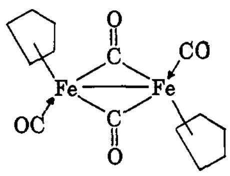
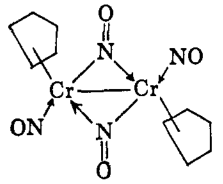


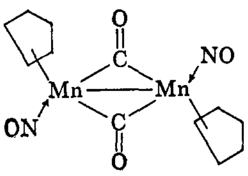
I



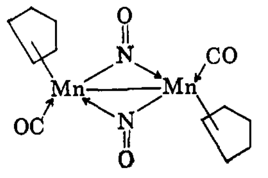
II

whereas the bridging carbonyl groups exhibit an infrared band at 1756 cm.$^{-1}$, *i.e.*, at a frequency of $\sim$90% of the frequency of the terminal carbonyls. In this connection it is of interest that the chromium derivative $[C_5H_5Cr(NO)_2]_2$ exhibits a band at 1672 cm.$^{-1}$ which may be attributed to the terminal nitrosyl groups and a band at 1505 cm.$^{-1}$ due to *bridging* nitrosyl groups. As in the case of the iron carbonyl derivative the frequency of the bridging nitrosyl groups is $\sim$90% of the frequency of the terminal nitrosyl groups. Moreover, it is of interest to compare the position of this band at 1505 cm.$^{-1}$ in $[C_5H_5Cr(NO)_2]_2$ with that of the band at 1510 cm.$^{-1}$ in $(C_5H_5)_3Mn_2(NO)_3$ assigned[1] to bridging nitrosyl groups. This infrared evidence indicates that the chromium complex $[C_5H_5Cr(NO)_2]_2$ has structure II. This structure is entirely analogous to the structure of $[C_5H_5Fe(CO)_2]_2$ (I) but with chromium atoms replacing iron atoms and nitrosyl groups replacing carbonyl groups.

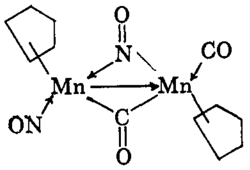
The situation with the manganese derivative $[C_5H_5MnCONO]_2$ is more complex due to possible structures with two bridging carbonyl groups (III), two bridging nitrosyl groups (IV), and possibly even one bridging carbonyl group and one bridging nitrosyl group (V).[7] The infrared spectrum of $[C_5H_5MnCONO]_2$ exhibits strong bands at 1956, 1781, 1707, and 1509 cm.$^{-1}$ which on the basis of the positions of the bands in $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_5Cr(NO)_2]_2$ may be assigned to terminal carbonyl groups, bridging carbonyl groups, terminal nitrosyl groups, and bridging nitrosyl groups, respectively. This suggests that $[C_5H_5MnCONO]_2$ either has structure V, is a mixture of isomers with structures III and IV, or is a mixture of III and/or IV with V. Attempts to separate $[C_5H_5MnCONO]_2$ into two or more isomers by chromatography on alumina were unsuccessful. It is possible, however, that III, IV, and V might be rapidly interconvertible in solution and that the products always isolated might be an equilibrium mixture of the three compounds.



III



IV



V

The compounds $[C_5H_5Cr(NO)_2]_2$ and $[C_5H_5MnCONO]_2$ are much less stable than $[C_5H_5Fe(CO)_2]_2$, decomposing slowly on prolonged storage at room temperature. The manganese compound is degraded by iodine to a carbony-free product under conditions where $[C_5H_5Fe(CO)_2]_2$ forms the iodide $C_5H_5Fe(CO)_2I$.[1] Sodium amalgam or sodium borohydride in *tetrahydrofuran* solution lead to very extensive destruction of $[C_5H_5MnCONO]_2$. The sensitivity of compounds of this type to strong reducing agents in ethereal solutions may explain the failure of Piper and Wilkinson to observe any $[C_5H_5Cr(NO)_2]_2$ as a product in the treatment of the halides $C_5H_5Cr(NO)_2X$ (X = Cl, Br, I) with ethereal Grignard reagents despite the fact that many of the reactions between $C_5H_5Fe(CO)_2I$ and the same Grignard reagents produced significant quantities of $[C_5H_5Fe(CO)_2]_2$.[9]

Further work on these and other nitrosyl derivatives is being carried out and will be described in forthcoming publications.

IR-9 machine with grating optics or on the Perkin-Elmer 112 machine with CaF_2 optics. Halocarbon oil mulls were used.

[7] In structure V the manganese–manganese bond instead of being analogous to the metal–metal bonds in structures I–IV may instead be regarded as analogous to the iron–iron bond in $C_4H_4Fe_2(CO)_6$ (ref. 8) and its derivatives where one metal atom donates a lone pair to the other metal atom.

[8] W. Hübel and E. Weiss, *Chem. Ind.* (London), 703 (1959); W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); A. A. Hock and O. S. Mills, *Proc. Chem. Soc.*, 233 (1958).

