Tetrahedron Letters No. 49, pp 4967 - 4968. 0040-4039/78/1201-4967$02.00/0

^{13}C TRACER STUDIES OF ALKYNES METATHESIS

A. Mortreux* and F. Petit
Laboratoire de Chimie Organique Appliquée, ERA CNRS 070458
Ecole Nationale Supérieure de Chimie de Lille, BP 40, 59650 VILLENEUVE D'ASCQ (France)
M. Blanchard
Laboratoire de Chimie XI, ERA CNRS 371, Faculté des Sciences
40, Avenue du Recteur Pineau, 86022 POITIERS Cédex (France)

Great interest has been devoted to the mechanism of the metathesis reaction of unsaturated hydrocarbons, and labeled olefinic molecules have been used to define whether this catalytic reaction proceeds via transalkylation or transalkylidenation, either in the homogeneous or in the heterogeneous phase[1].

An unsolved question in the course of our studies on the metathesis of alkynes

$$2\ R_1\text{-C}\equiv\text{C-}R_2 \rightleftarrows R_1\text{-C}\equiv\text{C-}R_1 + R_2\text{-C}\equiv\text{C-}R_2$$

with the homogeneous system $Mo(CO)_6$-PhOH[2,3], is whether a scission of the triple bond is involved during the catalytic process.

In order to obtain more information concerning this rearrangement, experiments have been carried out using ^{13}C labeled 1-phenyl-1-hexyne as starting material.

Preparation of 1-phenyl-1-hexyne-1 ^{13}C

Phenylacetylene-1 ^{13}C is first prepared from enriched ^{13}C barium carbonate according to a procedure previously described[4]. Alkylation of the sodium derivative by n-butyl-p-toluene sulfonate[5] gives the expected product Ph-C≡C-Bu (I) in which the ^{13}C acetylenic NMR shifts relative to TMS are as follows ($CDCl_3$ solution) : Ph-C_1≡ 80.69 ppm; ≡C_2-Bu 90.32 ppm (lit[6]: 83.1 and 92 ppm, converted using $\delta_{C_6H_6} = 128.7$).

The sp ^{13}C content in C-1 and C-2 can be evaluated from the intensities of the corresponding signals as 7.5 ± 0.1% and 1.1% respectively.

Catalytic Reaction

The catalytic reaction is carried out for 1 hour at 120°C in a sealed tube containing 0.6 g (3.5 mmol) of (I) dissolved in 2 ml of n-heptane, 13 mg of molybdenum hexacarbonyl (0.05 mmol, $\frac{C\equiv C}{Mo} \doteq 70$) and 0.87 g (5 mmol) of 4-bromophenol.

After cooling, the supernatant solution is washed with aqueous potassium hydroxide, and dried over magnesium sulfate.

Chromatographic analysis shows approximately equal amounts of 5-decyne (II, 21.9%) and diphenylacetylene (III, 22%), and 56.1% of I.

Spectroscopic Analysis and Results

The product was concentrated by evaporation and dissolved in $CDCl_3$. Direct ^{13}C NMR analysis of the reaction mixture was then performed on a WP 60 BRUCKER spectrometer.

Comparison between the observed spectrum (fig, B) and that of unlabeled diphenylacetylene (A) clearly shows that most of the enriched ^{13}C is localized on the diphenylacetylene sp carbon atoms (d), and on the C-1 atom of the starting material (e), the relative intensities between C-1 and C-2 remaining unchanged.

