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THE ACYLATION OF 2-BUTYNE BY DERIVATIVES OF 1- and 2-ADAMANTANECARBOXYLIC ACIDS

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The reaction of monosubstituted alkynes with 1-adamantanecarbonyl cation (I) $Y = BF_4^{\ominus}$ or (II) $Y = SbF_6^{\ominus}$ leads to the formation of 1,2-disubstituted derivatives of adamantane [1].

In the present work, we show that, in the acylation of 2-butyne by salts (I) and (II), the intermediate Int-2 formed as a result of a 1,5-hydride shift is capable of stabilization not only by reaction with a nucleophile present in reagent (I) [$F^{\ominus}$ from $BF_4^{\ominus}$ to form (III)] but also by intramolecular Ad_E cyclization leading to the formation of condensed derivatives of adamantane.

When $Y = BF_4^{\ominus}$, both pathways are realized, yielding (III), (V), and (VI), but in going to the more stable counterion, $SbF_6^{\ominus}$, exclusive formation of electrophilic cyclization products (IV) and (VI) is observed.

The haloketones (IV) and (V) are readily converted to (VI) after twofold TLC on SiO_2 or neutral Al_2O_3 or GLC. This prevents an unequivocal statement on the composition of the reaction mixture. However, there is a complex signal at 101.2 ppm in the ^{19}F NMR spectrum of the mixture of ketones (V) and (VI) obtained immediately after preparative GLC, which indicates the presence of (V) in this mixture. Elemental analysis of the mixture of ketones (IV) and (VI) obtained after preparative TLC showed the presence of 30% Cl.

The observed formation of (IV), (V), and (VI) indicates that the α-ketocarbonium ion Int-3 which apparently arises as a result of Ad_E cyclization of Int-2 readily undergoes 1,2-hydride shift and converts to the more stable β-ketocarbonium ion Int-4, which subsequently may be stabilized by reaction with $BF_4^{\ominus}$ [to form (V)] or, when $Y = SbF_6^{\ominus}$, with the chlorine-containing solvent [to form (IV)], or by proton elimination [to form (VI)].

The structure of (III) is supported by the PMR spectrum [specifically, by the presence of proton signals for the COC(Me) = CHMe fragment and the methine proton of the >CHF group (J_{HF} + 49 Hz)] and the ^{13}C NMR spectral data (Table 1) and also by mass spectra, IR spectra, and elemental analysis. The structure of the cyclopentanone derivative of adamantane (VI) was rigorously proven by analysis of the ^{13}C NMR spectra [taken in the presence of $Eu(fod)_3$, see Table 1] and the PMR spectra. Under $\{^1H - ^1H\}$ conditions and irradiation at 2.76 ppm (H^3) (δ, ppm from TMS) and 2.6 ppm (H^{α}), simplification of the signals for the methyl group

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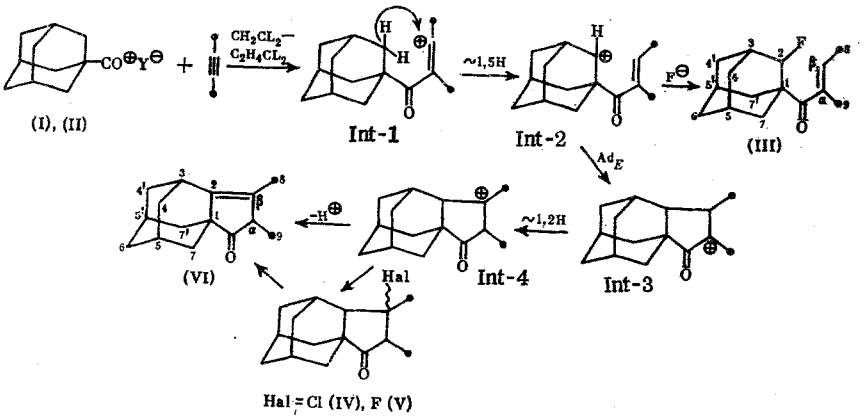
 0568-5230/79/2811-2330$07.50

Scheme 1



at C^{α} and C^{β} to singlets is observed and upon irradiation of the Me group at C^{β}, a change is observed in the proton signal at C^{3}.

