CONDENSATION OF ACETOPHENONE DIETHYL KETAL

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Among the known heat resistant polymeric materials the polyphenylenes are one of the most promising types of compounds [1]. However, the known methods for the synthesis of the polyphenylenes [2] have a number of disadvantages, which consist either in the complexity of synthesizing the starting compounds or in the difficulty of processing the polymer. The method proposed by us for the synthesis of polyphenylenes by the polycondensation of diacetylarylene ketals [3] has a number of important advantages and makes it possible to obtain polymers of variable structure under mild conditions. The method is based on the trimerization of the ketals of methyl aryl ketones in the presence of HCl to give a 1, 3, 5-substituted benzene ring system [4]. Detailed data on this reaction are lacking in the literature. By analogy with the condensation of acetophenone [5], it could be expected that the condensation of acetophenone ketal (AK) will give, together with 1, 3, 5-triphenylbenzene (TPB), condensation products of the polyvinylene type. Such fragments in the polyphenylene chain are defects and can importantly affect the properties of the polymer.

In the present paper we studied the condensation of AK, which modeled the formation of a 1, 3, 5-substituted benzene ring in the synthesis of polyphenylenes by the polycondensation of bis-ketals, and an attempt was made to ascertain its principal rules and the mechanism.

TABLE 1. Yield of 1, 3, 5-Triphenylbenzene when Acetophenone Ketal is Condensed in the Presence of Various Catalysts

Catalyst	Amount of catalyst,%	Solvent*	Temperature, °C	Yield† of TPB,%
HCl	20	Toluene	—15	33
HCl	20	Benzene	20	78
HCl	20	"	60	52
HF	20	"	20	0
H_3PO_4	10	"	20	0
H_2SO_4	10	"	20	0
H_2SO_4	10	Without a solvent	200	39‡
H_2SO_4	10	Ditolylmethane	200	35‡
$TsOH \cdot H_2O$	10	Benzene	20	0
$TsOH \cdot H_2O$	10	"	60	45
$TsOH \cdot H_2O$	10	Without a solvent	200	63‡
$TsOH \cdot H_2O$	10	Ditolylmethane	200	58‡
$BF_3 \cdot O(C_2H_5)_2$	10	Benzene	20	0
$SOCl_2$	10**	"	20	75
CH_3COCl	10**	"	20	70‡

*Solution concentration of ketal = 1 M/liter.

†Reaction time = 1 h.

‡Reaction time = 4 h.

**Calculated on the basis of the amount of alcohol that is liberated in the condensation of the AK.

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TABLE 2. Condensation Rate of AK at 20°C in Benzene (Initial AK concentration = 1.0 M / liter; catalyst = HCl)

t, min	Ketal concn. [x], M /liter	$k_{II} = \frac{1}{2[X]_0 t} \cdot \frac{[X]_0 - [X]}{[X]}$, liter· M^{-1}· min^{-1}
1	0,654	
2	0,566	0,129
3	0,500	0,121
4	0,425	0,113
5	0,403	0,110
6	0,369	0,115
7	0,341	0,114
8	0,316	0,108
9	0,299	0,114
10	0,284	0,113
		$k_m = 0,115$*

The value of the rate constant, determined for an initial AK concentration of 0.5 and 1.5 M/liter, is respectively 0.122 and 0.117 liter· M^{-1}· min^{-1}.

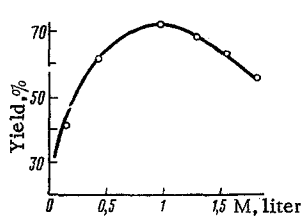


Fig. 1. Yield of TPB as a function of the initial AK concentration in benzene solution (catalyst = HCl, temperature = 20°).

We evaluated the efficiency of various acid catalysts in the formation of TPB on the basis of its yield. It proved that the most efficient catalysts are HCl gas, the acid chlorides of inorganic and organic acids, which form HCl when they react with the liberated alcohol, and p-toluenesulfonic acid (Table 1).

The high catalytic activity of HCl is probably associated with its dissociation in aprotic solvents according to the scheme: $2HCl \rightleftharpoons H^+ + HCl_2^-$ [6]. As a result, it becomes understandable why HF, which is weakly dissociated in aprotic solvents [7], does not catalyze the condensation of AK. The maximum formation of TPB in the presence of HCl is observed when the initial solution concentration of the ketal is 1 M/liter (Fig. 1). The extreme character of the yield of TPB as a function of the initial ketal concentration is probably explained by the increase in the portion of the side reactions.

