Tetrahedron Letters,Vol.23,No.43,pp 4419-4422,1982
Printed in Great Britain
0040-4039/82/434419-04$03.00/0

DISCRETE INTRODUCTION OF THE ELECTROPHILE AND NUCLEOPHILE IN Ad_E -REACTIONS OF DICOBALT HEXACARBONYL COMPLEXES OF CONJUGATED ENYNES.

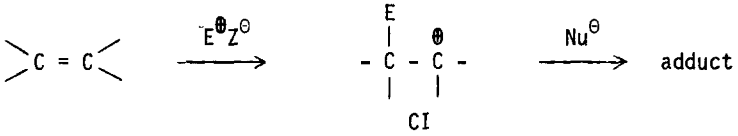
A. A. Schegolev* and W. A. Smit
Zelinsky Institute of Organic Chemistry, Leninsky Prospect 47
Moscow, USSR

Y. B. Kalyan and M. Z. Krimer*
Institute of Chemistry, Academicheskaya 3
Kishinev, USSR

R. Caple*
Department of Chemistry, University of Minnesota, Duluth
Duluth, Minnesota, USA 55812

Summary: The dicobalt hexacarbonyl complex of the enyne isopropenylacetylene (1) is effective in permitting stepwise Ad_E reactions to the double bond of 1 via stabilization of the intermediate carbenium ion.

We have been interested for some time in stepwise Ad_E reactions of alkenes where the electrophile and nucleophile could be introduced independently. A study of electrophilic reagents of the type $E^{\oplus}Z^{\ominus}$, where $Z^{\ominus}$ is a non-nucleophilic counterion, has shown that, in principle, it is possible to effect a discrete Ad_E -process but only under conditions where the carbenium ion intermediate (CI) exhibits significant stabilization under the reaction conditions.[1,2]

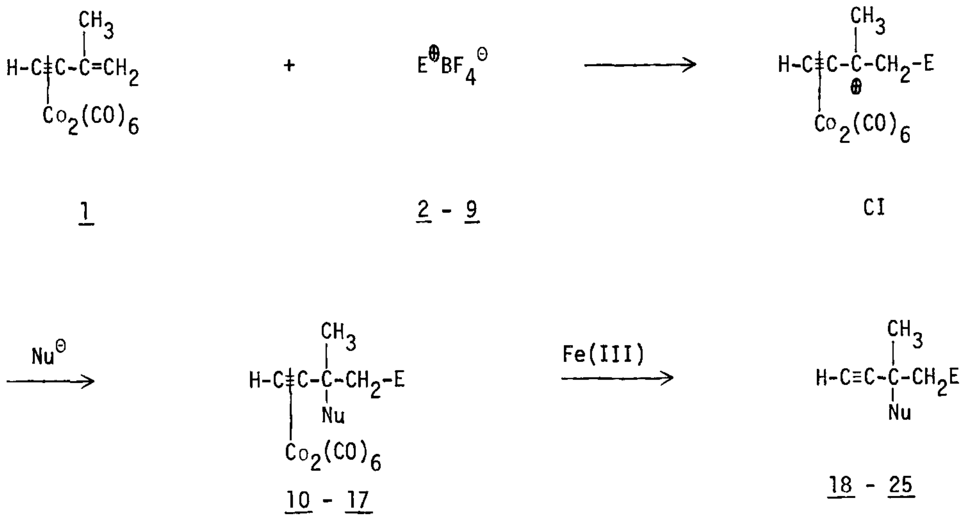


$$>C=C< \xrightarrow{E^{\oplus}Z^{\ominus}} \underset{\text{CI}}{-\overset{E}{\underset{|}{\overset{|}{C}}}-\overset{\oplus}{\underset{|}{C}}-} \xrightarrow{Nu^{\ominus}} \text{adduct}$$

The origin of the necessary stabilization may arise either in the electrophile or the alkene if they permit substantial delocalization of the positive charge. Bridged CI of the type halonium[3], mecurinium[3], or episulfonium ions[4] are known to be effective in this regard. With the episulfonium ions it is possible to carry out Ad_E reactions of alkenes with $RS^{\oplus}Z^{\ominus}$ reagents as a sequence of independent steps with the $RS^{\oplus}$ electrophile and a select "external" $Nu^{\ominus}$ being introduced separately.[4]

In the present study we wish to describe stabilization of a CI, formed upon an Ad_E reaction, that originates in the substrate itself. The approach is based on the known ability of transition metal complexes to enhance carbenium ion stability.[5] In particular, the recent work of Nicholas et al[6] has shown that very stable propargyl cations can be obtained upon solvolysis of dicobalt hexacarbonyl (DCHC) complexes of a variety of propargyl derivatives or upon protonation of DCHC complexes of conjugated enynes. The latter route suggested to us the possibility of using DCHC complexes of enynes as a method for the discrete introduction of electrophiles via the Ad_E pathway.

