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ACYLATION OF ALKYNES BY CATIONOID REAGENTS WITH THE FORMATION OF CYCLOPENT-2-ENONE DERIVATIVES

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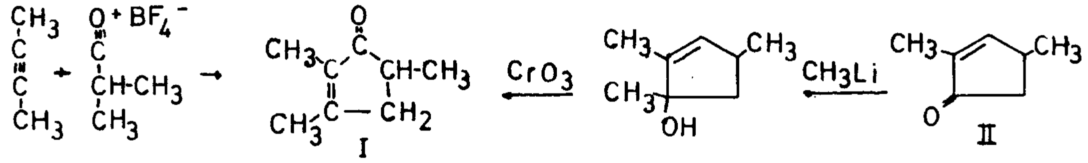
We have recently described the successful use of carbocationic reagents in electrophilic additions to the triple bond and demonstrated that vinyl cations, presumably formed as intermediates in these reactions, could be trapped even by such poor nucleophilic solvents as nitromethane /1/ or chlorobenzene /2/. These results encouraged us to undertake a more thorough investigation of the reactivity of these intermediates in different solvent systems.

Presently we wish to report a new and unusual reaction leading to the formation of cyclopent-2-enone derivatives, which was observed in several cases of alkyne acylation under the action of acyl tetrafluoroborates in non-nucleophilic solvents. Thus it was discovered that the reaction between butyne-2 and $(CH_3)_2$ $CHCOBF_4$ at $-60^{\circ}C$ in the mixed solvent system, CH_2Cl_2-$C_2H_4Cl_2$, leads to the formation of 2,3,5-trimethylcyclopent-2-enone(I) as a major reaction product (isolated yield 55%). The structure of I was suggested from its spectral data (see Table 1) and this structure was confirmed by the independent synthesis from 2,4-dimethylcyclopent-2-enone (II) /3/ by known procedures /4/.



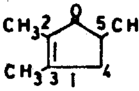
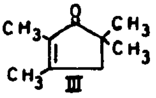
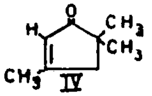
Under similar conditions the acylation of butyne-2 by $(CH_3)_3CCOBF_4$ resulted in the formation of 2,3,5,5-tetramethylcyclopent-2-enone (III) and the reaction of propyne with the same reagent gave 3,5,5-trimethylcyclopent-2-enone (IV). The general experimental procedure runs as follows: To the solution of

$AgBF_4$ (7.5mmoles) and alkyne (5 mmoles) in the CH_2Cl_2-$C_2H_4Cl_2$ mixture(3:2, 10 ml) at - 60°C was added the solution of the corresponding acid chloride (7.5 mmoles) in CH_2Cl_2 (3ml). The mixture was kept at this temperature for an additional 5 min and then decomposed by the addition of a saturated sodium bicarbonate solution. The aqueous solution was extracted twice with ether and the combined ether extracts were washed with water and dried over sodium sulfate. After ether removal the product was isolated by distillation under reduced pressure and purified, if necessary, by t.l.c. on silicagel (CH_2Cl_2-CH_3OH,99:1, R_f0.4-0.5).

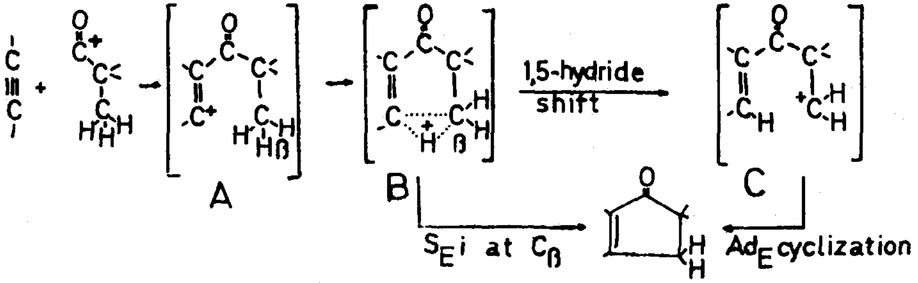
The structures of the compounds III and IV were deduced from the similarity of their IR,- UV, and PMR-spectral data with those for product I (see Table 1) and with corresponding data reported for some related cyclopent-2-enone derivatives /5/.

Preliminary data have shown that other alkynes,e.g. hexyne-1 or decyne-5 could also be transformed by the similar treatment with $(CH_3)_3$ $CCOBF_4$ or $(CH_3)_2$ $CHCOBF_4$ into the corresponding cyclopent-2-enone derivatives,their structures being tentatively identified by the spectral comparison with I,III and IV.