Thus, the acylation of 2-butyne by salts (I) and (II) leads to cyclopentanone derivatives, whose most likely pathway for formation involves consecutive 1,5-hydride shifts and an Ad_E cyclization. This is indirect support for our previous proposal [3] of possible analogous processes in the acylation of alkynes by aliphatic acylium cations.

We might expect that in going to derivatives of 2-adamantanecarboxylic acid [2-$AdCO^{+}Y^{-}$, $Y = BF_4^{\ominus}$ (VII) and $SbF_6^{\ominus}$ (VIII)], a relatively stable tertiary carbonium ion will form as the result of a 1,5-hydride shift and the addition of an arbitrarily selected "external" nucleophile will be possible at the stage of decomposition of the reaction mass.

Preliminary experiments showed that the acylium salt (VII) is unstable and readily undergoes decarbonylation. Thus, we used acylium salt (VIII) as the acylating reagent.

In the reaction of 2-butyne with (VIII), the single reaction product is a compound which corresponded to the addition of 2-butyne molecules (mass spectral data), and its IR spectrum lacked a carbonyl group absorption band. These results indicated that the intermediate Int-6 which forms as a result of a 1,5-hydride shift reacts with a second molecule of 2-butyne, and the intermediate Int-7 thus formed is stabilized by intramolecular attack at the oxygen atom of the carbonyl group with the formation of a pyran derivative of adamantane (IX) according to Scheme 2. The reaction cannot be halted at the formation of Int-6 by varying the conditions (slow addition of 2-butyne to an excess of the acylating reagent). In all cases, the single product is (IX) and its yield was 50% under optimal conditions.

The structure of (IX) follows from the ^{13}C NMR spectral data recorded under complete and partial proton decoupling. Examination of spatial models indicates that the molecule has a plane of symmetry passing through the pyran ring. Indeed, three signals with double intensity are observed in the ^{13}C NMR spectrum (δ, ppm from TMS): 42.74 t (C^{7} and $C^{7'}$), 38.79 t (C^{4} and $C^{4'}$), and 29.38 d (C^{5} and $C^{5'}$). In the region of adamantane signals, there are also signals at 36.97 t (C^{6}), 35.69 s (C^{1}), and 31.57 d (C^{3}) as well as six signals in the olefinic region: 142.97 s, 140.67 s, 130.29 s, 124.32 d, 115.47 s, and 106.37 s. The structure of (IX) was also supported by PMR, IR, and mass spectral data, elemental analysis, and the readiness of opening of the pyran ring by the action of $HClO_4$ in aqueous dioxane with the formation of diketone (X) (see Scheme 2).

The structure of diketone (X) was supported by the presence of proton signals for the COC(Me) —CHMe and CH(Me)COMe fragments in the PMR spectrum. Under $\{^{1}H - ^{1}H\}$ conditions, upon irradiation of the methyl group protons of the $CH(CH_3)COCH_3$ fragment, a simplification is observed for the proton signal at 2.6 ppm to a singlet. The presence of a doublet at 2.65 ppm (J ~12 Hz) in the PMR spectrum is a part of the AB system of protons at C^{4} of the adaman-

