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Cationic Telomerization of Isobutylene

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SUMMARY

Cationic telomerization has been attempted by reacting BF_3 onto isobutylene in the presence of acetic anhydride: Under proper experimental conditions, we obtained only one product - a ceto-ester monoadduct $CH_3COCH_2\text{-}C(CH_3)_2\text{-}O\text{-}COCH_3$ -. In order to study the initiation step, we have reacted a preformed salt $CH_3CO^+SbF_6^-$ onto isobutylene in the presence of acetic anhydride and shown that the acetylium salt is efficient and that termination by esterification is surprisingly high.

INTRODUCTION

Functionalisation of polyisobutylene is an active field of research, particularly in order to obtain telechelic oligomers. Several tentatives are to be mentioned:

- oxydative cleavage of carbon-carbon double bonds of butyl-rubber which gives oligomers with a ketone function at one end of the chain and a carboxylic group at the other one (1-3).
- the "inifer" method, developped by Kennedy, which gives polyisobutylene carrying two chlorine termini (4).

Acetic anhydride (AA) has been used by several authors to try to prepare some telechelics:

- Bockhoff and al.(5) report obtaining oligostyrene samples carrying either an acyl group or one ester end group by using $CH_3CO^+SbF_6^-$ as an initiator for styrene.
- Stix and al. (6) prepared poly-THF samples carrying two ester end groups using the same initiating system.

We report here our results concerning the cationic telomerization of isobutylene using the complex acetic anhydride-boron trifluoride as an initiator. In order to characterize easily and unambiguously the products obtained, we have used low monomer concentrations and studied the influence of solvent, temperature and proportions of the reagents.

EXPERIMENTAL

I - Telomerization with acetic anhydride/BF_3

Isobutylene and methylene chloride were distilled twice

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over CaH_2 . AA, BF_3 and $AgSbF_6$ were used as received; we checked by NMR that AA did not contain acidic protons. SO_2 was dried twice over P_2O_5 under vacuum. Our reactions were carried out under a dry argon atmosphere. Methylene chloride, AA and isobutylene were mixed and cooled down to the chosen temperature, then BF_3 was added by condensation.

After the reaction was over (30 mn unless otherwise stated) the reaction mixture was poured over a cold emulsion of ether and sodium hydroxide water solution. We checked that no isobutylene-containing compounds were dissolved in the water phase. The ether phase was evaporated and the products characterized.

II - Telomerization with $CH_3COCl/AgSbF_6$

CH_3COCl (2.8×10^{-2} mol) is dissolved in 100 ml of SO_2 and reacted with a stoichiometric amount of $AgSbF_6$: Ag Cl precipitates out and $CH_3CO^+SbF_6^-$ is formed; 100 ml of CH_2Cl_2 is added and the solution cooled down to - 70°C: 2.8×10^{-2} mol of isobutylene and of AA are added; the reaction mixture is maintained at this temperature for 3 hours, then SO_2 is evaporated; the insoluble salts are filtered and the products distilled.

The ^1H and ^{13}C NMR spectra were recorded on a 90 MHz Bruker spectrometer. The mass spectra were obtained on a GC/MS system Ribermag R 10/10.

RESULTS AND DISCUSSION

The compounds obtained have been characterized and their spectroscopic data are shown in table 1; they are of two different kinds.

Two olefines are found

- 4-methyl-4 pentene-2-one (A) $CH_3-CO-CH_2-C(CH_3) = CH_2$
- 4-methyl-3 pentene-2-one (B) $CH_3-CO-CH = C(CH_3)_2$,

as well as two esters

- 1,1 dimethyl-3-one-butylacetate (C): $CH_3-CO-CH_2-C(CH_3)_2-OCOCH_3$
- tertiobutylacetate (D) : $CH_3-COO-C(CH_3)_3$.