The condensation rate of the AK was studied by the amount of alcohol that was liberated during the synthesis, which amount was determined by GLC. The running concentration of the ketal was calculated on the basis of its conversion to the alcohol, on the assumption that 2 molecules of alcohol are liberated per ketal group:

$$[X] = [C^{\circ}_{\text{ket}}] - [C_{\text{ket}_1}]$$

where $[C_{\text{ket}_1}]$ is the ketal conversion in M/liter, which was determined using the equation:

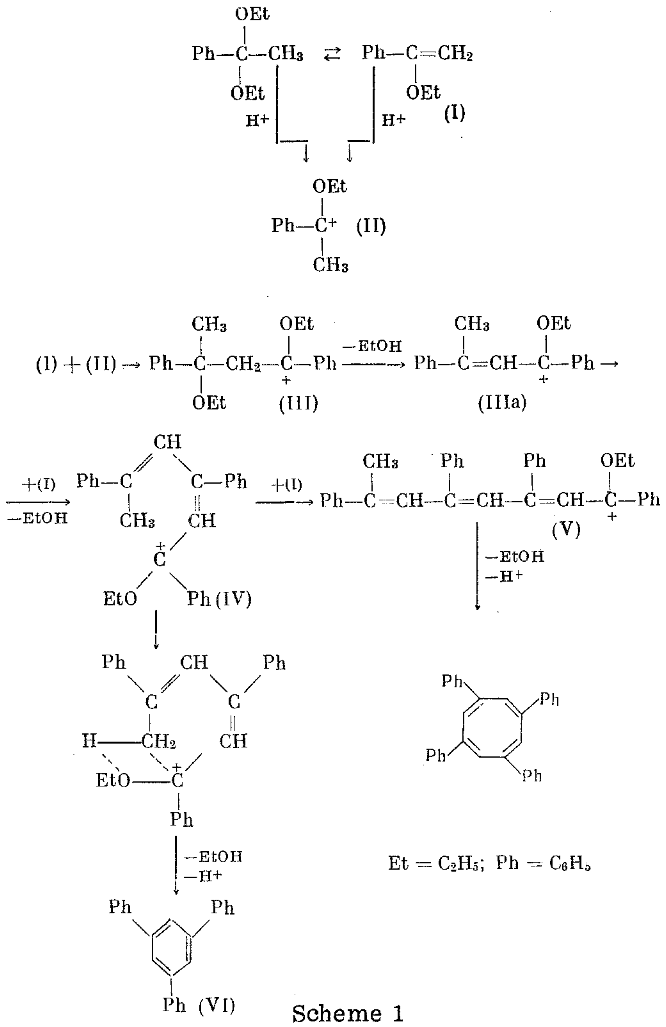
$$[C_{\text{ket}}] = (a_{\text{run}}/a_{\max})\,[C^{\circ}_{\text{ket}}]$$

where a_{run} is the running concentration of the alcohol in the sample in %, and $a_{\max}$ is the alcohol concentration in the reaction mass when all of the ketal has been converted, in %.

The constancy in the value of the rate constant, determined at various initial AK concentrations (Table 2), indicates the second order of the reaction. Starting with the second order of the reaction in AK, and taking into consideration the existing data both on the mechanism of the crotonic condensation [8] and on the chemical properties of ketals [9, 10], the process can be depicted by the following scheme (see Scheme 1).

As is known, equilibrium is established in acid medium with the formation of the AK of α-ethoxystyrene (I) [9, 10]. The addition of a proton to the AK and to (I) leads to the formation of the carbcation (II). The further reaction of (I) and (II) represents electrophilic attack of the methylene group of α-ethoxystyrene (I) by carbcation (II) with the formation of dimer (III). The intramolecular cleavage of alcohol from (III) leads to the formation of carbcation (IIIa), which is more stable due to conjugation. The further reaction of (I) with (IIIa) gives trimer (IV), which is capable of forming TPB (VI) via the intermediate complex and subsequent cyclic electron transfer [11]. The further reaction of (IV) with (I) gives tetramer (V), the intramolecular cyclization of which leads to (VII), etc.

The data on the cyclocondensation of α-ethoxystyrene itself corroborate the proposed scheme of the process. The yield of TPB in this case reaches 65%. The reaction has an induction period, which is associated with the formation of the carbcation (the color changes to dark red), after which the formation



Scheme 1

of the TPB, either without a solvent or in solution, bears an explosive character. A somewhat lower yield of TPB in this case can be explained by an increase in the role of the side reactions, as is evidenced by the appearance by halo compounds in the products.

As is known, the polarity of the solvent can exert an effect on the progress of the condensation. A decrease in the TPB yield is observed with increase in the polarity of the solvent (Table 3). This is probably explained by a decrease in the amount of α-ethoxystyrene with increase in the polarity of the solvent.

Taking into account the fact that the second step in the synthesis of polyphenylenes from ketals is accomplished at high temperatures [3], we made a more detailed study of the condensation of AK in the range 100-400°, and using p-toluenesulfonic acid ($TsOH \cdot H_2O$), H_2SO_4, $ZnCl_2$ and $SnCl_4$ as the catalysts. It proved that the efficiency of the catalysts decreases in the order: $TsOH > H_2SO_4 > ZnCl_2 > SnCl_4$ (Table 4). In addition, a decrease in the TPB yield occurs with increase in the temperature, although the ketal is consumed completely, which testifies to the formation of other products along with TPB.