TABLE 1

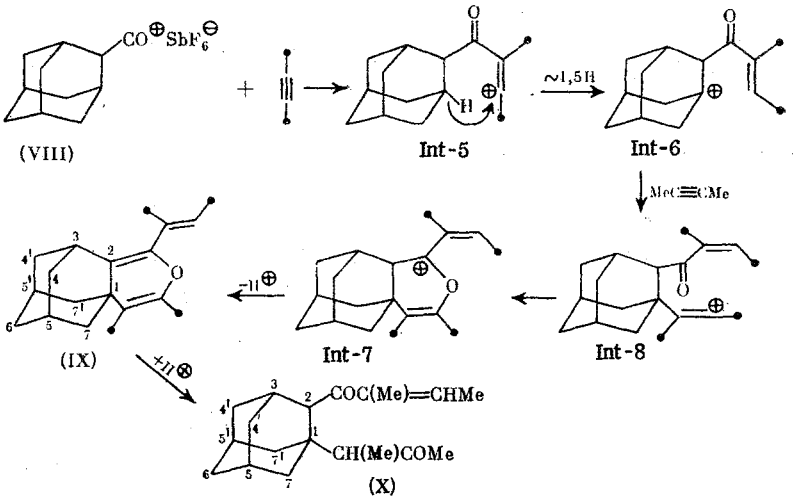
Compound	Parameters	C¹	C²	C³	C⁴	C⁴′	C⁵	C⁵′	C⁶	C⁷	C⁷′	C=O	Cᵅ	Cᵝ	C⁸	C⁹
(VI)	δ, ppm, in $CDCl_3$	51,36	122,82	30,42	37,82	37,61	28,96	28,84	36,61	40,91	39,16	220,3	50,09	142,61	14,87	10,99
	Pseudocontact shift (ΔC_i), $Eu(fod)_3$: (VI) = 0.3 : 0.5 (g)	2,06	1,64	0,73	0,73	0,55	0,85	0,79	0,55	2,19	2,13	2,74	2,16	1,15	2,47	0,61
(III)	δ, ppm, in $CDCl_3$	50,7	94,9	33,0	35,35	30,6	27,4	27,4	36,3	39,55	33,1	209,9	137,8	126,9	13,4	14,2
	Additive calculation using increments for the F and COR groups [2]	48,4	93,9	32,8	34,9	30,8	27,3	27,3	36,3	37,8	32,2					

TABLE 2*

Parameters (XI)	C²	C¹	C³	C⁴′	C⁴	C⁵	C⁶	C⁷	C⁸′	C⁸	C=O	Cᵅ	Cᵝ	CH_3	C_6H_5
δ, ppm	53,91	38,69	32,42	35,55	31,2	28,17	37,22	29,38	47,66	38,73	201,5	138,91	134,11	14,57 11,41	149,11 128,04 125,51 125,19
δ, ppm, in the presence of $Eu(fod)_3$ under "off-resonance" conditions	55,73 d	42,01 s	35,39 d	38,0 t	33,15 t	29,45 d	38,0 t	30,48 d	48,99 t	38,77 t	207,3 s	143,09 s	138,97 d	15,48 q 15,12 q	151,66 s 129,07 d 127,31 d 126,2 d
Pseudocontact shift (ΔC_i)	1,82	3,32	2,97	2,45	1,95	1,28	0,78	1,1	1,33	1,04	5,89	4.19	4,86	0,97 3,71	

*Spectra taken in $CDCl_3$ relative to TMS internal standard. $Eu(fod)_3$:(XI) = 0.2:0.15 (g).

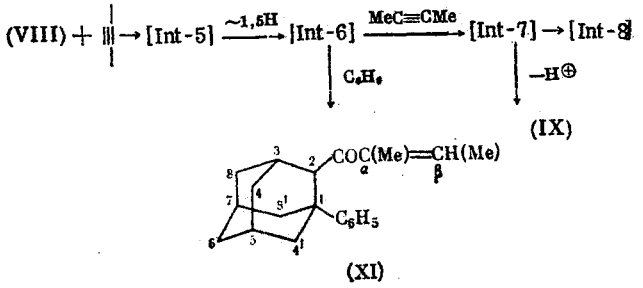
Scheme 2



tane system, which was demonstrated by the INDOR method. The second component of the AB system is found at 1.55 ppm. Under $\{^1H-^1H\}$ conditions, upon irradiation at 2.65 ppm, the component of the AB system at 1.55 ppm is simplified into a broad singlet. The structure of diketone (X) is also supported by IR and mass spectral data and elemental analysis.