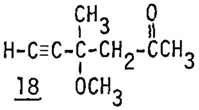
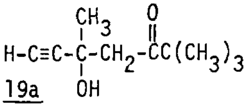
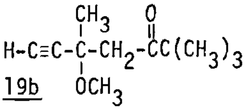
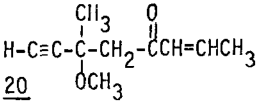
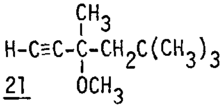
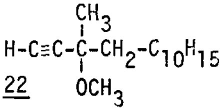
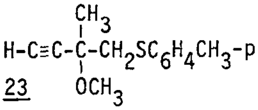
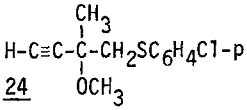
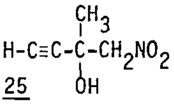
As a model compound we chose the DCHC complex of isopropenylacetylene (1),[7] and as electrophiles we chose cations of the type $RCOBF_4$, RBF_4, $ArSBF_4$, and NO_2BF_4 (see TABLE 1). The Ad_E reactions of these cations, in fact, proceed to provide the same type of stable cationoid intermediate that was observed upon protonation of I.[6,7] The interaction of the CI complex with a nucleophile, and a subsequent decomplexation, lead to products of net addition of $E^{\oplus}$ and $Nu^{\ominus}$ across the double bond of 1 (see TABLE 1).[8,9] No evidence of a side reaction was observed in any of these examples.[10]



where $E^{\oplus} = R\overset{\oplus}{C}O, R^{\oplus}, ArS^{\oplus}, NO_2^{\oplus}$ and $Nu^{\ominus} = {}^{\ominus}OH, {}^{\ominus}OCH_3$

The results in TABLE 1 confirm the utility of this two-step Ad_E sequence as a method of introducing the $E^{\oplus}$ and $Nu^{\ominus}$ addends in a distinct manner and, furthermore, show that the nature of $E^{\oplus}$ and $Nu^{\ominus}$ can be varied independently and over wide limits. The results suggest an obvious synthetic potential in so far as they illustrate the possibility of selective and various functionalizations of a double bond in a conjugated enyne. It is also evident that the present procedure, using 1 as an easily accessible C_5 prenyl synthon, opens new perspectives in the

TABLE I

Electrophile[a] (as $E^{\oplus}BF_4^{\ominus}$)	Nucleophile (as SOH)	Adduct After Decomplexation	% Yield[d]
$CH_3\overset{\oplus}{C}O$ 2	$CH_3O^{\ominus}$	 $H\text{-}C{\equiv}C\text{-}C(CH_3)(OCH_3)\text{-}CH_2\text{-}C(=O)CH_3$ 18	65%
$(CH_3)_3C\overset{\oplus}{C}O$ 3	$HO^{\ominus}$	 $H\text{-}C{\equiv}C\text{-}C(CH_3)(OH)\text{-}CH_2\text{-}C(=O)C(CH_3)_3$ 19a	72%
$(CH_3)_3C\overset{\oplus}{C}O$ 3	$CH_3O^{\ominus}$	 $H\text{-}C{\equiv}C\text{-}C(CH_3)(OCH_3)\text{-}CH_2\text{-}C(=O)C(CH_3)_3$ 19b	64%
$CH_3CH{=}CH\overset{\oplus}{C}O$ 4	$CH_3O^{\ominus}$	 $H\text{-}C{\equiv}C\text{-}C(CH_3)(OCH_3)\text{-}CH_2\text{-}C(=O)CH{=}CHCH_3$ 20	78%
$(CH_3)_3C^{\oplus}$ 5	$CH_3O^{\ominus}$	 $H\text{-}C{\equiv}C\text{-}C(CH_3)(OCH_3)\text{-}CH_2C(CH_3)_3$ 21	90%
$C_{10}H_{15}^{\oplus}$ 6[b]	$CH_3O^{\ominus}$	 $H\text{-}C{\equiv}C\text{-}C(CH_3)(OCH_3)\text{-}CH_2\text{-}C_{10}H_{15}$ 22	94%
$p\text{-}CH_3C_6H_4S^{\oplus}$ 7	$CH_3O^{\ominus}$	 $H\text{-}C{\equiv}C\text{-}C(CH_3)(OCH_3)\text{-}CH_2SC_6H_4CH_3\text{-}p$ 23	70%
$p\text{-}ClC_6H_4S^{\oplus}$ 8	$CH_3O^{\ominus}$	 $H\text{-}C{\equiv}C\text{-}C(CH_3)(OCH_3)\text{-}CH_2SC_6H_4Cl\text{-}p$ 24	60%
$NO_2^{\oplus}$[b] 9	$HO^{\ominus}$	 $H\text{-}C{\equiv}C\text{-}C(CH_3)(OH)\text{-}CH_2NO_2$ 25	55%

