

scission reaction, being unimolecular, may be in the "fall-off" range when measured (see particularly ref 3d).

The unequivocal value of the heat of formation of allyl radicals is obtained from the third law enthalpy change for reaction 1. $K_{r,d}$ may be measured by determining equilibrium concentrations of A and BA, or by measuring both k_r and k_d under *exactly*⁴ the same reaction conditions. We have accomplished the latter by observing the decomposition of BA and of diallyl oxalate (DAO) in the same stirred-flow reactor VLPP⁵ apparatus. DAO decomposes to give 2A + 2CO₂ and the A's combine to yield BA, the appearance of which is monitored at both 67 and 54 amu.

Table I shows the current results. Several items are especially noteworthy. First, $K_{r,d}$ has been determined at temperatures such that it varies by 200-fold in a manner consistent with the expected parameters. Second, although we expect the rate constants determined here to be below the high-pressure limit, the value of k_r is as high, or higher, than we expect the high-pressure value to be.

The first point gives us some confidence in the results and the second may mean either that the high-pressure limit is attained or that there is some contribution from a heterogeneous recombination of allyl radicals. (The latter would not effect the value of $K_{r,d}$ since, of course, diallyl decomposition would be similarly affected.)

The value of 9.6 kcal/mol for ARE may be uncertain by as much as 2 or 3 kcal/mol, and this result will be refined with continued experiment, but it must surely lay to rest any thought that ARE is much greater than 12 kcal/mole!

Acknowledgment. This work was supported in part by Contract NAS7-472 with the National Aeronautics and Space Administration. We thank Dr. G. Neil Spokes and Mr. R. Jackson for help in the design and construction of the apparatus. Professor D. G. L. James suggested that DAO would be a good source of allyl radicals and kindly supplied us with a preprint of his own work on the high-pressure pyrolysis of DAO.

(4) Both k_r and k_d may be pressure dependent, but not their ratio, if k_r and k_d are determined under the same conditions.

(5) S. W. Benson and G. N. Spokes, *J. Am. Chem. Soc.*, **89**, 2525 (1967).

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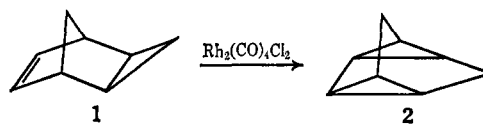
Received January 8, 1969

Coordination and Transition Metal Catalyzed Ring Opening of Some Hydrocarbons Containing Condensed Cyclopropane Rings

Sir:

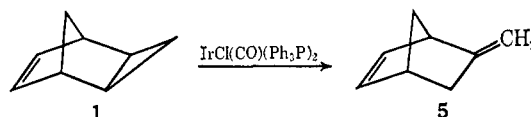
Previously¹ we have reported on the valence isomerization of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (**1**) into tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (**2**) in the presence of catalytic amounts of Rh₂(CO)₄Cl₂.

(1) H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *J. Am. Chem. Soc.*, **91**, 218 (1969).

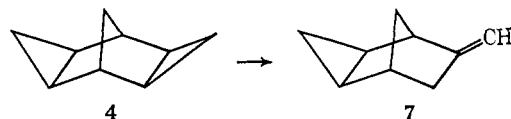


The isomeric *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (**3**) fails to undergo a similar reaction, which was attributed to the fact that the valence isomerization requires a simultaneous coordination of the hydrocarbon *via* the cyclopropane ring (edgewise) and the double bond.

In this communication we report on the interaction of other transition metal complexes with the hydrocarbons **1** and *exo,exo*-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane (**4**). We found that in the presence of catalytic amounts of IrCl(CO)(PPh₃)₂, **1** rearranges quantitatively to 5-methylenebicyclo[2.2.1]hept-2-ene (**5**) upon heating at 130° in benzene. The ring opening was very selective;

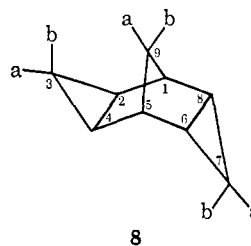


no traces of **2** and of bicyclo[3.2.1]octa-2,6-diene (**6**) could be detected. Under similar conditions **4** rearranges to *exo*-6-methylenetricyclo[3.2.1.0^{2,4}]octane (**7**). The structural assignment of **7** was based on its



nmr spectrum which shows the characteristic pattern of an *exo*-fused cyclopropane ring² and the presence of two signals for the methylene group at 4.95 and 4.70 ppm (compare **5**, 4.93 and 4.65 ppm from TMS).