When running the reaction of 2-butyne with (VIII) in the presence of benzene, in addition to (IX) formed in 15-20% yield, product (XI) is formed which corresponds to the addition of the acyl cation and an aromatic nucleophile, i.e., in this scheme (Scheme 3), intermediate Int-6 is stabilized by two competing processes: a) reaction with a second 2-butyne molecule or b) reaction with an aromatic nucleophile present in the medium.

Scheme 3



Upon changing the reaction conditions to provide for slow addition of 2-butyne to an excess of the acylating agent, it was not possible to obtain complete repression of the formation of (IX) and to direct the process exclusively towards the formation of products of the type of (XI). The structure of (XI) was supported by the presence of PMR signals for the COC(Me) = CHMe fragment, the proton at C^2, and the phenyl group protons. The doublet at 3.1 ppm (J ~ 12 Hz) is a component of the AB system of protons at C^4, as shown by the INDOR method. The second component is found at 1.55 ppm. Under $\{^1H-^1H\}$ conditions, upon irradiation at 1.55 ppm, the doublet at 3.1 ppm is simplified into a broad singlet. The structure of (XI) is also supported by the IR data, the ^{13}C NMR spectra taken under complete and partial proton decoupling in the presence of $Eu(fod)_3$ (Table 2), and mass spectral data.

These results indicate that the sequence of transformations (see Schemes 2 and 3) cannot be stopped at the stage of formation of intermediate I_6, at least under the conditions employed, and the reaction proceeds to the formation of covalent products with the participation of nucleophiles present in the medium.

EXPERIMENTAL

Gas-liquid chromatography was performed on chromatographs of the LKhM-8MD system with a 2-3 m × 2-3 mm column and preparative 4-6 m × 4-6 mm column with flame-ionization detector using OV-17, OV-101, SE-30, and polyethylene glycol-20000 stationary phases for monitoring the purity of the starting materials, analysis of the reaction mixtures, and, in some cases, for the preparative separation and purification of the products.

The IR spectra were taken on a UR-20 spectrometer, usually in CCl_4. The PMR spectra were taken on Varian DA-60-IL and Tesla BS-497 spectrometers and an experimental spectrometer operating at 300 MHz. The ^{13}C NMR spectra were taken on Bruker WP-60 (15.08 MHz) and XLFT-100 (20 MHz) spectrometers. The chemical shifts are given in the δ scale (ppm) relative to TMS or HMDS internal standard. The mass spectra were taken on Varian CH-6 and MAT-112 spectrometers.

A sample of 1-adamantanecarboxylic acid was obtained according to Koch and Haaf [4].

1-Adamantanecarboxylic Acid Chloride. To 18 g (0.1 mole) 1-adamantanecarboxylic acid, 22 ml (0.3 mole) freshly distilled $SOCl_2$ was added with stirring until a homogeneous solution was formed and the solution was then maintained for 3 h. (At longer reaction times, decarbonylation of the acid chloride was observed with the formation of 1-chloroadmantane.) The excess of $SOCl_2$ was removed in vacuum. A yield of 17.9 g (90%) 1-AdCOCl was obtained which gave a single GLC peak, mp 53-54°C [5].

2-Cyanoadmantane. To a freshly prepared solution of 5.9 g (0.087 mole) EtONa in 40 ml abs. ethanol and 90 ml THF, a solution of 10 g (0.067 mole) admantanone and 16 g (0.08 mole) tosylmethyl isocyanate [6] in 200 ml THF was added at 20°C. The mixture was stirred at this temperature for 2 h and then the solvent was removed and 100 ml water was added. The solution was extracted with ether and the extract was dried with Na_2SO_4. After removal of the solvent in vacuum, the residue was dried in benzene and heated for 10 min at 50-60°C with activated charcoal. A yield of 8 g (74%) 2-AdCN was obtained with mp 170-180°C [6] which gave a single GLC peak.

2-Adamantanecarboxylic Acid. To 8 g 2-cyanoadamantane, 100 ml 48% HBr and 25 ml acetic acid were added and the mixture was heated at reflux for 5 h. The mixture was cooled and 100 ml water was added. The mixture was extracted with chloroform and the extract was dried with Na_2SO_4. After removal of the solvent, the acid was recrystallized by freezing from pentane at −20°C. A yield of 7 g (83%) 2-adamantanecarboxylic acid was obtained with mp 142-143°C [7].

