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CATIONOID COMPLEXES AS REAGENTS IN ELECTROPHILIC ADDITION REACTION

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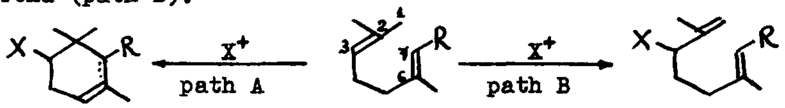
Strongly polarized complexes of general formula X^+Y^-, where X is a cationoid species such as an alkyl- or acyl-cation, nitronium ion, etc., and Y^- is a strong acid anion, e.g. BF_4^-, SbF_6^-, etc., are well-known as very efficient Friedel-Crafts reagents for aromatic substitution reaction /1/. It was also shown /2/, that these reagents are able to react with nonaromatic unsaturated compounds initiating rapid polymerization according to the scheme: $X^+Y^- + n\text{-(C=C)-} \longrightarrow X\text{-(C-C)}_n\text{- }Y$. Recently we have demonstrated /3/, that such a polymerization is not the only possible result of this reaction which can take a rather different course for 1,5-polyenes. In this case the initial electrophilic X^+ attack to the terminal (2,3) double bond may be followed either by ring formation due to nucleophilic participation of the second (6,7) double bond (path A) or by C_1-proton loss with the regeneration of a new double bond (path B):



These results, useful as they are for the synthesis of functionally substituted terpenoids /4/, gave us good reasons to suggest that similar formation of monomeric products in reactions with the cationoid complexes might be feasible in the case of more common unsaturated compounds such as monoolefines, acetylenes, etc. For this reason we reinvestigated the possibility of the use of strongly polarized cationoids as agents of electrophilic addition reactions.

The main result of the present study /5/ may be formulated as follows: cationoid complexes, X^+Y^-, of different nature ($X^+ = RCO^+$, R^+, NO_2^+, RS^+ and

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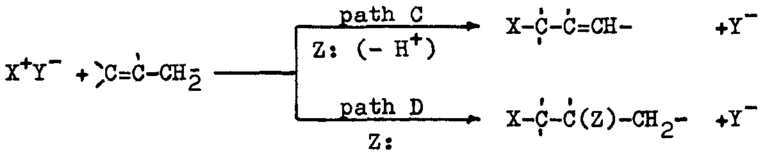
$Y^- = BF_4^-$) are able to react with various unsaturated compounds the monomeric adducts being formed in reasonably good yields provided the reaction is carried out under the conditions preventing polymerization processes (low temperatures, the absence of any excess of olefine in the reaction media).

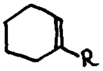
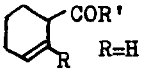
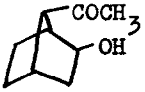
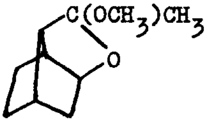
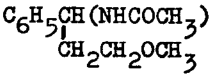
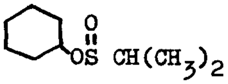
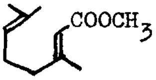
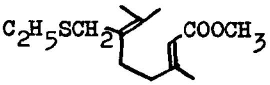
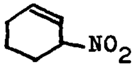
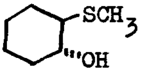
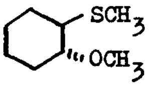
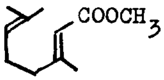
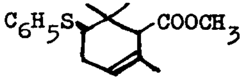
In general the reaction is carried out by the addition of unsaturated compound to a solution of cationoid reagent /6/ in an inert solvent at temperatures of -70 to 0°C and the process is complete within several minutes. Usual treatment of the reaction mixture (neutralization with a convenient base, extraction and so on) allows isolation of the reaction products in sufficiently pure form as judged by g.l.c. and t.l.c.-data. This study of the reaction shows that it may proceed along two alternative paths:



The reaction course and the structure of products formed varies depending on such factors as the nature of starting unsaturated compound and reagent X^+Y^-, the reaction conditions (temperature, solvent) and the nature of nucleophile Z used in the neutralization. Some typical examples of these reactions listed in the Table 1 show the scope and utility of the method. Full account will be published elsewhere.

