

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!

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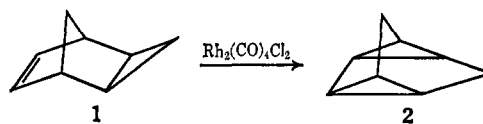
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Coordination and Transition Metal Catalyzed Ring Opening of Some Hydrocarbons Containing Condensed Cyclopropane Rings

Sir:

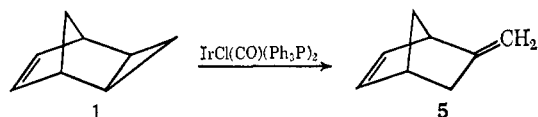
Previously¹ we have reported on the valence isomerization of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (1) into tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (2) in the presence of catalytic amounts of Rh₂(CO)₄Cl₂.

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

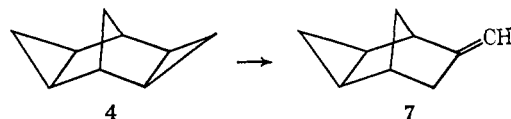


The isomeric *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (3) fails to undergo a similar reaction, which was attributed to the fact that the valence isomerization requires a simultaneous coordination of the hydrocarbon *via* the cyclopropane ring (edgewise) and the double bond.

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;

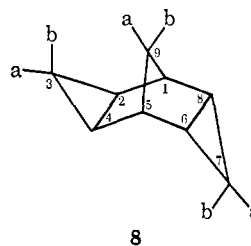


no traces of 2 and of bicyclo[3.2.1]octa-2,6-diene (6) could be detected. Under similar conditions 4 rearranges to *exo*-6-methylenetricyclo[3.2.1.0^{2,4}]octane (7). The structural assignment of 7 was based on its



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).