2-Adamantanecarboxylic Acid Chloride. To 7 g (0.041 mole) 2-adamantanecarboxylic acid, 11 ml (0.15 mole) freshly distilled $SOCl_2$ was added and the mixture was left overnight. The excess $SOCl_2$ was removed in vacuum and the residue was distilled. A yield of 6 g (73%) 2-adamantanecarboxylic acid chloride was obtained with bp 105-108°C (1.5 mm Hg) which gave a single GLC peak.

Acylation of 2-Butyne by 1-$AdCO^+BF_4^-$ (I). To a solution of 0.84 g (4.3 mmoles) $AgBF_4$ in 20 ml abs. CH_2Cl_2 – $C_2H_4Cl_2$ (1:1) at −40°C, a mixture of 0.8 g (4 mmoles) 1-AdCOCl and 0.27 g (5 mmoles) 2-butyne in 5 ml CH_2Cl_2 was added. The mixture was maintained at this temperature for 30 min and decomposed as usual. After removal of the solvent, a yield of 0.96 g ketones (III), (V), and (VI) was obtained. In preparative TLC compounds (III), (V), and (VI) move in one band. A yield of 0.5 g (55%) ketones (III), (V), and (VI) was obtained. Preparative GLC yielded 0.2 g (III) with mp 58-60°C and 0.15 g of a mixture of (V) and (VI). In an attempt at further GLC purification, the mixture of ketones (V) and (VI) was converted completely to (VI).

The PMR spectrum of (III)* (δ, ppm): $COC(\overset{C}{C}H_3)=\overset{B}{C}H\overset{A}{C}H_3$, 5.76 d.q. (1H, J_{AC} = 1.2 Hz, J_{AB} = 6.5 Hz), $\rangle CHF$, 4.98 d.d. (1H, J_{HF} = 49, $J_{H^2H^3}$ = 3 Hz), 2.2-1.4 (19H, unresolved multiplet of the admantane system and two methyl groups). IR spectrum (ν, cm^{-1}): 1695 (C=O), 1632 (C=C), 3040 (=CH). Mass spectrum, m/e: 226 $(M)^+$, 153 $(AdF)^+$, 83 $(COC(CH_3)=CHCH_3)^+$. Found: C 76.21; H 9.12; F 7.88%. Calculated for $C_{15}H_{21}OF$: C 76.20; H 8.90; F 7.88%.

*Signals of an unresolved multiplet of admantane system are present in the PMR spectra of all the compounds obtained.

PMR spectrum of (VI) (δ, ppm): 2.76 m (1H), 2.6 q (1H), 1.7 d (3H, J =1.2 Hz), 1.07 d (3H, J =7 Hz), 2.2-1.4 (13H, unresolved multiplet of the admantane system). IR spectrum (ν, cm^{-1}): 1745 (C =O). Mass spectrum, m/e: 206 $(M)^+$.

Acylation of 2-Butyne by 1-Ad$CO^+SbF_6^-$ (II). To a solution of 0.41 g (1.2 mmole) $AgSbF_6$ in 20 ml abs. CH_2Cl_2 —$C_2H_4Cl_2$ (1:1) at —40°C, a mixture of 0.2 g (1.0 mmole) 1-AdCOCl and 0.054 g (1.0 mmole) 2-butyne in 3 ml abs. CH_2Cl_2 was added. The mixture was held at this temperature for 30 min and decomposed by the usual method. Preparative TLC yielded 0.11 g (50%) of a mixture of ketones (IV) and (VI). Upon repeated chromatography on silica, the ketone mixture was converted almost entirely into (VI), which was identical in its spectral data (^1H and ^{13}C NMR, IR, and mass spectra) to the previously obtained sample.

