PARTIAL CHAIN-TRANSFER CONSTANTS IN TELOMERIZATION OF PROPYLENE WITH CCl_4, INITIATED BY MOLYBDENUM AND TUNGSTEN HEXACARBONYLS

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UDC 541.124.7 :66.095.2 :547.313.3

As a continuation of studying the initiation of radical reactions by Group VI metal carbonyls [1] we studied the telomerization of propylene with CCl_4 in the presence of the molybdenum and tungsten hexacarbonyls. As was established by the EPR method using spin traps, these carbonyls react with CCl_4 under UV irradiation to give $\dot{C}Cl_3$ radicals [2]. Starting with this, it could be expected that the telomerization of propylene with CCl_4, initiated by $Mo(CO)_6$ and $W(CO)_6$, as well as by $Cr(CO)_6$ [1], will proceed by the free-radical mechanism, since the $\dot{C}Cl_3$ radical propels the kinetic chain in peroxide-initiated telomerization. The fact that the values of the partial chain-transfer constants for telomerization, initiated by peroxides and by the studied initiators, coincide can also serve as proof for the free-radical mechanism. The possibility of initiating telomerization by the molybdenum and tungsten hexacarbonyls was first shown in [3] for the examole of reacting ethylene with CCl_4.

EXPERIMENTAL

The GLC analysis was run in a helium stream (6 liters/h) on an LKhM-8MD instrument equipped with a katharometer and a 2000 × 3 mm steel column packed with 15% SKTFT-50 deposited on Chromaton N-AW, and the temperature was programmed from 40 to 160°C (8 deg/min). The reactions were run in sealed 4-ml glass ampuls. The experimental procedure is described in [1]. The amounts of starting reactants, the experimental conditions, and the GLC analysis results for the reaction mixtures are given in Tables 1-3. The partial chain-transfer constants C_n were calculated using the Mayo equation.

DISCUSSION OF RESULTS

The telomerization of propylene with CCl_4, initiated by $W(CO)_6$, proceeds at 140° with good conversions and without the formation of side products (see Table 1, Expts. 4 and 5). The reaction is considerably slower at 120°. Thus, the conversions of propylene and CCl_4 in 150 min were a total of 4.8 and 9.4%, respectively, while at 140°, with the same amounts of the reactants, they were respectively 15 and 30% in 60 min. The distribution of the T_1-T_3 telomer homologs in this reaction at 120° (33.0, 59.3, and 7.7%) did not differ from the experiments run at 140° (see Table 1, Expt. 3). In the studied range of $W(CO)_6$ amounts ($7.5 \cdot 10^{-2}$-$30.0 \cdot 10^{-2}$ mmole) and time (30-90 min) the distribution of the telomer homologs was independent of the reaction time (see Table 1, Expts. 6, 7, and 3) and the amount of $W(CO)_6$ (Expts. 2-5), and coincided with the distribution when initiation was by tert-butyl peroxide (TBP) (Expt. 1). Higher concentrations of $W(CO)_6$ or a longer reaction time led to the formation of side products and tarring of the reaction mixture.

Initiation of the telomerization with $Mo(CO)_6$ at 140° leads to tarring of the reaction mixture, which is absent at 120°. Like in the initiation with $W(CO)_6$, the distribution of the telomer homologs was independent of the $Mo(CO)_6$ concentration (see Table 1, Expts. 9-12) and coincided with the distribution when initiation was by benzoyl peroxide (BP) (Expt. 8). The use of $Mo(CO)_6$ in an amount exceeding $30 \cdot 10^{-2}$ mmole leads to the appearance of side products in the reaction mixture.

To achieve approximately the same conversions of the reactants at a constant initiator concentration and reaction time a temperature of 20° lower is required for $Mo(CO)_6$ than for $W(CO)_6$ (see Table 1, Expts, 3, 11 and 5, 12). As a result, $Mo(CO)_6$ is a more efficient initiator than $W(CO)_6$ for the telomerization of propylene with CCl_4.

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2583-2586, November, 1982. Original article submitted February 10, 1982.