Several of the results presented deserve some special comments. Acylation with acyl-cations appears to be a most versatile and general method /7/ for the preparation of β, γ-unsaturated ketones (path C, examples 1-3). The examples 4 and 5 demonstrate the application of the reaction for the synthesis of functionally substituted ketones (along the path D). Since the addition of electrophil X^+ (X^+ - acyl) and nucleophile Z (Z - H_2O, CH_3OH) is carried out in stepwise manner as the separate and independent stages /8/, it is conceivable that a variety of products could be prepared from a given electrophile -olefine pair just by changing the nature of the external nucleophile Z used for neutralization of the reaction mixture. Preliminary data show that such a "double addition" reaction course is typical not only for norbornene acetylation but for acylation of other unsaturated compounds as well as for the reactions with other electrophiles X^+ (see below).

Table 1

No.	Initial Compound	Reagent	Nucleophil Z:	Conditions Solvent, t°C	Product /9/	Yield
1.		$R'COBF_4$	-	CH_3NO_2, -25°	 $R=H, R'=CH_3$ $R=H, R'=C(CH_3)_3$ $R=R'=CH_3$	I*, 80% II, 86% III*,70%
2.	$CH_3H_7CH=CH_2$	CH_3COBF_4	-	CH_3NO_2, -25°	$C_3H_7CH=CH-CH_2COCH_3$	IV*,51%
3.	$CH_3CH=CH_2$	$C_6H_5COBF_4$	-	CH_3NO_2, -25°	$CH_2=CH-CH_2COC_6H_5$	V*,61%
4.		CH_3COBF_4	H_2O	CH_3NO_2, -25°		VI*,60%
5.	-"-	CH_3COBF_4	CH_3OH	CH_3NO_2, -25°		VII*,74%
6.	$C_4H_9C\equiv CH$	CH_3COBF_4	H_2O	CH_3NO_2, -25°	$C_4H_9COCH_2COCH_3$	VIII*,64%
7.	$C_6H_5CH=CH_2$	$CH_3OCH_2BF_4$	CH_3CN	CH_3NO_2, -25°	 $C_6H_5\underset{CH_2CH_2OCH_3}{CH}(NHCOCH_3)$	IX, 63%
8.		$(CH_3)_2CHBF_4$	SO_2	SO_2, -70°		X, 20%
9.		$C_2H_5SCH_2BF_4$	-	CH_3NO_2, -25°		XI, 72%
10.		NO_2BF_4	-	SO_2-CH_3CN,-70°		XII*,40%
11.	-"-	CH_3SBF_4	H_2O	CH_3NO_2- $-CH_2Cl_2$, -25°		XIII*,50%
12.	-"-	CH_3SBF_4	CH_3OH	CH_3NO_2- $-CH_2Cl_2$, -25°		XIV*,45%
13.		$C_6H_5SBF_4$	$\Delta^{6,7}$	CH_3NO_2, -25°		XV, 57%

Example 6 shows that the proposed procedure is equally effective for the conversion of acetylenic compounds into β-diketones.

Alkylation (examples 7,8,9) as a rule proceeds less smoothly than acylation which is certainly due to the relative instability of alkyl--cations. "Double addition" seems to be the preferred course for the reactions with alkyl- or alkoxyalkyl-cations. The first example (example 7) demonstrates the usefulness of this reaction as a method for one-step transformation of olefine into bifunctional compounds. It is worthwhile to emphasize the ability of nucleophylic participation for such a weak nucleophyl as SO_2 as examplified in example 8 /10/. The use of alkylthiomethyl-cations as in No.9 might prove to be useful as a method for the introduction of a "masked" methyl group into a molecule.

Heterocations may also react both by the path C and D. The use of NO_2BF_4 (example 10) for olefine nitration constitutes an interesting alternative to the conventionally used methods for the synthesis of $\beta\gamma$-unsaturated nitrocompounds /11/. The reactions with alkyl- (examples 11,12) or aryl (example 13) - sulfenyl cations have some interest as a method for preparation of various substituted sulfur-containing compounds along the path D. It could also provide some new insight into the chemistry of episulfenium-ions since the latter seem to be the most logical intermediates in the reactions studied.

