, *Izvest. Akad. Nauk S.S.S.R. Otdel Khim Nauk*, 665 (1952).
2. The mp of the benzoyl derivative of 3, reported in Ref. 1 is most probably incorrect. The structure of 3 is supported by its mass spectrum, ir and nmr data. Spin decoupling indicates that the vinylic protons are coupled to H-4 (α C to N). Furthermore the N-benzoyl-3-anilino-cyclohexene¹ was prepared and found to differ from 3.
3. O.L. Chapman and W.R. Adams, *J. Amer. Chem. Soc.*, **89**, 4243 (1967).
4. In the following references the ranges of the vicinal protons couplings in β -lactams are 2.4-3.0 cps (trans) and 5.0-7.0 cps (cis): H.B. Kagan, J.J. Basselier and J.L. Luche, *Tetrahedron Lett.*, 941 (1964); K.D. Barrow and T.M. Spotwood, *Tetrahedron Lett.*, and reference 3.
5. M.L. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).
6. M.A. Hashmi, J.D. Munro, P.L. Pauson and J.M. Williamson, *J. Chem. Soc.*, (A), 240 (1967).
7. A.J. Birch, P.E. Cross, J. Lewis, D.A. White and S.B. Wild, *J. Chem. Soc.* (A), 332 (1968).