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TRANSITION METAL CATALYSED CYCLOPROPANATION OF OLEFINS

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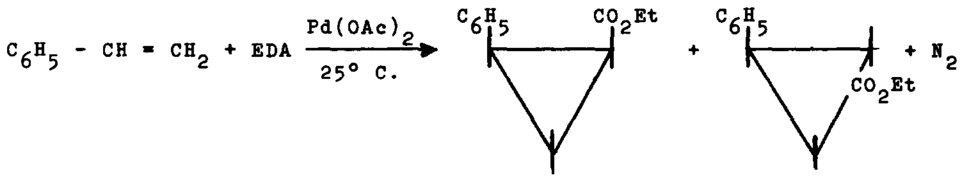
The metal-catalysed decomposition of diazoalkanes is a well-known reaction which has been the subject of several recent investigations (1-5). In particular, *MOSER*, studying the decomposition of *ethyl diazoacetate (E.D.A.)* in cyclohexene with various phosphite-copper (I) catalysts, has proposed (6) a cyclopropanation mechanism involving a carbene-metal-olefin complex.

We now wish to report a palladium-catalysed cyclopropanation of olefins which can be practically quantitative even under very mild thermal conditions.

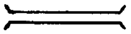
The model system selected for this study in homogeneous catalysis is shown in Eq. 1.



Palladium dichloride, rhodium trichloride and tris (triphenylphosphine) rhodium (I) chloride are also able to catalyse this reaction although being definetely less effective than palladium acetate.

Both, this striking rate enhancement and the ligand influence on the stereochemistry of the reaction would be consistent with a coordination mechanism; e.g., the trans/cis isomeric ratio in Eq. 1 decreases from 2,0 (no ligand) to 1,0 under addition of 3 moles of triphenylphosphite per mole of palladium acetate.

The model reaction has been extended to various diazocompounds and olefins with satisfactoring yields : some of these results are summarized in the following table.

R_2CN_2		Diazo/Pd(OAc)$_2$	T°C	Yield
N_2CH_2 (a)	Ph CH = CH_2	250	0	90 (7)
N_2CHCO_2Et	Ph CH = CH_2	200	25	96 (8)
N_2CHCO_2	PhC(CH_3) = CH_2	200	25	42 (b)

a) Gazeous CH_2N_2 produced by the procedure of TH.J. DEBOER and H.J. BACKER, Recueil 73, 229 (1954)

b) Boiling point 114-116° C. under 5 mm.

Further work is in progress to define the mechanistic and preparative implications ot these systems.

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REFERENCES.

1. E. MÜLLER, B. ZECH and H. KESSLER, Fortchr. Chem. Forsch, 7, 128 (1966).
2. H. NOZAKI, S. MORIUTI, M. YAMABE and R. NOYORI, Tetrahedron, 24, 3655 (1968).
3. R.K. ARMSTRONG, J. Org. Chem., 31, 618 (1966).
4. I. MORITANI, Y. YAMAMOTO, H. KONISHI, Chem. Com., 1457 (1968).
5. B.W. PEACE and D.S. WULFMAN, Tetrahedron Letters, 3799 (1971).
6. W.R. MOSER, J. Am. Chem. Soc., 91, 1135, (1969)
   ibid, 91, 1141 (1969).
7. H.E. SIMMONS and R.D. SMITH, J. Am. Chem. Soc., 81, 4256 (1959).
8. E. BÜCHNER and J. GERONIMUS, Ber., 36, 3782 (1903).