

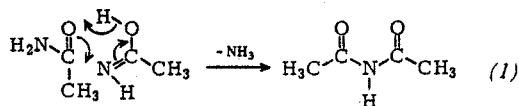
© Verlag Chemie, GmbH, Weinheim/Bergstr. 1979

Registered names, trademarks, etc. used in this journal, even without specific indication thereof, are not to be considered unprotected by law. Printed in Germany

## Intermolecular Ene Reactions in a High-Pressure/High-Temperature Flow Apparatus<sup>[\*\*]</sup>

By Jürgen Metzger and Peter Köll<sup>[\*]</sup>

In the thermal degradation of chitin in supercritical acetone<sup>[1]</sup> we were able to demonstrate the presence of large amounts of diacetamide (1), which can be formed by dimerization of the acetamide molecules in the sense of an ene reaction.

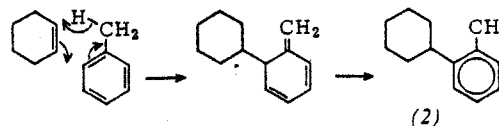


This finding encouraged us to investigate some ene reactions<sup>[2]</sup>, as example of the numerous types of thermal pericyclic reactions<sup>[3]</sup>, in the same high-pressure/high-temperature apparatus ("HP-HT" apparatus)<sup>[1]</sup>, which enables relatively unproblematical operation at pressures of up to ca. 500 bar and temperatures of up to ca. 700 K, and is readily built from commercially available HPLC and GC equipment. The apparatus offers all the advantages of a flow reactor, such as exceptionally rapid withdrawal of sensitive products from the reaction zone and the possibility of quickly changing the reaction parameters with slightest consumption of substances.

Whereas numerous intramolecular ene reactions, even with nonactivated enophiles, have already been reported<sup>[4]</sup>, intermolecular ene reactions generally require active enophiles<sup>[2]</sup>. It was predicted, however, that if the latter reactions were to be carried out at high pressures, besides the usual conditions employed for ene reactions, namely high temperatures and long reaction times, then intermolecular ene reactions with nonactivated enophiles should also be possible. Thus, the reactions carried out at high temperatures under pressure by Nemtsov et al.<sup>[5]</sup> in 1938 with the aim of polymerizing olefins

may be regarded as ene reactions. The reaction of acetylene as moderately active enophile with olefins at 623 K and 170 bar to give 1,4-dienes—likewise in a flow reactor—also demonstrates the influence of pressure in such reactions<sup>[6]</sup>.

In all the examples so far investigated by us (cf. Table 1) the expected products were seen to be formed in the overall main reaction. Even toluene was found to react as "deactivated" ene component with non-activated enophiles; reaction with cyclohexene afforded *o*-cyclohexyltoluene (2).



The yields quoted in Table 1 are not optimized and might easily be increased to preparatively satisfactory values by increasing the residence time of the reactants (incorporation

Table 1. Some intermolecular ene reactions with non-activated enophiles. Reaction conditions: 673 K, 450 bar, 10 min residence time, ene:enophile = 10:1, conversion based on enophile. Characterization of the products by GC-MS.

Ene	Enophile	Reaction product(s)	Conversion [%]
1-Hexene	1-Hexene	Mixture of isomeric dodecenes	5
Cyclohexene	Cyclohexene	3-Cyclohexylcyclohexene	4.5
Acetone	Cyclohexene	Cyclohexylacetone	0.5
Toluene	Cyclohexene	<i>o</i> -Cyclohexyltoluene	1.2
Toluene	Tolan	1,2-Diphenyl-1-tolyethylene	15

of a longer reaction capillary or reduction in the rate of flow of reactants). A typical example here is the synthesis of 3-cyclohexylcyclohexene from cyclohexene (see Experimentally). Such a dimerization apparently proceeds regioselectively, corresponding to the expected pericyclic mechanism. (With longer residence times, however, about 5% of the primary product isomerizes to 1-cyclohexylcyclohexene.) Thus, the thermal olefin-dimerization and the alkylation of toluene described here are superior to the catalytic methods, at least as far as regioselectivity is concerned.

### Experimental

Synthesis of 3-cyclohexylcyclohexene: Cyclohexene (20 g) is pumped through the "HP-PT" apparatus<sup>[1]</sup> at 673 K and 460 bar at a flow-rate of 0.12 ml/min and with a residence time of ca. 50 min. A 15-m long stainless steel capillary (O.D. 1.6 mm, I.D. 0.7 mm) can be used as reactor. Unreacted cyclohexene (16 g) is removed by distillation. The residue (3.4 g, 17%) mainly consists of pure 3-cyclohexylcyclohexene, which is further purified by distillation: b.p. 98°C/10 torr,  $n_D^{20} = 1.4912$  (b.p. 224°C/760 torr,  $n_D^{20} = 1.4941$ <sup>[7]</sup>). The IR, NMR, and mass spectra are consistent with the given structure.

Received: September 29, 1978 [Z 130a IE]  
German version: Angew. Chem. 91, 74 (1979)

[\*] Prof. Dr. P. Köll, Dr. J. Metzger  
Fachbereich 4 (Naturwissenschaften) der Universität  
Ammerländer Heerstr. 67–99, D-2900 Oldenburg (Germany)

[\*\*] Part 2 of High-Pressure/High-Temperature Reactions in a Flow Reactor.—Part 1: [1].

[1] P. Köll, J. Metzger, Angew. Chem. 90, 802 (1978); Angew. Chem. Int. Ed. Engl. 17, 754 (1978).

[2] H. M. R. Hoffmann, Angew. Chem. 81, 597 (1969); Angew. Chem. Int. Ed. Engl. 8, 566 (1969).

[3] J. B. Hendrickson, Angew. Chem. 86, 71 (1974); Angew. Chem. Int. Ed. Engl. 13, 47 (1974).

- [4] W. Oppolzer, V. Snieckus, *Angew. Chem.* 90, 506 (1978); *Angew. Chem. Int. Ed. Engl.* 17, 476 (1978).
- [5] M. S. Nemitsov, T. V. Nizovkina, E. A. Soskina, *J. Gen. Chem. (USSR)* 8, 1303, 1324 (1938); *Chem. Abstr.* 33, 4206 (1939).
- [6] N. F. Cywinski, *J. Org. Chem.* 30, 361 (1965).
- [7] W. Hüchel, R. Bross, O. Fechtig *et al.*, *Justus Liebigs Ann. Chem.* 624, 142 (1959).