(*Anal.* Calcd. for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 72.90; H, 9.51), then ester hydrolysis to give the diol VII and finally Sarett oxidation to give D-norandrostane-3,16-dione (VIII), m.p. 148.5–149.5° (*Anal.* Calcd. for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.80; H, 9.55). The infrared spectrum of VIII gives unmistakable evidence for the presence of a cyclobutanone ring (intense infrared band at 5.64 μ, in addition to cyclohexanone absorption at 5.83 μ).

For elaboration of hormone analogs, it would be desirable to have D-norsteroids with a Δ^4-3-ketone system. With this requirement in view, a similar reaction sequence starting from 16-oximinoandrost-5-ene-3β-ol-17-one[6] (IX) has been carried out. In this series, the irradiation of the corresponding diazo ketone (X), m.p. 200–201° (dec.), $[\alpha]_D - 187°$ (*Anal.* Calcd. for $C_{19}H_{26}O_2N_2$: C, 72.58; H, 8.34; N, 8.91. Found: C, 72.57; H, 8.46; N, 9.06), gave a mixture of acids. Diazomethane esterification and chromatography gave the methyl ester XI, m.p. 164–165° (*Anal.* Calcd. for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.44; H, 9.51). Proof that these Δ^5-compounds have structures analogous to those established in the saturated series is provided by the catalytic hydrogenation of XI which gave rise to the saturated ester XII identical in all respects (infrared, rotation, mixture m.p.) with an authentic sample of XII, m.p. 133–134°, $[\alpha]_D + 55°$ (*Anal.* Calcd. for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06. Found: C, 74.95; H, 10.02), obtained by treatment of III with diazomethane.

The important problems of establishing the stereochemistry of these D-norsteroids and of elaborating hormone analogs are currently receiving our attention, and we hope to be able to report the full details of these studies in a subsequent publication.

Acknowledgments.—We wish to express our thanks to Professor D. H. R. Barton, who encouraged us in this work, and to the Schering Corporation for generous gifts of starting materials.

[6] F. Stodola, E. C. Kendall and B. F. McKenzie, *J. Org. Chem.*, **6**, 841 (1941).

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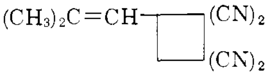
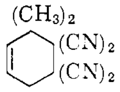
COMPETING CYCLOBUTANE FORMATION AND DIELS–ALDER REACTION

Sir:

We wish to report what appears to be the first observed instance of competitive formation of cyclobutane and cyclohexene adducts under mild conditions. The only previous instances of such competition are the condensation of tetrafluoroethylene with cyclopentadiene[1a] and the thermal dimerization of butadiene,[1b] both of which involve rather drastic conditions and are relatively unsuited for the determination of differences in reaction parameters. We have found that 4-methyl-1,3-pentadiene,[2] which will not undergo a normal Diels–Alder reaction with maleic anhydride, reacts overnight at room temperature with the more potent dienophile, tetracyanoethylene[3] to form in good yield a mixture of 3-(2-methylpropenyl)-1,1,2,2-tetracyanocyclobutane (I) and 3,3-dimethyl-4,4,5,5-tetracyanocyclohexene-1 (II). The cyclobutane (I) is isolated readily by ether extraction of the crude solid reaction product from tetracyanoethylene and excess methylpentadiene in tetrahydrofuran solution at room temperature,[3] to give a 69% yield of insoluble white crystals, m.p. 136–137° after recrystallization from benzene–cyclohexane (*Anal.* Calcd. for $C_{12}H_{10}N_4$: C, 68.5; H, 4.8; N, 26.6. Found: C, 68.8; H, 4.9; N, 26.1). The cyclohexene adduct (II) was obtained in 11% yield by passage of the ether extract through a short column of alumina, evaporation, recrystallization from benzene, cyclohexane and subsequent sublimation. The melting point of this compound appeared to lie in the range of 155–165°, but was obscured by sublimation and/or phase change even in a sealed tube (*Anal.* Calcd. for $C_{12}H_{10}N_4$: C, 68.5; H, 4.8; N, 26.6. Found: C, 68.8; H, 5.0; N, 26.2, by difference). Nuclear magnetic resonance and infrared spectra are in agreement with the assigned structures.[4]