Opening of the cyclopropane ring in **7** was not observed; the stability of **7** can again be ascribed to its inability to coordinate as a bidentate. For similar reasons, the *endo* isomer **3** and *exo,endo*-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]octane (**8**)³ fail to react at 130° using IrCl(CO)(PPh₃)₂.



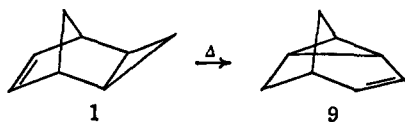
The thermal isomerization of **1** yields a different product. Compounds **1** and **4** are stable for at least 16 hr at 200°. Simmons reports that **1** is converted at 240° into tricyclo[3.2.1.0^{2,7}]oct-3-ene (**9**).⁵

(2) R. E. Pincock and J. Haywood-Farmer, *Tetrahedron Letters*, 4759 (1967).

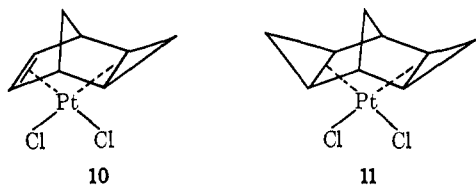
(3) The hydrocarbons **1**, **4**, and **8** are prepared according to the Simmons-Smith procedure⁴ and purified by preparative glpc. For nmr data of **1** and **4** see ref 1; nmr for **8** (ppm from TMS): H-1,5, 2.25, H-2,4, 0.70, H-3a, -0.08, H-3b, 0.32, H-6, 8.7a,7b, 1.25-1.47, H-9a, 0.95, H-9b, 0.59; $J_{2-3a} = 7.2$ cps, $J_{2-3b} = 3.2$ cps, $J_{3a-3b} = 6.5$ cps, $J_{6-9a} = 2.0$ cps, $J_{1-9a} < 1.0$ cps, $J_{9a-9b} = 10.5$ cps.

(4) S. D. Koch, R. M. Kliss, D. V. Lopiekes, and R. J. Wineman, *J. Org. Chem.*, **26**, 3122 (1961); H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(5) H. E. Simmons, quoted (in ref 15) by H. Prinzbach, W. Eberbach, M. Klaus, G. V. Veh, and U. Scheidegger, *Tetrahedron Letters*, 1681 (1966).



The catalytic activity of a number of other transition metal complexes was also studied. $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, Cu_2Cl_2 , $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, $(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2$, $\text{IrHCl}_2(\text{PPh}_3)_3$, and $\text{Rh}_2(\text{nor-C}_7\text{H}_8)_2\text{Cl}_2$ were found to be inactive. With $[(\text{C}_2\text{H}_4)_2\text{PtCl}_2]$ or $\text{K}[(\text{C}_2\text{H}_4)\text{PtCl}_3]$ **1** and **4** form the insoluble, stable pale yellow complexes **10** and **11**, respectively. The structures of these com-



plexes⁶ follow from elementary analyses, the absence of the uncoordinated $\text{C}=\text{C}$ stretching frequency for **10** and the presence of a terminal $\text{Pt}-\text{Cl}$ bond at 355 cm^{-1} , and from the quantitative displacement of coordinated **1** and **4** by reaction with bicyclo[2.2.1]hepta-2,5-diene.

Complex **11** did not give rise to the formation of tetracyclo[3.3.1.0^{2,8}.0^{4,6}]nonane (triassterane) upon being heated.

(6) Edgewise coordination of cyclopropane derivatives toward platinum has been reported previously by Mason⁷ and Irwin and McQuillin.⁸

(7) N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, *Chem. Commun.*, 396 (1966).

(8) W. J. Irwin and F. J. McQuillin, *Tetrahedron Letters*, 1937 (1968).

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New Reactions of Phenyl(bromodichloromethyl)mercury. Preparation of Perchlorothiirane

Sir:

Dichlorocarbene is known to be an electrophilic reagent, and there are quite a few of its reactions which can be understood best in terms of initial CCl_2 interaction with a lone pair atom present in the compound undergoing reaction.¹ The previously reported² reaction of dichlorocarbene (*via* sodium trichloroacetate) with di-*t*-butyl disulfide, which gives $\text{Me}_3\text{CSSCHCl}_2$ and isobutylene, presumably *via* CCl_2 attack at sulfur, suggested to us that a study of the reactions of dichlorocarbene with other sulfur compounds, including elemental sulfur itself, might be of interest. In its reaction with sulfur, electrophilic attack by CCl_2 at a sulfur atom might be expected to result in opening of the S_8 ring and ultimately in the formation of thiophosgene.

