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Preliminary communication

REACTION OF DIPHENYLCARBENEPENTACARBONYLTUNGSTEN WITH ETHYL VINYL ETHER IN NON-POLAR SOLVENTS

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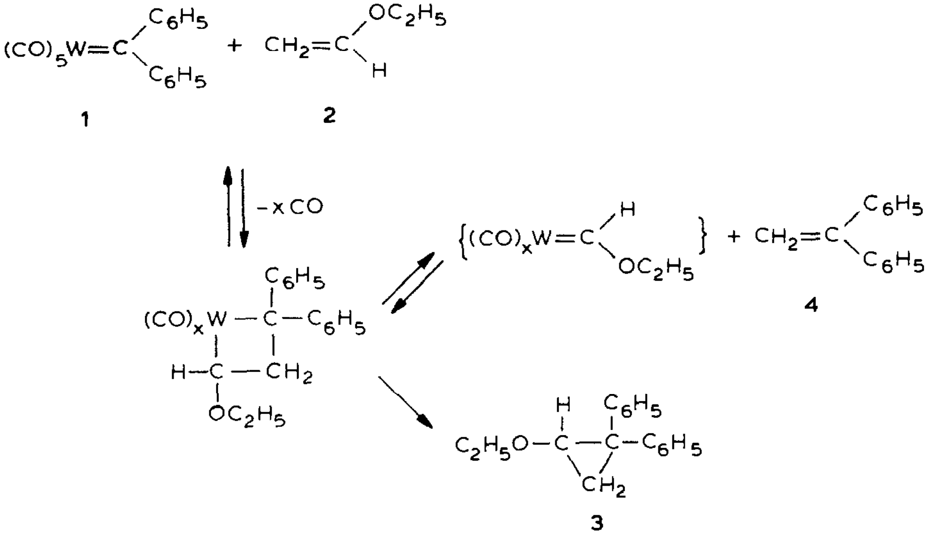
Summary

The reaction of $(CO)_5WC(C_6H_5)_2$ with ethyl vinyl ether in benzene or pentane yields predominantly the two metathesis products 1,1-diphenylethylene and 1-ethoxy-2,2-diphenylethylene along with some 1-ethoxy-2,2-diphenylcyclopropane.

The reaction of $(CO)_5Cr[C(OCH_3)(C_6H_5)]$ with ethyl vinyl ether (2) at 50°C to yield α-methoxystyrene was observed by Fischer and Dötz [1]. It represents the first example of a stoichiometric metathesis reaction of this



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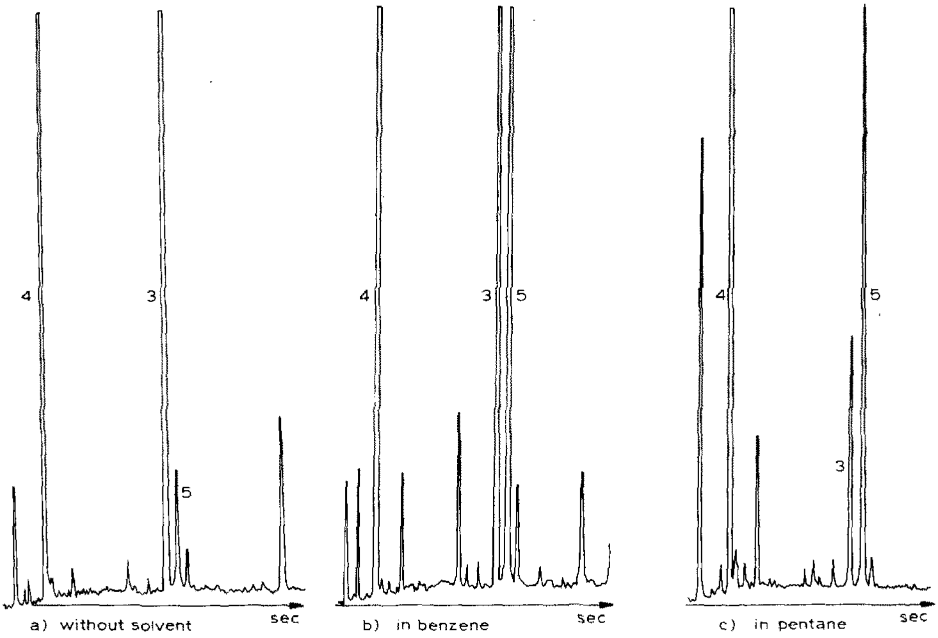
type. Casey studied the metathesis reaction of ethyl vinyl ether with the non-heteroatom-stabilized carbene complex $(CO)_5WC(C_6H_5)_2$ (1) [2]. The reaction (3 h, 37°C) yielded 65% of 1-ethoxy-2,2-diphenylcyclopropane (3) and 11% of 1,1-diphenylethylene (4). Casey proposed a mechanistic scheme involving a metallacyclobutane intermediate, to account for both the cyclopropanation and the metathesis [3,4].