[9] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

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RECEIVED JUNE 24, 1963

Even-Electron Paramagnetic Chelates[1]

Sir:

Certain even-electron metal chelates of formula $M^{+2}(R^-)_2$ have been found to be paramagnetic. Electron spin resonance studies of these compounds show that they contain two unpaired electrons. All combinations in which M is Be, Mg, Ca, Sr, or Zn and R is 2,2′-bipyridine, 4,7-diphenyl-1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 2,2′-biquinoline, or 4,4′-diphenyl-2,2′-bipyridine have been investigated. The beryllium chelates were formed by the method of Coates and Green.[2] The other metal chelates were prepared by the reduction of R with a metal–mercury amalgam.

Solutions of most of the substances in rigid 2-methyltetrahydrofuran exhibited e.s.r. spectra characteristic of triplet molecules.[3-6]

The temperature dependence of the spectra indicate that the ground state is either triplet or lies within 100 cm.$^{-1}$ of the triplet state. The splittings in the $\Delta M = 1$ region of the magnetic resonance absorption lie in the range between 50 and 135 gauss. These splittings, which are due to the intramolecular spin–spin interaction, generally vary as would be expected if the spins reside singly on each ligand and are separated by M^{+2}. The zinc chelates, however, are an exception. In each series, apart from 2,2′-bipyridine,[3] the splitting for the zinc compound is largest. The increased dipolar interaction is probably accounted for by: (i) admixtures of states in which either one or two electrons are removed from the 3d shell of the zinc ion and are placed singly on either ligand and/or (ii) a spin polarization

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[1] This work has been supported by the United States Air Force under contract, the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and an equipment loan contract with the Office of Naval Research.

[2] G. E. Coates and S. I. E. Green, *J. Chem. Soc.*, 3340 (1962).

[3] The products of 2,2′-bipyridine with calcium and strontium were paramagnetic but were insoluble in 2-methyltetrahydrofuran and showed a single e.s.r. line. Solutions of zinc amalgam and 2,2′-bipyridine were not paramagnetic.

[4] M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **3**, 190 (1960).

[5] R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962).

[6] N. Hirota and S. I. Weissman, *Mol. Phys.*, **5**, 537 (1962).

of the zinc ion produced by an interaction of the spins on the ligand with an excited state of the zinc ion.

Another exception is that in all cases, within the experimental error (the maximum value is ±3%), the splittings for the beryllium and corresponding magnesium compound are the same. This may imply that in the beryllium chelates the ligands are kept apart, not by the size of the cation, but by the repulsion between the ligands.

In addition to presenting many possibilities for the study of electronic interactions, the compounds described here may be useful in synthetic procedures where it is desirable to have pairs of electrons available for reduction purposes.

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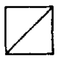
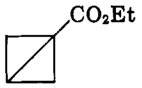
RECEIVED JUNE 28, 1963

Bicyclobutane

Sir:

Interest in the chemical and physical properties of highly strained molecules induced us to attempt the synthesis of the simplest bicyclic compound, [1.1.0]-bicyclobutane (**1**). Although two substances (**2**[1] and **3**[2]) possessing the carbon skeleton of bicyclobutane have appeared in the literature, for reasons of symmetry and simplicity the parent substance was uniquely suited for certain studies.

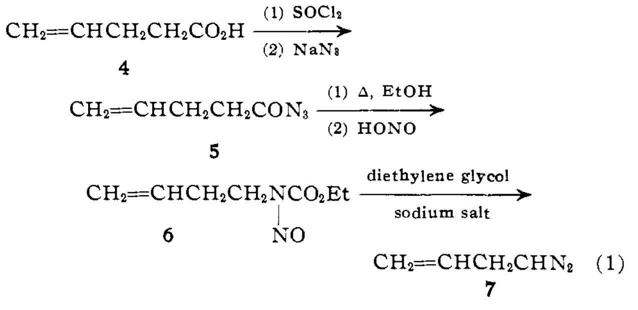

1



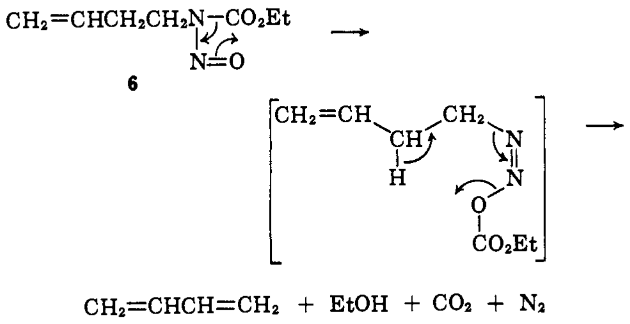
2


3

We hoped that intramolecular addition of a divalent carbon atom to an olefinic double bond, a process known to be successful when the reactive sites are well separated,[3] could lead to the highly strained system. Allyldiazomethane (**7**) was an appropriate substrate for this attempt. It was prepared from allylacetic acid (**4**) *via* the acid chloride, the azide (**5**), allylcarbinylurethan (b.p. 62–64° (1.5 mm.); infrared $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.90, 5.84, 6.10 μ; *Anal.* Found: C, 58.61, H, 9.05, N, 9.84), and N-nitrosoallylcarbinylurethan (**6**) (eq. 1).[4] Thermal decomposition of the nitroso compound **6** at temperatures above 150° gave butadiene, ethanol, carbon dioxide, and nitrogen as the only products detectable by v.p.c. A possible mechanism for the fragmentation is shown at the top of the next column.[5]