<u>Table 1</u>

Alkyne + Acylating agent	Product	Yield /6/ %	PMR - spectra /7/						IR/8/ cm^{-1}	UV/8/ λ_{max}, nm (ε)
			2-CH_3	3-CH_3	5-CH_3	2-H	4-H	5-H		
$CH_3C{\equiv}CCH_3$ $(CH_3)_2CHCOBF_4$		55	1.53	1.95	1.0	-	2.1 - 3.0		1705 1665	235 (9450)
$CH_3C \equiv CCH_3$+ $(CH_3)_3CCOBF_4$	 III	73	1.6	1.97	1.0	-	2.3	-	1700 1660	235 (10300)
$CH_3C \equiv CH$ + $(CH_3)_3CCOBF_4$	 IV	66	-	2.05	1.0	5.72	2.35	-	1710 1630	226 (8950)

The formation of the cyclic products in the described reaction appears to be a somewhat unusual process since its net result necessarily implies the involvement of the saturated chain of the acyl residue in the ring closure. While considering the possible mechanistic routes for the description of the process, one may find attractive the suggestion that the reaction proceeds in a stepwise manner as shown on the scheme:



The initial attack of the acyl cation at the triple bond could result in the formation of the vinyl cation A. Subsequent transformation of the latter into a cyclopent-2-enone derivative may be envisaged as the result of intramolecular electrophilic attack of the electron-deficient center of the vinyl cation directed at the C_β-H single bond /9/. The question can be raised whether the formation of the new C-C bond proceeds via direct substitution or as a sequence of two steps via a 1,5-hydride transfer with intermediate formation of cation C which can undergo further Ad_E-cyclization. According to the recently developed concepts on electrophilic substitution at saturated carbon /10a,b/, in both cases the identical triangular transition state B can be involved and at present the experimental evidence does not allow one to identify which of these mechanisms, if either, is operating in the ring forming step.

The interest in the field of vinyl cations is now ever growing. These intermediates have been suggested for a number of different reactions /11/ and they are well-known for their ability to be trapped inter- and intramolecularly by the various π-/2,11/ or n-donors /1,11/. Several intramolecular reactions, including 1,2-hydride migration and skeletal rearrangements, have been also reported /11/, thus indicating the ability of these intermediates to interact with σ-donors. We believe that the unusual course of the cyclization reaction reported in this paper clearly demonstrates the exceptionally "hot" nature of vinyl cations generated under non-nucleophilic conditions. Further studies of other possible routes of inter-and intramolecular stabilization of these intermediates are now under way in this laboratory with the purpose both to gain more insight into the properties of vinyl cations and to elaborate synthetically useful procedures based on the alkyne reactions with powerful cation sources.

References

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3. I.N.Nazarov and I.I.Zaretskaya, Iszvestia Akad.Nauk SSSR, Otd.Chim.Nauk,1944, 65.
4. G.Büchi and B.Egger, J.Org.Chem.,36, 2021 (1971).
5. a) For example, pmr-spectrum of 3,5-dimethylcyclopent-2-enone revealed the presence of signals with chemical shifts;(δ)5.71 (2-H);2.33(4-H) 2.01(3-CH$_3$), 0.99 (5-CH$_3$), V.F.Bistrov,T.E.Pozdniakova,A.N.Elizarova and A.A.Achrem, Iszvestia Akad.Nauk SSSR, Otd.Chim.Nauk,1963,66; b)see also data reported by H.N.A.Al-Jallo and E.S.Waight, J.Chem.Soc.(B),1966,73.
6. Yields are given for the distilled products.The homogeneity of I,III and IV was estimated by g.l.c.-data and checked by PMR. Analytical data correspond to the proposed structures and mass-spectra revealed the presence of corresponding molecular ions for all products.
7. PMR-spectra were recorded with Varian DL-60 spectrometer. Chemical shifts(δ) are given in p.p.m. with HMDS as internal standard. Peak area and splitting correspond to the expected values.
8. IR-spectra were recorded for the solutions in CCl$_4$; UV were taken for the solutions in n-hexane.
9. Several examples of S_E i reactions at saturated carbon atom are to be found in the literature but they usually involve hydride transfer (1,2 or 1,3) or methyl migrations (alkyde transfer); see for examples ref.10b.
10. a) See series of papers by G.Olah, et al.,under the title "Electrophilic Reactions at Single Bonds",e.g. Part XI, J.Amer.Chem.Soc.,95,6827 (1973); b) D.M.Brower and H.Hogeveen, "Electrophilic Substitution at Alkanes and in Alkylcarbonium Ions", in "Progress in Physical Organic Chemistry", vol.9, p.179 (1972), Wiley, Interscience, N.Y.
11. For a recent review see: G.Modena,U.Tonellato, "Vinyl Cations", in "Advances in Physical Organic Chemistry", v.9, p.185 (1971), Acad.Press, N.Y.