0568-5230/82/3111-2280$07.50 © 1983 Plenum Publishing Corporation

TABLE 1. Telomerization of Propylene with CCl_4, Initiated by $W(CO)_6$, $Mo(CO)_6$, tert-Butyl Peroxide (TBP), and Benzoyl Peroxide (BP)*

Expt. No.	Initiator (mmole·10^2)	T, °C	Time, min	Conversion, %		Amount of telomers $CCl_3[CH_2CH(CH_3)]_nCl(T_n)$ with n = 1-3, mole%			Amount of racemic diastereomeric modification of T_3, %		
				C_3H_6	CCl_4	T_1	T_2	T_3	h-T_3	s-T_3	i-T_3
1	ПТБ (2,0)	140	60	6,0	12,1	35,4	56,3	8,3	32,9	49,3	17,8
2	$W(CO)_6$ (7,5)	140	60	6,9	13,7	35,2	56,6	8,2	34,4	50,5	15,1
3	$W(CO)_6$ (18,5)	140	60	15,0	30,8	35,6	55,7	8,7	34,1	52,9	13,0
4	$W(CO)_6$ (25,0)	140	60	23,8	49,3	36,0	55,1	8,9	34,1	52,1	13,8
5	$W(CO)_6$ (30,0)	140	60	33,6	67,3	37,2	54,4	8,4	34,0	53,6	12,4
6	$W(CO)_6$ (18,5)	140	30	4,8	9,8	39,0	54,0	7,0	34,7	50,5	14,8
7	$W(CO)_6$ (18,5)	140	90	15,4	33,0	39,8	53,2	7,0	35,5	51,2	13,3
8	BP (1,2)	120	60	7,7	15,9	29,8	61,0	9,2	33,2	53,0	13,8
9	$Mo(CO)_6$ (0,8)	120	60	5,4	10,5	30,0	60,2	9,8	33,1	51,5	15,4
10	$Mo(CO)_6$ (2,5)	120	60	16,5	33,7	29,2	61,2	9,6	34,4	52,5	13,1
11	$Mo(CO)_6$ (18,5)	120	60	19,9	42,4	30,6	58,8	10,6	32,9	52,6	14,5
12	$Mo(CO)_6$ (30,0)	120	60	19,2	36,3	32,0	58,2	9,8	33.5	54,3	12,2

*17.6 ± 2.6 mmoles C_3H_6, 4.9 ± 0.1 mmoles CCl_4, C_3H_6/CCl_4 = 3.6 ± 0.1.

TABLE 2. Telomerization of C_3H_6 with CCl_4 in Presence of 0.03 mmole of $Mo(CO)_6$ (120°, 20 min)

C_3H_6	CCl_4	Conversion, %		$\left(\frac{C_3H_6}{CCl_4}\right)_{av}$	Amount of T_n telomers, mole %			Partial chain-transfer constants C_n	
mmole		C_3H_6	CCl_4		T_1	T_2	T_3	C_1	C_2
12,87	9,99	9,5	8,9	1,28	63,6	35,0	1,4	2,24	32,1
15,27	7,13	6,2	8,6	2,20	47,8	49,6	2,6	1,99	41,4
17,51	5,63	5,4	9,9	3,26	36,6	58,8	4,6	1,80	39,8
18,51	4,57	3,5	8,2	4,26	34,0	58,9	7,1	2,14	34,5
20,11	3,87	3,0	8,3	5,50	24,0	67,8	8,2	1,69	44,2
18,00	2,91	3,8	12,4	6,79	22,7	67,3	10,0	1,90	43,6
20,94	2,60	2,9		8,89	18,5	67,7	13,8	1,92	41,6
20,50	2,15	2,6	12,3	10,38	18,7	65,1	16,1	2,39	42,0
23,11	2,14	1,5	7,9	11,21	15,1	64,9	20,0	1,99	36,4
30,41	2,37	0,5	2,8	12,98	14,7	62,8	22,5	2,24	36,2
							Average	2,03	39,2
							σ*	0,03	0,6

*Arithmetical mean error.

TABLE 3. Telomerization of C_3H_6 with CCl_4 in Presence of 0.19 mmole of $W(CO)_6$ (140°, 25 min)

C_3H_6	CCl_4	Conversion, %		$\left(\frac{C_3H_6}{CCl_4}\right)_{av}$	Amount of T_n telomers, mole %			Partial chain-transfer constants C_n	
mmole		C_3H_6	CCl_4		T_1	T_2	T_3	C_1	C_2
13,90	9,43	10,9	11,0	1,47	57,6	39,2	3,2	2,00	18,0
16,13	7,18	5,9	8,2	2,28	44,0	49,4	6,6	1,79	17,1
16,63	4,90	4,8	9,8	3,48	39,0	54,0	7,0	2,22	26,8
21,93	4,59	4,8	12,3	4,98	28,7	57,7	13,6	2,00	21,1
21,16	3,86	4,4	12,6	5,74	22,9	61,9	15,2	1,70	23,4
21,82	2,59	2,0	8,3	8,71	19,6	60,8	19,5	2,12	27,2
21,96	2,16	3,8	18,7	11,10	18,0	60,0	22,0	2,44	30,3
24,30	2,17	3,8	20,5	12,38	15,6	59,1	25,3	2,29	28,9
31,42	2,43	2,2	13,1	13,74	11,0	57,4	31,6	1,70	25,0
30,85	2,06	1,5	10,2	15,70	9,8	61,2	29,0	1,70	33,1
							Average	2,00	25,2
							σ*	0,04	0,9

*Arithmetical mean error.