---

a) The addition to the complex 1 was carried out at -60° in a 50:50 mixture of CH_2Cl_2 and $C_2H_4Cl_2$. Reaction times varied from 15 to 240 min.

b) 1-Adamantyl cation.

c) SO_2 employed as solvent.

d) isolated

synthesis of isoprenes. We are presently pursuing work in this direction.

REFERENCES AND NOTES

1. G. H. Schmid and D. Garrattin "The Chemistry of Double Bonded Functional Groups," S. Patai, Ed., Wiley, New York, 1977, Chap. 9.
2. (a) W. A. Smit, A. V. Semenovsky, O. V. Lybinskaya, T. N. Chernova, M. Z. Krimer, and V. F. Kucherov, Tetrahedron Lett., 1971, 33, 3101; (b) W. A. Smit, A. V. Semenovsky, O. V. Lybinskaya, and V. F. Kucherov, Dok. Acad. Sci., 1972, 203, 604.
3. (a) G. A. Olah, "Halonium Ions," Wiley-Interscience, New York, 1977; (b) G. A. Olah and S. Yu, J. Org. Chem., 1975, 40, 3638.
4. (a) W. A. Smit, M. F. Krimer, and E. A. Vorob'eva, Tetrahedron Lett., 1975, 29, 2451; (b) W. A. Smit, H. S. Zefirov, I. V. Bodrikov, and M. Z. Krimer, Accounts Chem. Res., 1979, 12, 282.
5. For a review see "Transition Metal Organometallics in Organic Synthesis," H. Alper, Ed., Academic Press, New York, 1976, 1, and 1978, 2.
6. S. Padmanabhan and K. M. Nicholas, J. Organometal. Chem., 1981, 212, 115, and previous references cited therein.
7. Obtained according to the procedure described in S. Padmanabhan and K. M. Nicholas, Synthetic Communications, 1980, 10, 503.
8. The reagents 2 - 8 were generated in situ by the following general exchange reaction, $E{-}Cl + AgBF_4 \rightarrow AgCl + E^{\oplus}BF_4^{\ominus}$ and NO_2BF_4, 9, was obtained from Columbia Organic Chemicals Company, Inc., South Carolina.
9. The structures of the adducts 10 - 17 were established by 'H NMR. The structures of the adducts 18 - 25 are also consistent with their spectral data and microanalyses.
10. Typical reaction conditions are those for the generation of the adduct 21. A mixture of $AgBF_4$ (1.5 mmol), 1 (1 mmol), and $(CH_3)_3CCl$ (1.5 mmol) in 7 ml of 50:50 $CH_2Cl_2/C_2H_4Cl_2$ was stirred at -60^{o} for 3 hours under Argon. Methanol (0.4 ml) was then added and stirring was continued for an additional 30 min. Workup involved the addition of $NaHCO_3$ solution, ether extraction, and purification by TLC. Decomplexation was carried out as reported in reference 9.

ACKNOWLEDGMENT

We are indebted to Professor V. I. Sokolov, Institute of Elemental Organic Chemistry, Moscow, USSR, for helpful suggestions.

(Received in USA 13 April 1982)