Their formation could be explained by the following mechanisms:

1) formation of the initiating species

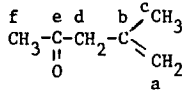
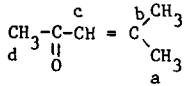
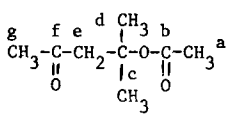
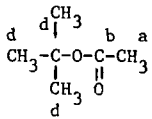
$$AA + BF_3 \longrightarrow CH_3CO^+(BF_3, OCOCH_3)^- ,$$

(Below, the anion will be omitted for the sake of simplicity)

2) initiation of isobutylene oligomerization

$$CH_3CO^+ + \text{isobutylene} \longrightarrow CH_3CO-CH_2 - C^+(CH_3)_2 ,$$

Table 1 - Spectroscopic data of compounds obtained in isobutylene telomerization

 A	NMR	a		b		c	d		e		f
	^1H	4.6,4.7				1.6	2.9				1.98
	^{13}C	114.9 T		139.5 S		22.5 Q	52.9 T		206.7 S		28.9 Q
	mass spectrum										
	m/e	43	44	39	27	15	29	40	83	98	
	I	100	23.9	19.5	18.8	14.5	10.8	72	6.9	2.2	
 B	NMR	a		b		c	d				
	^1H	1.9		2		5.9	2				
	m/e	39	43	55	83	53	41	98	99		
	I	100	68.7	48.5	48.1	29.2	25.3	15.3	2.5		
 C	NMR	a		b		c	d		e		f	g
	^1H	1.8 S					1.35 S		2.85 S			1.98 S
	^{13}C	22.5 Q J = 128 Hz		170.5 S		80.1 S	26.5 Q J =130 Hz		52.3 T J=128 Hz		205.8 S	31.7 Q J =126 Hz
	m/e	43	55	83	39	45	56	98	41	59	60	159
	I	100	12.1	10.2	7.7	7	5.9	5.6	5.6	4.2	4.2	0.3
 D	NMR	a		b		c	d				
	^1H	1.8 S					1.3 S				
	^{13}C	22 Q		170.6 S		72.8 T	28 Q				
	m/e	43	57	41	56	59	44	39	15	101	117	
	I	100	50.3	48.9	26.9	26.2	23.5	23	20.6	8.8	0.8	

3) transfer to monomer giving side product A

$$CH_3CO\text{-}CH_2\text{-}C^+(CH_3)_2 + \text{isobutylene} \longrightarrow CH_3\text{-}COCH_2\text{-}C(CH_3) = CH_2 + (CH_3)_3C^+ \quad ,$$
(A)

4) transfer to AA giving side product D and C

(a) $(CH_3)_3C^+ + AA \longrightarrow (CH_3)_3\text{-}C\text{-}OCOCH_3 + CH_3CO^+$,
(D)

(b) $CH_3COCH_2\text{-}C^+(CH_3)_2 + AA \longrightarrow CH_3COCH_2 - C(CH_3)_2\text{-}OCOCH_3 + CH_3CO^+$,
(C)

5) termination with the counter-ion

(a) $(CH_3)_3\text{-}C^+(BF_3,OCOCH_3)^- \longrightarrow (CH_3)_3C\text{-}OCOCH_3 + BF_3$
(D)

(b) $CH_3COCH_2\text{-}C^+(CH_3)_2(BF_3,OCOCH_3)^- \longrightarrow CH_3COCH_2\text{-}C(CH_3)_2\text{-}OCOCH_3 + BF_3$.
(C)

Product B is always found in small quantity; it is not present in the reacting mixture but is formed during the separation of the different compounds by decomposition of the ceto-ester monoadduct C.

Product A originates from a transfer to monomer while C and D stem from termination or transfer reactions: both yield products C and D and we have no way to determine which mechanism is operative.