The fact that the distribution of the telomer homologs under the studied conditions is independent of the time and concentrations of $Mo(CO)_6$ and $W(CO)_6$ enabled us to determine the partial chain-transfer constants C_n in these reactions (see Tables 2 and 3). The range of change in C_3H_6/CCl_4 in the corresponding experiments was selected within limits that excluded the formation of substantial amounts of telomers with n > 3. The average values of C_n when the telomerization was initiated with $Mo(CO)_6$ and $W(CO)_6$ proved to be close to the C_n values when using peroxide initiation (C_1 = 2.23, C_2 = 40.3, 105°; C_1 = 3.65, C_2 = 33.145° [4]). This fact indicates that the telomerization of propylene with CCl_4, initiated by $Mo(CO)_6$ and $W(CO)_6$, proceeds by the free-radical

chain mechanism. This mechanism is also confirmed by the coinciding of the stereodirectivity of the telomerization when it is initiated by molybdenum and tungsten carbonyls and by peroxides. The amount of racemic diastereomeric forms of the telomer $CCl_3CH_2\overset{*}{C}H(CH_3)CH_2\overset{*}{C}H(CH_3)CH_2\overset{*}{C}HClCH_3$ (T_3) is approximately the same for telomerization in the presence of $W(CO)_6$ and TBP, and also $Mo(CO)_6$ and BP (cf. Expt. 1 and 2-7, and Expt. 8 and 9-12 in Table 1).

CONCLUSIONS

1. The first and second chain-transfer constants in the telomerization of propylene with CCl_4, initiated by $Mo(CO)_6$ at 120° and by $W(CO)_6$ at 140°, were determined.

2. A coinciding of the partial chain-transfer constants and a retention of the same stereodirectivity of the reaction when it is initiated by either peroxides or the molybdenum and tungsten hexacarbonyls indicate the free-radical mechanism of the telomerization in the presence of $Mo(CO)_6$ and $W(CO)_6$.

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SOME CHEMICAL TRANSFORMATIONS OF 5-(PROPYN-2-YL)BICYCLO[2.2.1]-2-HEPTENE

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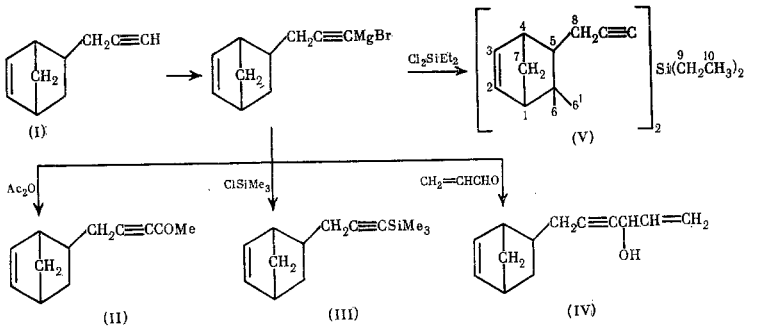
UDC 542.91:547.517.547.314

The 5-(propyn-2-yl)bicyclo[2.2.1]-2-heptene (I) previously obtained by us [1] contains three reactive centers, and specifically an acetylenic H atom, a double bond, and a triple bond, which makes it possible to use it for obtaining various unsaturated derivatives of the bicycloheptene series [2, 3]. In the present paper we studied the reactions of (I) at the acetylenic group in order to synthesize some functionally substituted derivatives that contain an alcohol, carbonyl, amino, or a di-(or tri) alkylsilyl group.

As it proved, (I) forms the corresponding Grignard acetylide, which easily reacts with the reactants indicated in the scheme to give the corresponding derivatives (II)-(V) in 85-90% yields:



Compound (I) enters into the Mannich reaction with HCHO and Et_2NH to give the acetylenic amine (VI) in 85% yield:

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2586-2589, November, 1982. Original article submitted February 12, 1982.

0568-5230/82/3111-2282$07.50 © 1983 Plenum Publishing Corporation