N—Cl-SULFONAMIDES AS COMPONENTS THAT RAISE THE EFFICIENCY OF INITIATING SYSTEMS INVOLVING METAL CARBONYLS

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Initiating binary systems based on $Fe(CO)_5$ and a nucleophilic cocatalyst make it possible to react unsaturated compounds with polyhalo derivatives in the cases where peroxides, azo compounds, etc. do not function as initiators [1, 2]. In [3] the theory was expressed that an N-chloroarylsulfonamide can take part in initiating the addition of CCl_4 to $p\text{-}ClC_6H_4SO_2N(Cl)CH_2CH{=}CH_2$ at 50°C, which is 50° lower than the usual temperature for the reaction of CCl_4 with olefins.

On the example of the studied addition of CCl_4 to 1-octene we studied the use as a component of the initiating system those arylsulfonamides that contain either one or two Cl atoms attached to the N, and arylsulfonamides that lack the N—Cl bond. The reaction practically does not go at room temperature (Table 1, Expts. 1-3). The binary systems: $Fe(CO)_5$ + hexamethylphosphoramide (HMPA) and $Fe(CO)_5 + p\text{-}ClC_6H_4SO_2NCl_2$ are ineffective at 50°. HMPA is more effective than DMF in the ternary system. Atmospheric oxygen inhibits the reaction (see Table 1, Expt. 8). In combination with $Fe(CO)_5$ and HMPA, arylsulfonamides that contain one N—Cl bond lead to the formation of the adduct in 21-25% yield. The best results were obtained in the experiments using $p\text{-}ClC_6H_4SO_2NCl_2$ as the third component of the initiating system, where the yield of adduct reaches 70%. Under the same conditions, $C_6H_5SO_2NCl_2$ (see Expt. 10) and $p\text{-}CH_3C_6H_4SO_2NCl_2$ are less efficient than $p\text{-}ClC_6H_4SO_2NCl_2$.

As a result, the ternary systems $Fe(CO)_5$ + HMPA + $p\text{-}ClC_6H_5SO_2NCl_2$ possess interest as initiators of free-radical addition and telomerization reactions.

The chloroamides of carboxylic acids are efficient in graft polymerization [4]. It is possible that the system proposed by us, which includes N—Cl-arylsulfonamides, will expand the gamut of compounds with a N—Cl bond that can be used to initiate polymerization.

EXPERIMENTAL

The N,N-Dichloroarylsulfonamides (Ar = $p\text{-}ClC_6H_4$, C_6H_5, $p\text{-}CH_3C_6H_4$) were recrystallized from CCl_4, and the purity was checked by the melting point and amount of active Cl. The N-chloro-N-sodio-p-chlorobenzenesulfonamide and p-chlorobenzenesulfonamide were recrystallized from water. The other arylsulfonamides were obtained as described in [5]. The GLC analysis of the reaction mixture was run on an LKhM-8MD instrument, using a katharometer, a 1 m × 3 mm column packed with 5% Silicone SE-30 deposited on Chromosorb N-AW-HMDS (0.16-0.20 mm), a temperature of 160°, helium as the carrier gas, a flow rate of 40 ml/min, and 1,1,1,3-tetrachlorooctane as the internal standard.

Reaction of CCl_4 with 1-Octene. Expts. 1-16. With stirring, to a mixture of 1-octene, CCl_4, and catalyst that had been purged well with N_2 was rapidly added in a N_2 stream a CCl_4 solution of the arylsulfonamide. In Expts. 12 and 14 the 1-octene, CCl_4, and catalyst were added to the arylsulfonamide and CCl_4. The reaction mixture was passed through a 30-35 mm bed of Silica gel L 100/160 μ and washed with 20 ml of CCl_4. The GLC method was used to identify the 1,1,1,3-tetrachlorononane and determine its yield.

Expt. 17. Here the reactants were loaded twice and the experiment was run the same as described above. Fractional distillation of the reaction mixture gave 70 mmoles of pure 1,1,1,3-tetrachlorononane (GLC data), whose constants agreed with the data given in [6].

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TABLE 1. Reaction of CCl_4 (0.1 mole) with 1-Octene (50 mmoles) Using $Fe(CO)_5$ (5 mmoles) + Nucleophilic Cocatalyst (20 mmoles) + Arylsulfonamides

Expt. No.	Arylsulfonamide	Amt. mole. %	Nucleophilic cocatalyst	T., °C	Time h	Yield of $CCl_3CH_2CHCl\cdot(CH_2)_5CH_3$, %
1	p-$ClC_6H_4SO_2NCl_2$	5	None	25	6	0,3
2	The same	5	DMF	25	6	1
3	»	5	»	25	63	5
4	»	5	None	50	6	7
5	»	5	DMF	50	6	13
6	»	5	HMPA	50	6	69
7	None	5	»	50	6	4
8 *	p-$ClC_6H_4SO_2NCl_2$	5	»	50	6	7
9	The same	5	»	50	3	20
10	$C_6H_5SO_2NCl_2$	5	»	50	6	30
11	p-$CH_3C_6H_4SO_2NCl_2$	5	»	50	6	17
12	p-$ClC_6H_4SO_2NClNa$	10	»	50	6	21
13	p-$ClC_6H_4SO_2NCl$ $ClCH_2ClCHCH_2$	10	»	50	6	25
14	p-$ClC_6H_4SO_2NH_2$	10	»	50	6	4
15	p-$ClC_6H_4SO_2NH$ $ClCH_2ClCHCH_2$	10	»	50	6	4
16	p-$ClC_6H_4SO_2N(CH_2CHClCN)_2$	10	»	50	6	5
17 †	p-$ClC_6H_4SO_2NCl_2$	5	»	50	6	70

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*The reaction was run in the air.

†See the experimental part.

CONCLUSIONS

On the example of adding CCl_4 to 1-octene it was shown that N—Cl-arylsulfonamides are efficient components of initiating systems based on $Fe(CO)_5$, and make it possible to lower the reaction temperature substantially.

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