hexanes was likewise demonstrated by dehydrohalogenation to the same pair of Δ^1 and Δ^2 perfluoropropylcyclohexenes in each instance. C gave a 15/85 mixture and A gave a 60/40 mixture of Δ^1/Δ^2 olefins according to gas chromatography, n.m.r. vinyl proton resonance areas and infrared analysis. D gave pure Δ^1 olefin. A study of related chemistry of these substances is being carried on.

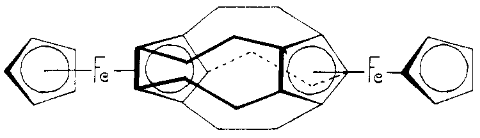
CONTRIBUTION NO. 325 FROM THE
PIONEERING RESEARCH SECTION
JACKSON LABORATORY NEAL O. BRACE
E. I. DU PONT DE NEMOURS AND CO.
WILMINGTON, DEL.

RECEIVED FEBRUARY 10, 1962

PENTAETHANODIFERROCENE

Sir:

Experimental results, obtained in this laboratory, provide evidence in serious contradiction to the recent assignment of Structure I to material obtained by prolonged treatment of ferrocene with aluminum chloride in the presence of ethylene dichloride.[1] The substance in question, whose formation is viewed as resulting from multi-alkylation of two ferrocene nuclei by five molecules of ethylene dichloride, possesses the name, "pentaethanodiferrocene";[1] and, the present experimental basis for rejection of I lies in the observation that material identical with "pentaethanodiferrocene" is produced by treatment of ferrocene with aluminum chloride *in the absence of ethylene dichloride.*



Structure I.

Careful repetition of the procedure reported by the original workers[1] gave rise to a yellow-colored solid possessing properties [dec., near 130°; mol. wt., 527 (benzene); d^{22}_4 1.37 ± 0.14 (methanol)] strikingly close to those reported for pentaethanodiferrocene [dec., near 130°; mol. wt., 545, 568 (benzene); d^{20}_4 1.461 (methanol)].[1] A yellow-colored solid (dec., near 130°), then obtained from similar treatment of ferrocene—except that benzene was used in place of ethylene dichloride—was found to be identical with the material produced in ethylene dichloride. The identity was demonstrated by means of superimposable infrared spectra (chloroform) and, more definitively, by the congruence of X-ray powder patterns determined from the two purified solids.[2]

These results clearly show that the aliphatic carbons present in structural association with the two ferrocene nuclei of "pentaethanodiferrocene" must have as their source a third ferrocene nucleus or its equivalent; and, that the sequence of bonding for all of these units is different from that depicted by I. Since ferrocene is known to undergo oxidation to ferricinium cation in the presence of strong electrophile and air,[3,4,5] and decomposition of the unstable ferricinium species in the presence of a proton source[6] may be expected to result in generation of cyclopentadiene, it would appear likely that the aliphatic carbons exist as substituted cyclopentane rings either as such or in a modified form. Experiments designed to provide information to allow a choice among several structural possibilities are now in progress, and all results will be reported in a full account of this work.

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[1] A. N. Nesmeyanov and N. S. Kochetkova, *Doklady Akad. Nauk, S.S.S.R.*, **126**, 307 (1959).

[2] The author is indebted to Prof. Richard Layton of this Department for determination of these X-ray powder patterns.

[3] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

[4] V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955).

[5] M. Rosenblum and J. O. Santer, *ibid.*, **81**, 5517 (1959).

[6] Under the experimental conditions used,[1] it is not unreasonable to expect appreciable amounts of hydrogen chloride formed by the action of atmospheric moisture on aluminum chloride.

DEPARTMENT OF CHEMISTRY STANLEY I. GOLDBERG
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, S. C.