Table 2 shows the influence of temperature and the proportions of the different reagents on the yields and on the nature of the products. Several remarks can be made:

- The yield expressed in percentage of isobutylene incorporated ($100\Sigma/M$) varies from a few percent when AA is in large proportion to about 60% (runs N° 2,3,4) when AA is present in small quantity: it probably reflects the competition of AA and isobutylene towardsthe active cations.
- The proportion of compound D coming from proton initiation and ester termination is significant when the concentration in isobutylene is higher (runs N° 2,3,4).
- The formation of the ceto-ester monoadduct C is quantitative or near quantitative when a large excess of AA is used and when the proportions of BF_3 and isobutylene are small (runs N° 1,6,7,9,10).

Table 2 - Isobutylene telomerization : yield and proportions of the different compounds obtained

Run N°	T°C	$\frac{[M]}{[BF_3]}$	$\frac{[AA]}{[M]}$	$\frac{[AA]}{[BF_3]}$	Solvent (ml)		$\frac{100[\Sigma]}{[M]}$	$\frac{([A]+[B])\,100}{[\Sigma]}$	$\frac{[C]\,100}{[\Sigma]}$	$\frac{[D]\,100}{[\Sigma]}$
					AA	CH_2Cl_2				
1	- 20	0,94	17	16	100	-	16	10	90	-
2	- 20	0,94	1	1	17	83	56	55	33	12
3	- 20	0,97	1,48	1,4	20	80	63	39	33	28
4	- 20	0,97	1,94	1,89	20	80	55	40	38	23
5	- 20	2	5	10	30	70	37	20	80	-
6	- 40	3	13,3	40	100	-	7	10	90	-
7	- 40	2	16	32	100	-	4	10	90	-
8	- 40	2	4	8	30	70	37	25	75	-
9	- 40	1	20	20	100	-	15	-	100*	-
10 (5 hours)	- 40	1	20	20	100	-	26	-	100*	-
11	- 40	1	10	10	46	54	31	29	71	-
12	- 40	0,91	6,6	6	33	67	32	33	67	-
13	- 40	0,42	4,6	1,96	36	64	23	19	77	4
14	- 60	0,91	6,6	6	33	67	29	32	68	-

$[\Sigma] = [A] + [B] + [C] + [D]$ $[M]$ = molar concentration in isobutylene

* : determined by ^{1}H-NMR before separation of the mixture

. The influence of temperature is rather limited (runs N° 5, 12,14).

. The reaction time does not influence the nature of the product formed (quantitative formation of C in Table 2 for runs N° 9 and 10) and its influence on the yield is fairly limited : a six-fold increase of the reaction time only doubles the yield (runs N° 9 and 10).

Meerwein (7) showed that the reaction of BF_3 onto AA provokes the formation of a condensation compound containing 5 molecules of AA. In our experiments, the concentration in BF_3 is much lower so that this condensation is limited: besides the product obtained is soluble in water and eliminated this way. Nevertheless, a side reaction involving BF_3 must take place to inactivate it as the yield increases only moderately with time : several mechanisms could be evoked, involving either AA condensation or a complex formation with the ketones formed (8).

We see that BF_3, somehow gives side reactions and proves to be of rather low efficiency; in order to increase the efficiency of the initiator and to shed some light on the initiating step, we have used a preformed salt, the preparation of which is described in the experimental conditions (II).

Several features stand out:

. the yield in transformed isobutylene is quantitative.

. only two products are obtained namely 53% of C and 47% of D molewise.

Under the conditions chosen the acetylium salt is a fairly good initiator since about 50% of the isobutylene has been reacted this way. Lyubinkaya (9) had already shown that many substituted olefines are susceptible to attack by an oxocarbenium salt; more interestingly, termination occurs by esterification so that for each ketone formed by initiation, one finds one ester.

In conclusion the initiation of isobutylene by acetic anhydride $-BF_3$ complex produces only limited yields but quantitative formation of a ceto-ester monoadduct . A preformed oxocarbenium on the other hand can produce equal proportions of ester and ketone. Experimental conditions have to be studied in order to increase the molecular weights of the functionalized oligomers.

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