Acylation of 2-Butyne by 2-Ad$CO^+SbF_6^-$ (VIII). To a solution of 1.4 g (4.1 mmoles) $AgSbF_6$ in 30 ml CH_2Cl_2 —$C_2H_4Cl_2$ (1:1) at —60°C, a solution of 0.8 g (4.0 mmoles) 2-AdCOCl and 0.54 g (10.0 mmoles) 2-butyne in 5 ml CH_2Cl_2 was added. The mixture was held at this temperature for 30 min and decomposed by the usual method. Preparative TLC on silica gel L using 1:4 ether —hexane yielded 0.5 g (50%) pyran (IX), mp 57-59°C.

PMR spectrum (δ, ppm): 5.3 d. q. (1H, J =6.5 Hz, J =1.2 Hz), 2.55 br. s. (1H), 1.4-2.11 (unresolved multiplet of the adamantane system and four methyl groups). IR spectrum (ν, cm^{-1}): 1708 (= COC=), 1659 (C —C). Mass spectrum, m/e: 270 $(M)^+$, 215 $(M - C_4H_7)^+$, 255 $(M - CH_3)^+$. Found: C 84.25; H 9.85%. Calculated for $C_{19}H_{26}O$: C 84.44; H 9.63%.

Diketone (X). To a solution of 0.22 g pyran (IX) in 20 ml dioxane, 10 ml 30% $HClO_4$ was added. The mixture was stirred for 2-3 min and 50 ml water was added. The mixture was extracted with $CHCl_3$ and the extract was washed with aq. $NaHCO_3$ and dried with Na_2SO_4. After removal of the solvent, preparative TLC yielded 0.17 g (72%) (X) with mp 107-109°C (from hexane).

PMR spectrum (δ, ppm): $COC(CH_3)$ =$CHCH_3$, 6.72 q (1H, J =7 Hz), 1.77 d (3H, J =7 Hz), 1.65 s (3H), $CH(CH_3)COCH_3$, 2.6 q (J =7 Hz), 0.76 d (3H, J =7 Hz), 2.07 s (3H), 3.3 br. s (1H, CHCO), 2.65 d (J =12 Hz). IR spectrum (ν, cm^{-1}): 1711, 1665 (C =O), 1640 (C =C), 3061 (=CH). Mass spectrum, m/e: 288 $(M)^+$, 245 $(M - COCH_3)^+$, 83 $(COC(CH_3) =CHCH_3)^+$, 43 $(COCH_3)^+$. Found: C 79.31; H 10.03%. Calculated for $C_{19}H_{28}O_2$: C 79.17; H 9.72%.

Acylation of 2-Butyne by 2-Ad$CO^+SbF_6^-$ in the Presence of Benzene. To a solution of 0.93 g (2.73 mmoles) $AgSbF_6$ in 30 ml abs. CH_2Cl_2 —$C_2H_4Cl_2$ (1:1) at —60°C, a solution of 0.35 g (1.75 mmoles) 2-AdCOCl and 5 ml benzene in 5 ml CH_2Cl_2 was added, followed by the slow addition of 0.13 ml (1.5 mmoles) 2-butyne in 10 ml CH_2Cl_2 over about 10 min. The mixture was stirred at —60°C for an additional 10 min and then decomposed in the usual manner. Preparative TLC on silica gel L with 1:2 ether —hexane eluant yielded 0.2 g (45%) (XI), mp 152-155°C, and 0.06 g (15%) pyran (IX).

Compound (XI). PMR spectrum (δ, ppm): $COC(CH_3)$ =$CHCH_3$, 6.43 q (1H, J =7 Hz), 1.71 d (3H, J =7 Hz), 1.53 s (3H), CH —CO, 3.68 br. s (1H), 3.1 d (1H, J =12 Hz), 7.17 br. s (5H, C_6H_5). IR spectrum (in $CDCl_3$, ν, cm^{-1}): 1668 (C =O), 1641 (C =C), 840, 860 (C_6H_5). Mass spectrum, m/e: 294 $(M)^+$, 211 $(M - COC(CH_3) =CHCH_3)^+$, 83 $(COC(CH_3) =CHCH_3)^+$.