The initial step may be a nucleophilic attack of a vinyl ether carbon on a carbene carbon atom, leading to the formation of a metallacyclobutane. The formation of the carbene complex $(CO)_xWC(OC_2H_5)H$ should be favoured since not only is the electronic stabilization likely to be greater than in the carbene complex $(CO)_xWC{=}CH_2$ which contains a negatively polarized carbene carbon atom, but in addition there is less steric hindrance in the metallacyclobutane intermediate.



a) without solvent

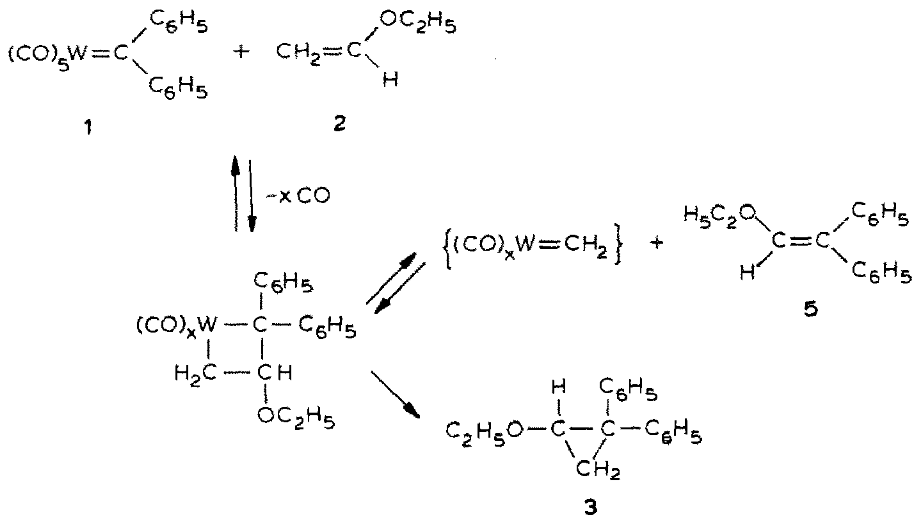
b) in benzene

c) in pentane

Fig. 1. GC Separation of the reaction products 3, 4 and 5. GC Carlo Erba HRGC with FID, column: quartz 11435 OV 1701 50 m. Temperature program: 100° C, 5° /min until 270° C.

In our search for cyclopropanation reactions brought about by metathesis catalysts we found that the composition of the products depends on the solvent used for the reaction of 1 with 2. When 2 is used as a polar solvent the main reaction product is cyclopropane (3) (61%), along with 4 (15%) and the previously unknown metathesis product 1-ethoxy-2,2-diphenylethylene (5) (2%). The formation of 5 can only be explained in terms of the opposite orientation in the metallacyclobutane intermediate.

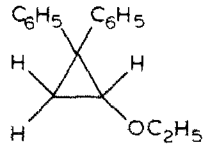
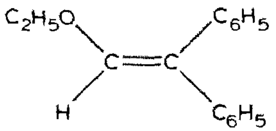
If the less polar solvents benzene and pentane are used, the proportions of the metathesis products 4 and 5 increase at the expense of the cyclopropane 3 [5]. (The analysis and identification of 3, 4 and 5 were by GC, GC/MS and GC/FT-IR. (Fig. 1, Table 1).



The results show that the reaction between 1 and 2, often used for a model reaction for metathesis, is more complicated than has been assumed previously.

TABLE 1

VARIATION OF THE RATIOS OF PRODUCTS 3, 4 AND 5 FROM THE REACTIONS OF $(CO)_5WC(C_6H_5)_2$ (1) WITH ETHYL VINYL ETHER (2) (a), WITHOUT SOLVENT (1/2, 1/200), (b) IN BENZENE (1/2, 1/20) AND (c) IN PENTANE (1/2, 1/20); CONDITIONS 4 h, 37°C.

	Reaction products (%)	(a) in 2	(b) in benzene	(c) in pentane
3		61	20	5
4	$(C_6H_5)_2C{=}CH_2$	15	46	43
5		2	11	15

References

1 E.O. Fischer and K.H. Dötz, Chem. Ber., 105 (1972) 3966.
2 C.P. Casey and T.J. Burkhardt, J. Am. Chem. Soc., 96 (1974) 7808.
3 C.P. Casey in H. Alper (Ed.), Transition Metal Organometallics in Organic Synthesis, Academic Press, New York, 1976, Vol. 1, p. 220.
4 C.P. Casey and M.C. Cesa, Organometallics, 1 (1982) 87.
5 Kinetic investigations of the reaction of 1 with isobutyl vinyl ether show the same trend but as yet no 1-isobutoxy-2,2-diphenylethylene has been detected. Personal communication from H. Fischer, Techn. Universität, München.