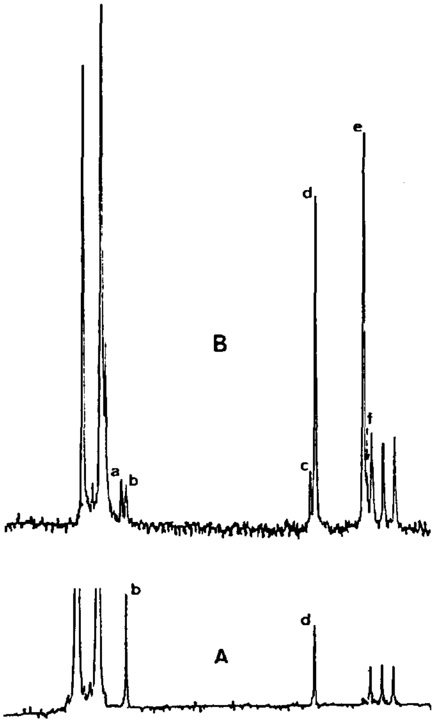
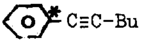
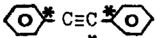


Figure.

^{13}C NMR spectra of unlabeled diphenylacetylene (A) and catalytic mixture from 1-phenyl-1-hexyne-1 ^{13}C (B)*.

Assignements in ppm relative to TMS :

	Carbon atom	δ
(a)		124.48
(b)		123.44
(c)	$Ph-C\equiv\overset{*}{C}-Bu$	90.32 (lit[6]:92)
(d)	$Ph-\overset{*}{C}\equiv\overset{*}{C}-Ph$	89.42 (lit[7]:90.7)
(e)	$Ph-\overset{*}{C}\equiv C-Bu$	80.69 (lit[6]:83.1)
(f)	$Bu-\overset{*}{C}\equiv\overset{*}{C}-Bu$	80.10 (lit[7]:79.9)

*The saturated carbon atoms have been omitted for clarity.

The ^{13}C content of the diphenylacetylene sp carbon atoms is evaluated from the ratio of the signals (d) and (b), which is 0.69 in the unlabeled compound, and 9.41 in the reaction product : if it is supposed that carbon (b) (α to the triple bond) is not affected during the catalytic process, and always contains 1.1% of ^{13}C, the ^{13}C content of the two sp carbon atoms in diphenylacetylene can then be estimated as 15%. The proximity of the signals (e) and (f) does not allow any accurate determination of the ^{13}C content in 5-decyne. However, as all the ^{13}C label is localized on the diphenylacetylene twice as much as in the starting material, it can be assumed that the reaction proceeds according to the following scheme :

$$2\ Ph-\overset{*}{C}\equiv C-Bu \rightleftarrows Ph-\overset{*}{C}\equiv\overset{*}{C}-Ph + Bu-C\equiv C-Bu$$

Conclusion

From these results, we can conclude that the alkylidyne R-C≡ moieties retain their identity during the catalytic process. Furthermore, they indicate that a scission of the triple bond occurs rather than a transalkylation process, since this would have led to a statistical distribution of the ^{13}C label among the three acetylenic compounds.

Whether this rearrangement occurs on the transition metal alone, or with the aid of the phenolic reagent[3] still remains an open question, for which further experiments are in progress.

Acknowledgments : We are grateful to Dr M. Guelton for helpful discussions and interpretations of NMR spectra obtained on facilities made available by Professor E. Derouanne in his laboratory (Namur, Belgium).

BIBLIOGRAPHY

1) For a recent review, sec J.J. ROONEY and A. STEWART, Catalysis (London), 1, 277 (1977)
2) A. MORTREUX, N. DY and M. BLANCHARD, J. Mol. Catal., 101 (1975/76)
3) A. MORTREUX, J.C. DELGRANGE, M. BLANCHARD and B. LUBOCHINSKY, J. Mol. Catal., 2, 73 (1977)
4) J. CASANOVA, M. GEISEL and R.N. MORRIS, Org. Prep. Proced., 1 (2) 81 (1969)
5) J.R. JOHNSON, A.M. SCHWARTZ and T.L. JACOBS, J. Amer. Chem. Soc., 60, 1882 (1938)
6) D.D. TRAFICANTE and G.E. MACIEL, J. Phys. Chem., 69, 1348 (1965)
7) J. BRANDT and W. DIETRICH, Magn. Res. Rel. Phenomena, Proc. Congr. Ampere 16th, 303 (1971)

(Received in UK 27 September 1978)