CONCLUSIONS

The acylation of 2-butyne by derivatives of 1- and 2-adamantanecarboxylic acid leads to the formation of 1,2-disubstituted and condensed adamantane derivatives.

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THE GENERATION AND PROPERTIES OF EPISULFONIUM INTERMEDIATES. 8.* REGIOSELECTIVITY IN THE NUCLEOPHILIC RING OPENING OF EPISULFONIUM ION DERIVATIVES OF SOME UNSYMMETRICAL ALKYL- AND ARYLOLEFINS

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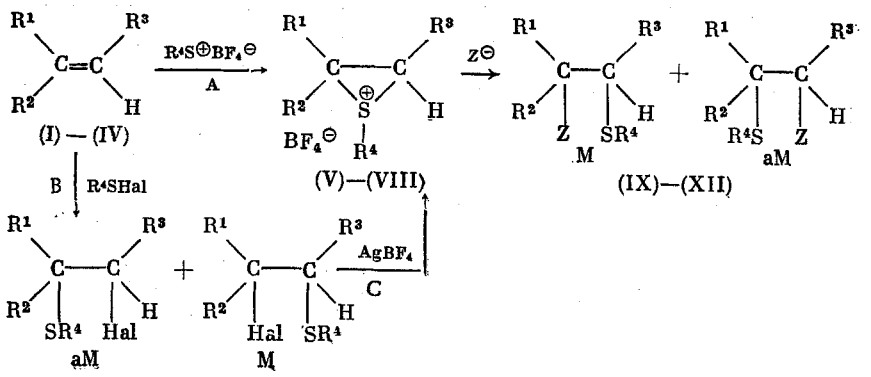
UDC 542.97:547.313

Episulfonium ion (ESI) derivatives of propylene and isobutylene are converted upon reaction with nucleophiles ($Z^{\ominus}$) to β-substituted thioethers, and M adducts greatly predominate in the mixture of M and aM adducts† formed [2, 3]. In order to determine whether this behavior is general, we studied the possible generation and regioselectivity of ring opening of ESI obtained from unsymmetrical alkenes: trimethylethylene (I), isopropylethylene (II), styrene (III), and 2,3,4,5,6-pentafluorophenylethylene (IV).

The conversion of these alkenes to ESI was carried out in accord with our previous methods [4]: by the reaction of the alkene with $RS^+BF_4^-$ (obtained in solution by the reaction of RSCl with $AgBF_4$) (path A) or through a step of the corresponding β-halothioethers with their subsequent treatment with a solution of $AgBF_4$ (path B + C) (see Scheme 1)

Scheme 1



$R^1 = R^2 = R^3 = Me$; $R^4 = Ar$ (I), (V), (IX); $R^1 = i\text{-}Pr$, $R^2 = R^3 = H$; $R^4 = Ar$ (II), (VI), (X); $R^1 = Ph$, $R^2 = R^3 = H$; $R^4 = Me$ (III), (VII), (XI); $R^1 = C_6F_5$, $R^2 = R^3 = H$; $R^4 = Me$ (IV), (VIII), (XII).

For the case of formation of the ESI of (V), $R^4 = 4\text{-}ClC_6H_4$, the ^{13}C NMR spectra support the structure presented for this complex (the chemical shifts of the bridge ^{13}C nuclei are 72.97 (^{13}CH) and 88.76 ($^{13}CR^1R^2$), compare with values for the derivatives of propylene, isobutylene [3], and di-tert-butylethylene [5]). The structures of the remaining ESI were taken by analogy.

The solutions of the ESI of (V)-(VIII) obtained were then reacted with various nucleophiles $Z^{\ominus}$ ($Z^{\ominus} = OCOMe^{\ominus}, MeO^{\ominus}, HO^{\ominus}, H^{\ominus}$), leading to the formation of the corresponding cova-

*Communication 7: [1].
†Here and subsequently, the terms M and aM refer to products of addition according and opposite to the Markownikoff rule (RS^+ is the electrophile).

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