$$\underset{\mathbf{4}}{\mathrm{CH_2{=}CHCH_2CH_2CO_2H}} \xrightarrow[\text{(2) NaN}_3]{\text{(1) SOCl}_2} \underset{\mathbf{5}}{\mathrm{CH_2{=}CHCH_2CH_2CON_3}} \xrightarrow[\text{(2) HONO}]{\text{(1) }\Delta\text{, EtOH}} \underset{\mathbf{6}}{\mathrm{CH_2{=}CHCH_2CH_2}\underset{\mathrm{NO}}{\underset{|}{\mathrm{N}}}\mathrm{CO_2Et}} \xrightarrow[\text{sodium salt}]{\text{diethylene glycol}} \underset{\mathbf{7}}{\mathrm{CH_2{=}CHCH_2CHN_2}} \quad (1)$$



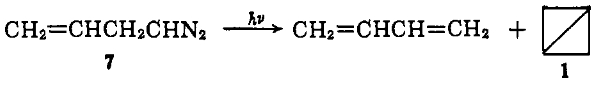
$$\mathrm{CH_2{=}CHCH{=}CH_2 + EtOH + CO_2 + N_2}$$

Because of its lability the nitroso compound was transformed without purification into allyldiazomethane by rapid addition to a vigorously stirred solution of excess diethylene glycol sodium salt in diethylene glycol at 0°. The system was maintained at a low pressure in order that the diazoalkane distil as it was formed into a trap cooled by Dry Ice. After three additional distillations in the cold, the orange diazo compound was stored in heptane solution at −78°.

Aliquots of the allyldiazomethane solution were added to acetic acid–heptane and the excess acid was titrated with methanolic sodium methoxide. Vapor phase chromatography indicated that butadiene as well as allylcarbinyl acetate was formed in the reaction with acetic acid[6]; the diene:ester ratio was markedly dependent upon the acid concentration. It was necessary to correct the titrimetric assay slightly for diene formation since this reaction consumes no acid. The yield of allyldiazomethane was calculated to be approximately 30% from the nitrosourethan, 16% from allylacetic acid.

A 5% solution of the diazo compound in heptane was photolyzed in Pyrex at −78° using a Hanovia 450-watt Type L lamp. The volume of nitrogen evolved was close to the theoretical, and v.p.c. analysis of the now colorless solution revealed in addition to heptane two compounds in the ratio 5:1. Not surprisingly, the major component was identified as butadiene by n.m.r. and mass spectral comparison with an authentic sample. Deuterium labeling studies demonstrated that most, but not all, of the butadiene arose by 1,2-hydrogen migration.

The striking similarity in mass spectra of the major and minor photolysis products established that the latter was isomeric with butadiene. Cyclobutene and methylenecyclopropane, both mechanistically plausible isomers, had in common with butadiene slightly shorter retention times on Ucon Polar than that of the unknown hydrocarbon. Critical evidence was provided by the n.m.r. spectrum ($\mathrm{CCl_4}$), which displayed a complex multiplet centered at 8.61 τ (relative area 2) and a "singlet" at 9.55 τ (relative area 1) that possessed fine structure under high resolution. Only the bicyclic structure for $\mathrm{C_4H_6}$ is consistent with these data.



$$\underset{\mathbf{7}}{\mathrm{CH_2{=}CHCH_2CHN_2}} \xrightarrow{h\nu} \mathrm{CH_2{=}CHCH{=}CH_2} + \mathbf{1}$$

Although the combined yield of butadiene and bicyclobutane was essentially quantitative, the content of bicyclic isomer in the photolysis mixture dropped to zero after a few days even at temperatures well below 0°, presumably as a result of radical polymerization or autoxidation. Thermal isomerization of the strained hydrocarbon to butadiene was complete within 4 min. at 150° but only slight during the same interval at 110°. At the latter temperature a small amount of cyclobutene accompanied the diene in the pyrolysate.

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[1] K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959).

[2] W. R. Moore, H. R. Ward, and R. F. Merritt, *ibid.*, **83**, 2019 (1961).

[3] G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961).

[4] P. A. S. Smith, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chapter 9, p. 337; W. W. Hartman and R. Phillips, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 464.

[5] E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1174 (1961).

[6] H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 120–136.