I



II

In view of the possibility of these compounds arising from a common intermediate as postulated by Woodward[5] for the Diels–Alder reaction, a brief examination of the effect of synthesis conditions on the ratio of products was made. The crude product obtained in essentially quantitative yield at 2° (2400 min. time for color fading[3]) contained 12% II while at 57° (35 min.) 17% II was observed, as estimated by comparison of infrared spectra with known mixtures. The differences of enthalpy and entropy of activation are calculated to be 1.4 ± 0.5 kcal. (favoring I) and 1.4 ± 1.5 cal./°C. (favoring II), respectively. Reaction in cyclohexane (180 min. at 65°) gave a product containing more than 30% II in addition to a small amount of degradation products. Reaction in nitromethane[6] gave essentially pure I in 7 minutes at room temperature. The very small differences in activation parameters are to be expected if the two products are formed from a common high-energy intermediate or transition state, but are more likely fortuitous in view of the remarkable solvent effect. As can be seen above, the formation of I is more

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[1] (a) J. J. Drysdale, W. W. Gilbert, H. K. Sinclair and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 245, 3672 (1958); (b) H. W. B. Reed, *J. Chem. Soc.*, 685 (1951).

[2] G. B. Bachman and C. G. Goebel, *J. Am. Chem. Soc.*, **64**, 787 (1942).

[3] W. J. Middleton, R. E. Heckert, G. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

[4] Elaboration of the spectra of these and related compounds will be reported in a forthcoming publication.

[5] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[6] D. W. Wiley, private communication, has found that the rates for cyclobutane formation from tetracyanoethylene and electron-rich olefins vary over a 10^{5-6} range depending on solvent, with nitromethane being one of the fastest and cyclohexane one of the slowest.

than a hundred times faster in nitromethane than in tetrahydrofuran while several related Diels–Alder reactions[4] are accelerated by a factor of about two for the same solvents. If both I and II were formed from a common, rate-limiting transition state, as would be expected for an intermediate of the type proposed by Woodward for the Diels–Alder reaction collapsing in either of two possible directions, the total rate of reaction would be expected to show only the slight solvent effect which is generally characteristic of Diels–Alder reactions. Since this is not the case, it is necessary to conclude either that a change in mechanism has occurred with a change in solvent or else that I and II are formed in either solvent through separate rate-limiting transition states, quite likely involving, respectively, the *transoid* and *cisoid* configurations of the diene. Attempts at thermal interconversion as demonstrated by Woodward[5] and Roberts[7] in related systems (at the suggestion of Prof. Roberts) were thwarted by the limited thermal stability of I under conditions such that II was virtually unchanged. Decomposition appeared to be accompanied by gas evolution and formation of conjugated structures (strong absorption at 4.5, 6.1, 6.3 microns) and may be related to elimination reactions previously described for tetracyanocyclobutanes.[8]

Acknowledgments.—The author wishes to thank Dr. P. D. Bartlett, in whose laboratories several aspects of this reaction are being investigated, and Dr. J. D. Roberts for helpful discussions.

(7) R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2199 (1961).

(8) J. K. Williams, D. W. Wiley, B. C. McKusick, 139th ACS Meeting, St. Louis, Mo. (1961) abstracts p. 9-O.

