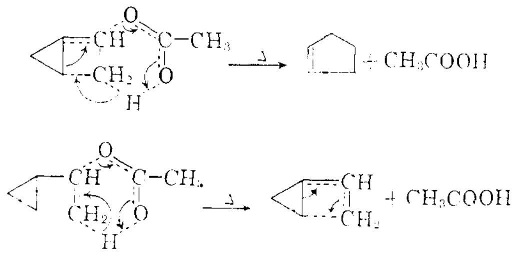
Thermally induced rearrangements have been found for the pyrolysis of medium ring cycloalkyl acetates,[4] the pyrolysis of cyclononyl acetate yielding mainly 1,8-nonadiene.[5] Our results are not an extension of these proposed transannular rearrangements. Elimination of the elements of acetic acid from 1-cycloalkylethyl acetates probably occur in the established fashion.[1,2] The rearrangement by ring expansion common to 3 and 4 membered carbocyclic systems can be concerted, similar to the preparation of 1,3-butadiene from cyclobutyl S-methyl xanthate[6] or else proceed through an intermediate vinylcycloalkane or result from a combination of these two choices. In this case, evidence is presented that the latter process accounts for a major portion of the reaction.



1-Cyclopropylethyl acetate, boiling at 139–140° (755 mm.), $n^{25}$D 1.4140, C, 65.71, H, 9.67, was pyrolyzed[1] at 510°; and a mixture of 6 olefins, as evidenced by G.P.C.,[7] 87% was obtained. Fractionation yielded cyclopentene, boiling at 44° (755 mm.), 69%, $n^{25}$D 1.4202, (lit. boiling at 41–42° (760 mm.), $n^{25}$D 1.4190).[8] 1,4-Pentadiene, 10%, vinylcyclopropane, 12%, and isoprene, trace amount, were similarly identified, in all cases a comparison with known samples was made for positive identification.

A thermal isomerization of vinylcyclopropane was responsible, at least in part, for the formation of cyclopentene. Vinylcyclopropane in acetic acid was pyrolyzed under identical conditions and 40% of this material was converted to cyclopentene, 95%, and 1,4-pentadiene, 5%.

1-Cyclobutylethyl acetate, boiling at 157–159° (755 mm.), $n^{25}$D 1.4230, was pyrolyzed[1] at 500°; and a five-component mixture boiling at 50–82° (755 mm.), 80%, was obtained. Fractionation yielded crude cyclohexene boiling at 80–84° (755 mm.), 65%, $n^{25}$D 1.4410, (lit. boiling at 82–84° (760 mm.), $n^{25}$D 1.4435).[9]

1-Cyclopentylethyl acetate[3] boiling at 91–92° (38 mm.), $n^{25}$D 1.4332, was pyrolyzed[1] at 520° and a mixture of olefins was obtained, 76%. The major isomer, vinylcyclopentane, boiled at 98.8–99° (755 mm.), 74%, $n^{25}$D 1.4336, (lit. boiling at 100.3° (760 mm.), 70%, $n^{20}$D 1.4367)[3]. Ethylidenecyclopentane boiled at 111–112° (755 mm.), 24%, $n^{25}$D 1.4470, (lit. boiling at 112.6° (760 mm.), 10%, $n^{20}$D 1.4490).[3]

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DEPARTMENT OF CHEMISTRY C. G. OVERBERGER
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 1, NEW YORK A. E. BORCHERT

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[4] A. T. Blomquist and P. R. Taussig, THIS JOURNAL, **77**, 6399 (1955).

[5] A. T. Blomquist and P. R. Taussig, *ibid.*, **79**, 3505 (1957).

[6] J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949).

[7] Gas phase chromatography.

[8] H. Adkins and S. H. Watkins, THIS JOURNAL, **73**, 2184 (1951).

[9] G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., H. Gilman, Ed., 1941, p. 183.

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## BISACRYLONITRILE NICKEL BISTRIPHENYLPHOSPHINE[1]