To our knowledge the results presented in this paper constitute the first example of successful application of strongly polarized cationoid complexes for normal electrophilic addition reactions. These results allow to suggest that many other cationoid complexes of different nature /12/ might be involved into the reactions similar to that described above. The use of such complexes as the reagents of electrophilic addition reaction will sensibly widen the traditional limits of this reaction /13/.

The studies of the scope and limitations of the reactions, their mechanisms and preparative applications are in progress in this laboratory.

References

1. "Friedel-Crafts and related reactions", G.Olah, ed., Interscience, N.Y., 1963, vol.I,IV.
2. G.Olah, H.Quinn, S.Kuhn, J.Amer.Chem.Soc., 82, 426 (1960).
3. W.A.Smit, A.V.Semenovsky, Tetrahedron Letters, 3651 (1965); M.Z.Krimer, W.A.Smit, A.V.Semenovsky, Iszvestia Acad.Nauk, Ser.chim., 1967, 1573; ibid., 1968, 866; ibid., 1968, 1590.
4. M.Z.Krimer, W.A.Smit, A.V.Semenovsky, V.F.Kucherov, Iszvestia Acad.Nauk, Ser.chim., 1968, 1352.
5. Preliminary communication see: W.A.Smit, A.V.Semenovsky, V.F.Kucherov, M.Z.Krimer, O.V.Lubinskaya, T.N.Chernova, Iszvestia Acad.Nauk, Ser.chim., 1970, 1681.
6. Cationoid reagents could be prepared by any of the known methods, e.g. by metathesis reaction $XCl + AgBF_4 — X^{+}BF_4^{-} + AgCl$, see /1/, /2/.
7. Usual Kondakov-like procedure of olefine acylation results in the formation of mixture of products /See for a review D.N.Belov, T.A.Rudolfi in "Reactions and Methods in Organic Chemistry", vol.7, 1958, Moscow/ or α,β-unsaturated ketones (e.g. C.Grob, H.Lutz, Helv.chim.acta 48, 791 (1965). Satisfactory yields of β,γ-unsaturated ketones have been reported recently for some special cases of alkylcyclohex-1-ene acylation (J.Groves, N.Jones, Tetrahedron Letters, 1161 (1970)).
8. The examples of nucleophilic participation in the course of electrophylic addition reactions are quite numerous (see, for example, D.Dalton, R.Smith, D.Jones, Tetrahedron, 26, 575 (1970) ; F.Boerwinkle, A.Nassner, Tetrahedron Letters, 3921 (1968) and references therein) but the usual procedure of these reactions necessarily limits the choice of the nucleophil involved because the latter should be present in the reaction media (as a solvent or as an anion of the added salt).
9. Yields in the Table 1 are given for isolated products. Satisfactory analytical data were obtained for all new compounds. Their IR- and n.m.r.-spectra are consistent with the structures shown. For some of the products

(denoted by asterick) additional chemical proof of structure was also given as follows: for VII, XII, XIII, XIV - by the direct comparison with authentical samples prepared by the known methods; for I, III, IV, V - by alkali isomerization to the known α,β-unsaturated ketones; VI - by the conversion via acetylation, Bayer-Villiger oxidation and saponification to the known cis-exo-norbornadiol-2,7 (H.Kwart, W.Vosburgh, J.Amer.Chem.Soc., 76, 5400 (1954)).

10. We were unable to find any data in the literature pertinent to sulfur dioxide participation in electrophylic addition reactions of unsaturated compounds and there is very little information about its use in Friedel--Crafts-like sulfination of aromatic compounds (G.Olah, R.Schlosberg, D.Kelly, Gh.Mateescu, J.Amer.Chem.Soc., 92, 2546 (1970) and references cited therein).
11. F.G.Bordwell, E.W.Gabrisch, J.Amer.Chem.Soc., 82, 3588 (1960).
12. D.Bethel, V.Gold, "Carbonium Ions. An Introduction", Academic Press, London, 1967; see also the series of papers published by G.Olah and coworkers in J.Amer.Chem.Soc., 1960-1970.
13. P.B.D.De La Mare, R.Bolton, "Electrophilic additions to unsaturated systems", Elsevier, Amsterdam, 1966.