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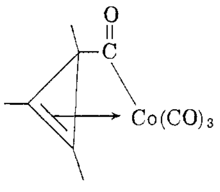
CYCLOPROPENYL COMPLEXES OF IRON AND COBALT

Sir:

π-Bonded metal complexes of the cyclic moieties C_nH_n are known for $n = 4, 5, 6, 7$ and 8. We attempted to prepare a complex containing a cyclopropenyl ligand π-bonded to a metal. Orgel[1] has mentioned the possibility of such complexes and noted the molecular orbitals involved. In practice, we have sought a complex of triphenylcyclopropenyl since triphenylcyclopropenyl bromide is synthesized readily[2] and is highly symmetrical.

Triphenylcyclopropenyl bromide reacted immediately with cobalt tetracarbonylate anion in acetonitrile at room temperature without gas evolution. Processing of the solution gave a 58% yield of yellow, air-stable crystals, m.p. 134–135.5°, soluble in organic solvents. *Anal.* Calcd. for $C_{25}H_{15}CoO_4$: C, 68.50; H, 3.45; Co, 13.4. Found: C, 68.26; H, 3.29; Co, 13.3. An infrared spectrum (KBr pellet) showed seven peaks in the 690–790 cm.$^{-1}$ region, an unsymmetrical doublet at 2015, 2080 cm.$^{-1}$ characteristic of the $Co(CO)_3$ group, and a band at 1710 cm.$^{-1}$ assigned to a ketonic carbonyl. The characteristic triphenylcyclopropenyl cation band at 1400 cm.$^{-1}$ was absent. These data suggest structure I or II for the product.



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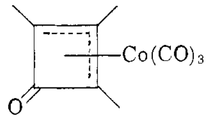

II

Similarly, $Fe(CO)_3NO^-$[3] reacted with triphenylcyclopropenyl bromide in methanol, producing a 14% yield of maroon crystals, m.p. 119–21°, somewhat less air-stable than the cobalt compound. *Anal.* Calcd. for $C_{24}H_{15}NFeO_4$: C, 65.94; H, 3.46; N, 3.20; Fe, 12.8. Found: C, 66.10; H, 3.99; N, 2.96; Fe, 13.3. An infrared spectrum showed a symmetrical doublet at 1950, 2005 cm.$^{-1}$ which was assigned to the carbonyl stretches in $Fe(CO)_2$, and an unsymmetrical doublet at 1720(s) and 1680 cm.$^{-1}$ (m) assigned to nitrosyl and ketonic carbonyl groups. Bands characteristic of the phenyl groups were present at 690 and 760 cm.$^{-1}$ with a shoulder at 750 cm.$^{-1}$. Structures analogous to I and II are possible for this complex, with Fe replacing Co and one CO replaced by NO.

Evidence in support of structure I was obtained by oxidizing the iron complex with 1,3-diphenylallyl chloride in hot toluene. This treatment gave yellow crystals of triphenylcyclopropenylium tetrachloroferrate (III), m.p. 253–254°, identified by comparison with the product obtained from triphenylcyclopropenyl bromide and $FeCl_3$ in ethanol. This suggests that the cyclopropene ring is intact in the complexes and therefore that structure I is correct.

These complexes are closely related to the expected π-$(C_6H_5C)_3$ complexes. In fact, the relation is the same as that existing between $RMn(CO)_5$ and $RCOMn(CO)_5$.[4] Complexes of cobalt tricarbonyl with acrylyl and 4-pentenoyl have been prepared.[5] These are similar to structure I in that bonding to cobalt occurs *via* a double bond and a bridging carbonyl.

(1) "An Introduction to Transition Metal Chemistry," L. F. Orgel, Editor, Methuen and Co., Ltd., London, 1960, pp. 153–157.

(2) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367, (1961).

(3) M. J. Hogsed, U. S. Patent 2,865,707 (1958).

(4) R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

(5) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

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RECEIVED NOVEMBER 10, 1961

PHOTOCHEMICAL REACTIONS OF 1,2-DIKETONES

Sir:

The photolysis of appropriate 1,2-diketones gives 2-hydroxycyclobutanones with striking selectivity and remarkable yields. Only 2-hydroxycyclobutanones, and none of the 1-alkanoylcyclo-