*Sir:*

In a recent paper[2] the discovery of a new class of highly reactive π-complexes of nickel with α-substituted olefins was described and exemplified for bisacrylonitrile nickel, $Ni(CH_2{=}CH{-}CN)_2$ (I). Due to extensive changes in the vinyl region and the presence of one practically unchanged nitrile band in the infrared spectrum of I[3] a structure was proposed in which the π-electrons of the double bond of the two acrylonitrile molecules were assumed to take part in the bonding, thus leading to the unusual coördination number of two for a zerovalent nickel complex. The nature of bonding between the metal and the olefinic ligand can be understood by applying the view of bonding of ethylene to a transition metal by Dewar[4] and Chatt.[5] Whereas vinylogs with electron donating α-substituents are not suitable as ligands, a sufficient bond stabilization is attained through the introduction of the strongly electronegative nitrile group. The effect of this substituent can be seen in that it lowers the energy levels of the antibonding π*-orbitals of the olefinic double bonds and thus facilitates the back-donation of electrons from the nickel atom. The combined effects of electron-donation to and back-donation from the nickel atom may lead to a rehybridization at the carbon atoms and thus to metal–carbon bonds with partial σ-character. In this respect the conditions of bond formation appear to be similar to a recently prepared bis-tetrafluoroethylene complex of iron carbonyl.[6] A zerovalent nickel complex with the coördination number of two would involve a $3d^{5}4sp$ configuration. A necessary requirement for such an electron distribution would be the possibility of filling the two empty 4 p orbitals with the electron pairs of two additional ligands to produce the stable $sp^3$ configuration. The catalytic activity of I in part can be attributed to this unusual coördinative unsaturation. So far, however, only a 1:1 triphenylphosphine adduct of I was isolated.[2] The preparation of a bistriphenylphosphine adduct of I now has been successful through reaction of I with excess of triphenylphosphine in diethyl ether in a specially designed apparatus in which all necessary operations were performed under exclusion of of oxygen. After filtration of the reaction solu-

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[1] Paper II on Bisacrylonitrile Nickel and Related Complexes.

[2] G. N. Schrauzer, THIS JOURNAL, **81**, 5310 (1959).

[3] A detailed description of the infrared spectra of I and related complexes in both the NaCl and CsBr region is in preparation.

[4] M. J. S. Dewar, *Bull. Soc. Chim.*, C 79, 18 (1951).

[5] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[6] K. F. Watterson and G. Wilkinson, *Chemistry and Industry*, 99 (1959).

tion and the removal of most of the solvent followed by the addition of *n*-hexane, the adduct separated in form of a yellow-red layer which subsequently crystallized. Bisacrylonitrile nickel bistriphenylphosphine, $Ni(CH_2{=}CH{-}CN)_2 \cdot 2P(C_6H_5)_3$ (II) forms yellow, somewhat fluorescent diamagnetic[7] crystals. When heated in a closed tube, II decomposes above 140° into nickel, triphenylphosphine and acrylonitrile. It is soluble in ether, benzene, acetone and alcohol but only sparingly soluble in *n*-hexane. It can be recrystallized from a concentrated etheral solution upon addition of *n*-hexane. II is sensitive to oxygen though not pyrophoric; solutions, however, are almost instantaneously decomposed when brought into contact with air. *Anal.* Calcd. for II Ni, 8.52; P, 8.99; N, 4.06. Found; Ni, 8.69; 8.63; P, 9.03; 9.20; N (Kjeldahl), 3.85%. Molecular weight calcd. 689.4; found (cryoscopic in benzene under nitrogen) 600 and 632. Dipole moment in benzene solution at 25°: 6.00 ± 0.07 *D*. The nitrile stretch is found at 2167 $cm.^{-1}$(Nujol) The slight shifts in comparison to the 1:1 triphenylphosphine adduct (CN: 2180 $cm.^{-1}$) and to I (CN: 2220 $cm.^{-1}$) can be attributed to an increasing positivation of the nitrile groups. The positivation of the nitrile groups can be the result of a decrease of electron back-donation into the double bonds due to the coördination of the nickel atom with triphenylphosphine. Bisacrolein nickel, $Ni(CH_2{=}CH{-}CHO)_2$ (*Anal.* Calcd. Ni, 34.37; acrolein, 65.63. Found: Ni, 34.5; acrolein, 63.2) appears to have a structure similar to I. It also forms adducts with triphenylphosphine. $Ni(CH_2{=}CH{-}CHO)_2 2P(C_6H_5)_3$ forms yellow-red, air-sensitive crystals which start to decompose above 140°. *Anal.* Calcd. Ni, 8.44; P, 8.91: found Ni, 8.34; P, 8.47. Details concerning these compounds will be reported later together with a description of further catalytic applications and reactions of representative members of this new class of nickel complexes.

INSTITUT FÜR ANORGANISCHE CHEMIE DER UNIVERSITAET
MUNICH, GERMANY
G. N. SCHRAUZER

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[7] Bisacrylonitrile nickel has a small paramagnetic moment of 0.68 Bohr magneton. Anomalous magnetic moments also were observed in the case of similar complexes (unpublished data). I am indebted to Mr. H. Olf of the Technische Hochschule at Munich for the magnetic measurements.