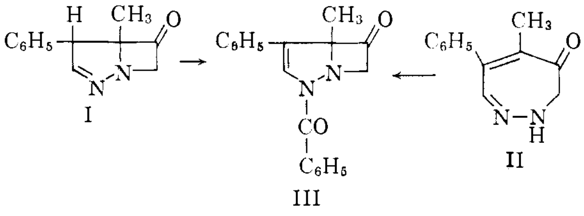
RECEIVED APRIL 25, 1962

HETEROCYCLIC STUDIES. IX. SOME TRANSFORMATIONS OF THE 1,2-DIAZABICYCLO[3.2.0]HEPTANE SYSTEM[1]

Sir:

Current interest in the chemistry of strained bicyclic systems prompts us to report very briefly the formation and some of the reactions of 2-benzoyl-5-methyl-4-phenyl-1,2-diazabicyclo[3.2.0]-3-hepten-6-one (III). This compound is produced by benzoylation of the bicyclic ketone (I)[2] with benzoyl chloride in pyridine; m.p. 126–127° (dec.), (Found: C, 75.07; H, 5.33; N, 9.15). The structure follows from the method of preparation and the physical properties (λ_{KBr} 5.56, 6.13 μ; n.m.r. (60Mc.): 3 proton CH_3 peak at 95 c.p.s., 2 proton quartet for CH_2 at 277 c.p.s., J_{AB} 17 c.p.s., 11 proton aryl and vinyl peak at 450 c.p.s. max.).

A more practical preparation of III is provided by a facile bridging reaction that occurs on treatment *of the diazepinone* II[3] with benzoyl chloride in pyridine or dimethylaniline; acetyl chloride furnishes the corresponding 2-acetylbicyclic ketone.



In contrast to the parent bicyclic ketone I, which is tautomeric with II and is rapidly converted to II or derivatives thereof under most reaction conditions, III displays a remarkably broad

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[1] Supported in part by a grant from the Geschickter Fund for Medical Research.

[2] J. A. Moore and R. W. Medeiros, *J. Am. Chem. Soc.*, **81**, 6026 (1959).

[3] J. A. Moore and J. Binkert, *ibid.*, **81**, 6029 (1959).

spectrum of structural changes with relatively mild reagents; the reactions are summarized in Fig. 1.[4]

In warm glacial acetic acid solution the bridging reaction is reversed and the diazepinone II is formed. This acyl transfer is reminiscent of the deacetylation of imido esters which occurs under these conditions.[5] In aqueous methanolic hydrochloric acid, the bicyclic system rearranges *without hydrolysis* to furnish the 1-benzamidopyridinium chloride V[6] (Found: C, 67.21; H, 5.16; N, 8.30) in 90% yield. This reaction can be depicted very simply as an allylic shift of the bridging bond from C-5 to C-3, initiated by protonation at N-1, followed by collapse of the resulting 1,7-diazabicyclo[4.1.0]heptanone IV to V.

On brief refluxing in methanol solution containing a catalytic amount of benzoic or *p*-toluenesulfonic acid, a product having the composition of a hemiketal is obtained (Found: C, 71.30; H, 5.99; N, 8.31; OCH_3, 9.23). This compound is similarly convertible to II and V, but from ultraviolet ($\lambda_{\max}^{\text{EtOH}}$ 261 mμ) and other data it appears not to be the bicyclo[3.2.0]hemiketal derived from III by simple carbonyl addition. (Carbonyl derivatives of III, such as the semicarbazone, have not been obtained despite numerous attempts).

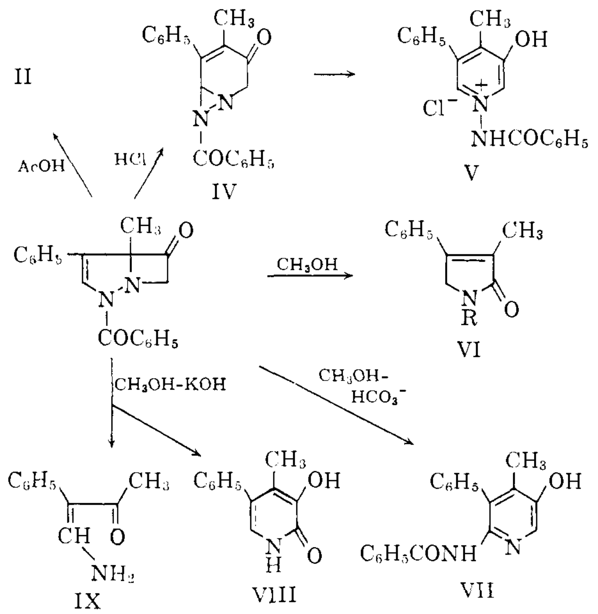
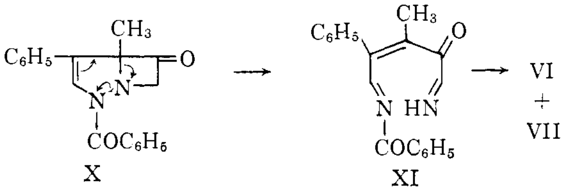
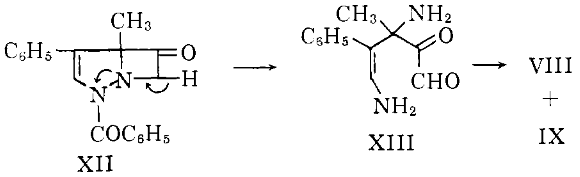