Phenyl(bromodichloromethyl)mercury³ was used as the dichlorocarbene source^{4,5} during the present study.

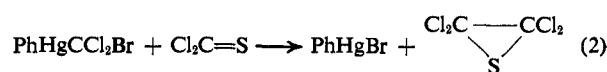
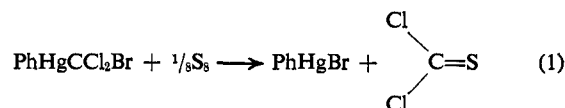
(1) (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 8; (b) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, Chapter 3.

(2) S. Searles, Jr., and R. E. Wain, *Tetrahedron Letters*, 2899 (1965).

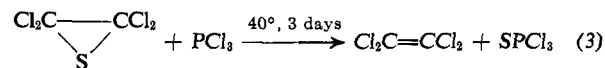
(3) D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).

(4) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

A reaction of 10 mmol of this mercurial with 0.16 g (5 mg-atoms of S) of S_8 in 30 ml of dry benzene under nitrogen at 70° for 1 hr resulted in the formation of phenylmercuric bromide in 93% yield. Concentration of the yellow filtrate at 14 mm to remove solvent was followed by trap-to-trap distillation of the residue *in vacuo*. Gas-liquid partition chromatographic (glpc) analysis (20% Dow Corning DC 200 silicone oil on 80-100-mesh WAW DMCS) of the distillate showed the presence of small amounts of benzene and tetrachloroethylene as well as of a third component. The latter was not the expected thiophosgene; its combustion analysis (C, Cl, S) and its mass spectrum showed it to be the as yet unknown 2,2,3,3-tetrachloro-1-thiirane (perchlorothiirane) (34% yield, by glpc). The formation of this product is understandable in terms of CCl_2 addition to the $\text{C}=\text{S}$ bond of the initially formed thiophosgene (eq 1 and 2). Perchlorothiirane is a colorless,



malodorous liquid, bp $36\text{--}38^\circ$ (0.1 mm), which is stable at room temperature for moderate lengths of time. On long standing at room temperature or on mild heating it turns yellow. It can be purified by glpc (DC 200 column at 90°). Its thermolysis at 150° (10 min) gives tetrachloroethylene and elemental sulfur. Quantitative desulfurization of perchlorothiirane is accomplished by reaction with phosphorus trichloride in slight excess under mild conditions (eq 3). On the



other hand, its reaction with triphenylphosphine in ether at room temperature was more complex. Triphenylphosphine sulfide was isolated in 46% yield, but tetrachloroethylene was formed in only trace amounts, and the reactants were converted mostly to intractable, resinous materials.

The fragmentation of perchlorothiirane in the mass spectrometer at 70 eV gave the chlorinated equivalents of thiirane itself:⁶ $\text{C}_2\text{Cl}_4\text{S}^+$ (17.5), $\text{C}_2\text{Cl}_3\text{S}^+$ (29.8), $\text{C}_2\text{Cl}_2\text{S}^+$ (62.9), CCl_2S^+ (3.2), C_2ClS^+ (12.3), CClS^+ (100.0), Cl_2S^+ (0.58), S^+ (3.2), C_2Cl_4^+ (78.8), C_2Cl_3^+ (46.2), C_2Cl_2^+ (26.8), C_2Cl^+ (8.7), CCl_3^+ (21.0), CCl_2^+ (23.5), and CCl^+ (21.7). Its infrared spectrum (liquid film) showed absorptions at 1145 (s), 1110 (w), 920 (sh), 910 (w), 835 (sh), 815 (s), 770 (w), 750 (s), 745 (sh), 705 (w), 675 (s), 670 (sh), and 650 cm^{-1} .

The ready occurrence of the reaction shown in eq 2 was demonstrated in a reaction of 27 mmol each of $\text{PhHgCCl}_2\text{Br}$ and thiophosgene under nitrogen in benzene at 40° for 3 days. The yields of phenylmercuric bromide and perchlorothiirane were 92 and 36%, respectively.

(5) D. Seyferth in "Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research. IX. Organometallic Compounds," Robert A. Welch Foundation, Houston, Texas, 1966, pp 89-135 (review).

(6) E. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **65**, 1177 (1961).