HOMOGENEOUS METATHESIS OF FUNCTIONALISED ACETYLENES

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SUMMARY The first examples of functionalised acetylenes metathesis are described (1) using molybdenum carbonyl-phenol complexes gave the expected tolane (2) and disubstituted acetylene (3).

It took a long time to establish metathesis of functionalised olefins and we are inclined to think that it is also important for acetylenes. The heterogeneous and homogeneous acetylene metathesis is well known but there are no reports on the metathesis of acetylene carrying a functional group.

We here report the metathesis of functional phenyl-1 but -1 yne derivatives $(1)^4$ with molybdenum carbonyls as homogeous catalyst

The complex Mo(CO)_3 $(\text{C}_6\text{H}_5\text{ OH})^{2b}$ or $(\text{Mo(CO)}_6, \text{C}_6\text{H}_5\text{ OH} - 1,1)$ in refluxing octane with the acetate (1b) in contrast with non functionalised acetylene like the phenyltolyacetylene 2b did not lead to an equilibrium. In the presence of an excess of 4-chlorophenol the equilibrium was rapidly observed. This fact was attributed to the complexation of the acetate group on the molybdenum.

Methathesis of acetate (1b) in refluxing octane

| catalyst | Mo/phenol/(1b) | %(1) transformed (time, h) |
|-------------------------------------|----------------|----------------------------|
| $A = Mo(CO)_{3}(C_{6}H_{5}OH)$ | 1 - / 20 | 4 (6) |
| $B = Mo(CO)_{6}, C_{6}H_{5}OH$ | 1/1 / 20 | 4 (6) |
| $C = Mo(CO)_{6}, 4-C1-C_{6}H_{4}OH$ | 1/1 /20 | 5 (6) |
| $D = Mo(CO)_{6}, 4-C1-C_{6}H_{4}OH$ | 1/20 / 20 | 52 (2) |

The D system was used with the other acetylenes. A typical procedure for metathesis of (1b) serves as an illustration $Mo(CO)_6$ (0.5mM), 4-ClC $_6H_4OH$ (10mM) and (1b) (10mM) was refluxed under argon in octane (50ml) during 16h. The mixture was analysed by gas chromatography (silicone S 30 10 %, 180°C). The acetylenes were separated by preparative thin layer chromatography (SiO $_2$, ethyle acetate-cyclohexane 1/1 for 1b, 2 and 3b) and identified by their spectra (I.R., N.M.R.).

| | Metai | hes | sis of | func | tionalis | sed ac | etylenes | ; |
|----|--------|-----|--------|-------|----------|--------|----------------------|---|
| (D | system | ın | reflu | ing (| octane, | 16h o | r 4.5h ^{a)} | |

| Acetylene | % (1) transformed | $\begin{cases} \frac{(2) + (3)}{(1) \text{ transformed}} = Y \end{cases}$ |
|-----------|-------------------|---|
| 1a | 14 | 31 |
| 1b | 56 ^a | 98 |
| 1c | 37 | 91 |
| 1d | 4 | o |
| 1e | 58 | 98 |
| 1f | 20 | 81 |
| | I | 1 |

In the same conditions (2) and (3b) gave the same mixture as (1b). Clearly the equilibrium was obtained with (1b), (1c) and (1e). The metathesis of esters (1b) and (1e) was clean, only some traces of transesterification with the phenol were observed. Whereas the carboxylic acid (1d) did not undergo any metathesis surprisingly the alcohol (1a) reacted in a low yield (Y). 2 % of acid (1d) did not inhibit the metathesis of the acetate (1b). These results contrast with those obtained from the olefin metathesis where alcohol and acid are poisons for the catalyst. The low conversion and the low selectivity of the nitrile (1f) was due to a strong complexation of the cyano group on the molybdenum catalyst and isomerisation of (3f) occurred.

The application of functionalised acetylene metathesis in synthesis will be further explored on our laboratory.

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