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Tetrahedron Letters No. 15, pp 1465 - 1466, 1972. Pergamon Press. Printed in Great Britain.

# TRANSITION METAL CATALYSED CYCLOPROPANATION OF OLEFINS

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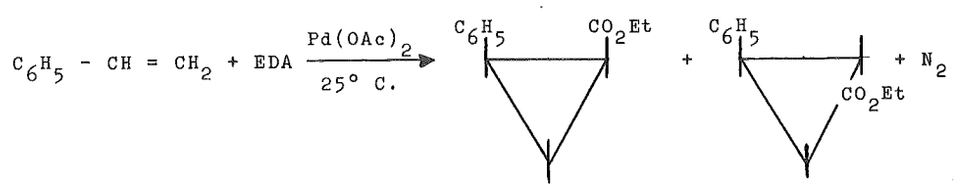
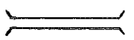
(Received in UK 23 February 1972; accepted for publication 2 March 1972)

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.

Acknowledgements : the authors are indebted to E.R.A. (Union Carbide Corp.) for its financial support and to Dr. Hans REIMLINGER for fruitfull discussions.

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Tetrahedron Letters No. 15, pp 1467 - 1468, 1972. Pergamon Press. Printed in Great Britain.

# A NOVEL REACTION OF 2-PHENACYLDIMEDONE WITH N,N-DISUBSTITUTED HYDRAZINES[1,2]

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(Received in UK 23 February 1972; accepted for publication 2 March 1972)

The reaction of acetonyldimedone (I) and 2-phenacyl-1,3-cyclohexanedione (II) with primary amines constitutes the basis for the synthesis of 'ketotetrahydroindoles' of type III[3] which have been further usefully exploited[4]. We wish to report that the reaction of 2-phenacyldimedone (IV) with N,N-dimethylhydrazine does not lead to the expected pyrrole V, but an anomalous product of structure VI. Addition of 2-3 molecular equivalents of the hydrazine to IV resulted in an exothermic reaction. The initially formed paste became a crystalline solid. The reaction was completed by adding alcohol and refluxing the mixture for ½ hr. The product, $C_{18}H_{22}N_2O$, m.p. 255-257°, was obtained in about 60% yield. Its U.V. (95% EtOH) [$\lambda_{max}$ 248, 276, 320 (inflex) nm (log ε 4.21, 4.25, 3.84)], IR (nujol mull) (bands at 1620, 3200 $cm^{-1}$) and NMR spectra (in DMSO-$d_6$ on Varian A60; TMS internal standard) [signals at δ 1.07 ppm (s, $-C-Me_2$), 2.27 (s, $CH_2$), 2.67 (8H, $NMe_2$, $CH_2$), 7.1-7.6 (m, 3 aromatic H), 7.7-8.0 (m, 2 aromatic H) and 11.2 (broad s, NH, washed out by $D_2O$)] were in agreement with structure VI. With N-aminomorpholine, IV likewise gave in 51% yield, the morpholino pyrrole VII, $C_{20}H_{24}N_2O_2$, m.p. 297-8°, forming an oxime, m.p. 285°(d), and with N,N-dibenzylhydrazine, the 3-dibenzyl-aminopyrrole VIII, m.p. 205-7°, in 43% yield. The U.V. spectra of VI, VII and VIII resembled those of the pyrrôles X and XI, which were prepared by standard procedures[3].

Catalytic debenzylation of VIII afforded IX, m.p.221-3°, whose diazonium sulfate on being heated in boiling alcohol, yielded X, m.p. 235-6°, thus confirming the structures of these novel products.