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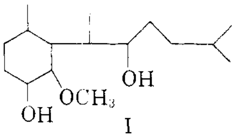
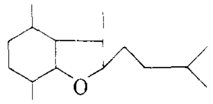
## THE STRUCTURE OF FUMAGILLIN; FORMATION OF TETRAHYDROFURAN RINGS BY METHOXYL CLEAVAGE AND THE SYNTHESIS OF A DEHYDROGENATION PRODUCT, 2-ISOAMYL-3,4-DIMETHYLBENZOFURAN[1]

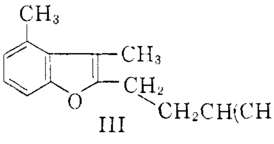
*Sir:*

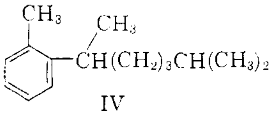
The preceding communication reported evidence allowing assignment of structures to fumagillin and its derivatives.[2] The present paper describes the conversion of a fumagillin derivative to a benzofuran, and proof of structure of the latter by synthesis.

Treatment of the desoxyhexahydroalcohol (I) with tosyl chloride–pyridine gives in good yield the perhydrobenzofuran II, with loss of methanol and cyclization; reduction of II with lithium aluminum hydride gives IIa, and this on selenium dehydrogenation gives a good yield of a mixture of the benzofuran III and the hydrocarbon IV.


I


II, R = OTs
IIa, R = H


III


IV

We have observed four other cases of cyclization similar to that above with different conditions and different derivatives related to I. The secondary hydroxyl group adjacent to the methoxyl in I is not involved in the cyclization, because a compound related to I, in which the secondary hydroxyl is etherified with tetrahydropyran, also cyclizes.[3] The formulation of II and related compounds is consistent with the n.m.r. spectra showing two protons on carbon adjacent to oxygen at τ6.2–6.5; in one derivative of II, where R is carbonyl, one proton has τ5.68, indicating that it is adjacent to the carbonyl and to the heterocyclic oxygen.

The proof of the perhydrobenzofuran ring in IIa by dehydrogenation to III and synthesis of the latter supports the structures suggested previously.

The structure of III was apparent from its analysis, ultraviolet, infrared and n.m.r. spectra. It was synthesized from 3-methyl-4,6-dichlorophenol (V) by alkylation with 3-bromo-6-methyl-2-heptanone to give VI, with subsequent cyclization by cold sulfuric acid, to give the crystalline 2-isoamyl-3,4-dimethyl-5,7-dichlorobenzofuran (m.p. 52°) in 43% over-all yield. The chlorines were removed by hydrazine 5% palladium on carbon in refluxing methyl cellosolve,[4] giving III in 94% yield. The bromo ketone was prepared by formation of the enol acetate[5] from 6-methyl-2-heptanone[6] with subsequent bromination and decomposition in methanol.[7]

The identity of synthetic III with that obtained by degradation was demonstrated by the complete

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[1] Supported in part by Grant E-1138 of the U. S. Public Health Service. Compounds described in this and the preceding communication have been characterized by elementary and group analysis, infrared spectra, optical rotation, ultraviolet absorption where applicable, and n.m.r. spectra in most cases.

[2] D S. Tarbell, R. M. Carman, D. D. Chapman, K. R. Huffman and N. J. McCorkindale, THIS JOURNAL, **82**, 1005 (1960).

[3] Analogy for this cyclization is provided by the formation of 2-methyltetrahydrofuran by lithium aluminum hydride treatment of $CH_3O(CH_2)_3CH(OBs)CH_3$ and $CH_3CH(OCH_3)(CH_2)_3OBS$: E. L. Allred, Ph.D. Dissertation, University of California, Los Angeles, 1959, pp. 146–160. We are indebted to Professor S. Winstein for communicating these results prior to publication. Other cyclizations accompanied by methoxyl cleavage are reported by S. Winstein, E. Allred, R. Heck and R. Glick, *Tetrahedron*, **3**, 1 (1958); *cf.* D. S. Noyce and H. I. Weingarten, THIS JOURNAL, **79**, 3093, 3098 (1957).

[4] W. L. Mosby, *Chem. and Ind.*, 1348 (1959).

[5] *Cf.* E. H. Man, F. C. Frostick, Jr., and C. R. Hauser, THIS JOURNAL, **74**, 3228 (1952).

[6] D. H. Hey and D. S. Morris, *J. Chem. Soc.*, 48 (1948).

[7] *Cf.* P. Z. Bedoukian, THIS JOURNAL, **67**, 1430 (1945).