Fig. 1

Refluxing III in neutral methanol solution (containing benzoic acid and sodium benzoate) gives the 1-benzoylpyrrolone VI ($R = C_6H_5CO$) (Found: C, 78.39; H, 5.70; N, 5.31) in 40% yield. This substance was characterized by mild alkaline hydrolysis to the pyrrolone VI ($R = H$).[3] In methanol solution containing a catalytic amount of ammonia or bicarbonate, the major product (70%) is the isomeric 6-benzamidopyridine VII.[7] In stock methanol, without added reagents, both VI and VII are obtained, and it appears that these compounds may arise from a common precursor. One possibility is the concerted rupture of the N–N and C–5—N bonds, as in X → XI, then recyclization by two different paths, although the driving force for these reactions is not obvious. A polar solvent is necessary; heating III in benzene or toluene leads to another, highly reactive isomer whose structure is not yet known.



In cold methanolic potassium hydroxide a mixture of products is formed from III which includes the enamine IX,[8] m.p. 98° (Found: C, 74.42; H, 7.13; N, 8.60) (35% yield), characterized by conversion to 3-methyl-4-phenylpyrazole and by synthesis from 1-phenyl-1-ethoxymethyleneacetone, an unidentified compound $C_{17}H_{17}O_2N$ (6%), and a compound (5%) which has been identified as the pyridone VIII (Found: C, 71.13; H, 5.58; N, 7.44) by comparison with a product obtained by Elbs oxidation of 3-hydroxy-4-methyl-5-phenylpyridine[9] (the other possible oxidation product, the previously known[7] 3-hydroxy-4-methyl-5-phenyl-6-pyridone, also was obtained). The cleavage observed in this reaction probably is initiated by removal of a proton at C-7 followed by elimination at the N—N bond (XII) and hydrolysis to give a species such as XIII which can be conceived as a common precursor of VIII and IX. Dismutation of the α-dicarbonyl system and ring closure would furnish VIII; fragmentation with loss of glyoxal and further hydrolysis would give IX.



Further discussion and details of these reactions will be presented in forthcoming papers.

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[4] Most of the reactions described have also been observed with the 2-acetyl derivative as well.

[5] W. Z. Heldt, *J. Am. Chem. Soc.*, **80**, 5880 (1958).

[6] J. A. Moore and J. Binkert, *ibid.*, **81**, 6045 (1959).

[7] J. A. Moore and F. J. Marascia, *ibid.*, **81**, 6050 (1959).

[8] Lit. m.p. 96°, H. Rupe, A. Metzger and H. Vogler, *Helv. Chim. Acta*, **8**, 848 (1925).

[9] J. A. Moore and H. Puschner, *J. Am. Chem. Soc.*, **81**, 6041 (1959).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF DELAWARE
NEWARK, DELAWARE

JAMES A. MOORE
FRANK J. MARASCIA
ROBERT W. MEDEIROS
EDMOND WYSS

RECEIVED MAY 4, 1962

BIOSYNTHESIS OF THE TETRACYCLINES. IV.[1] BIOLOGICAL REHYDRATION OF THE 5a,6-ANHYDROTETRACYCLINES

Sir:

In our studies on the pathways of biosynthesis of the tetracyclines, we have examined, for pre-

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[1] Previous series paper: J. R. D. McCormick, J. Reichenthal, U. Hirsch and N. O. Sjolander, *J. Am. Chem. Soc.*, **84**, in press (1962).