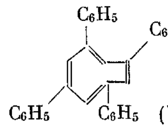
According to the GLC, the condensation products of AK in the presence of $SnCl_4$ contain TPB with a relative retention time of 17 min, and also of compounds with a longer retention time, which can be explained by the formation, along with TPB, of other cyclic compounds, like tetraphenylcyclooctatetraene (VII) and pentaphenylcyclodecapentaene, which should exist as 9, 10-dihydronaphthalene (VII) [12]. The formation of a substituted cyclooctatetraene was observed during the trimerization of some carbonyl-substituted olefins [13], in which connection it was postulated that the process proceeds via the intermediate formation of β-acetoxyvinyl acetate, which subsequently underwent condensation of the aldol type. Also in support of the formation of macrocycles in the experiment with $ZnCl_2$ at 200° is the good agreement of the mass number of the identified compounds with the molecular weight of compounds (VII) and (VIII).

TABLE 3. Effect of Polarity of Solvent on Yield of 1, 3, 5-Triphenylbenzene (Catalyst HCl, 20°, 1 hour)

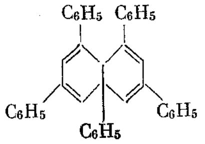
Catalyst	μ	Yield of TPB,%
Benzene	0,00	78
Toluene	0,29	76
CCl_4	0,00	72
Dioxane	0,45	69
Chloroform	1,15	60
Chlorobenzene	1,56	41,5
m-Cresol	1,54	43
Dimethyl-formamide	3,37	26,5
Nitrobenzene	3,99	28,6

TABLE 4. Yield of 1, 3, 5-Triphenylbenzene when Acetophenone Ketal is Condensed in the Presence of Acid Catalysts at Various Temperatures (Reaction time = 4 hours)

Catalyst	Yield of TPB, %			
	100°	200°	300°	400°
$TsOH \cdot H_2O$	40	48	37	23
H_2SO_4	—	31	26,4	10,3
$ZnCl_2$	—	24	18,6	11
$SnCl_4$	—	11	9,5	5



(VII)



(VIII)

In the NMR spectrum of the condensation products (with a mol. wt. of 675), remaining after recrystallization of the solid products, besides the signal of the protons of the benzene ring at 2.6-2.9 ppm (τ scale) and the CH_3 protons at 8.05 ppm, a signal is present at 3.25 ppm, which can be assigned to the proton of a vinylene structure, which suggests the possibility of forming linear polyvinylenes.

As a result, the condensation of AK represents a complex process, where together with the main product, namely TPB, a certain amount of condensation products is formed that have both a cyclic and a linear structure.

METHOD

Acetophenone diethyl ketal was obtained as described in [14] by the treatment of acetophenone with orthoformic ester. α-Ethoxystyrene, with bp 61-63° (2 mm) and $n_D^{23.5}$ 1.5275 [15], was obtained by the Claisen method [10], by heating AK in the presence of pyridine and CH_3COCl.

Condensation of Acetophenone Ketal. A stream of HCl was passed for 1 h into a solution of 2.5 g of AK in 10.5 ml of the solvent. The excess HCl and solvent were removed in vacuo at 30-35°. The residue was worked up to give triphenylbenzene with mp 172-173° (from glacial CH_3COOH) [4]. The condensation of AK in the presence of the other catalysts was run in a similar manner. The amount of acid chlorides, used as catalysts, was calculated on the basis that they reacted completely with the liberated alcohol, i.e., 2 M of acid chloride per mole of AK. We took 1.4 g of acetyl chloride for 2.5 g of the ketal, which represents 10%.

The amount of alcohol in the reaction mass was determined by GLC. The 1000 × 3 mm column was filled with 19% of Apiezon L deposited on Teflon, and the temperature was 45°. The relative retention time of the alcohol was 15 sec, and that of benzene was 150 sec. The column was calibrated using an alcohol–benzene mixture. The mass spectrometric measurements were run on MKh-1309 and RMI-6 (Hitachi) instruments, at a temperature of 50° in the ionization chamber and an ionization energy of 70 eV. The NMR spectra were taken on a Perkin–Elmer R-12 instrument in CCl_4 solution.

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CONCLUSIONS

1. A study was made of the formation of triphenylbenzene by the condensation of acetophenone diethyl ketal under various conditions and the optimum conditions were determined.

2. Some of the kinetic rules of the reaction were studied and it was shown that the condensation of acetophenone ketal is described by a second order kinetic equation. A probable mechanism of the reaction was proposed.

3. Employing chromatographic and mass-spectrometric analysis methods it was shown that, together with triphenylbenzene, macrocyclic compounds and polyvinylene oligomers are formed.

LITERATURE CITED

1. V. V. Korshak, Heat Resistant Polymers [in Russian], Nauka, (1970).
2. J. C. Speight, P. Kovacic, and F. W. Koch, J. Macromol. Chem. (Revs), C, 5, 295 (1971).
3. V. V. Korshak, M. M. Teplyakov, and V. P. Chebotarev, Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva, 17, 702 (1972).
4. H. O. Wirth, W. Kern, and E. Schmitz, J. Macromol. Chem., 68, 69 (1963).
5. V. A. Kargin, V. A. Kabanov, V. P. Zubov, I. M. Papisov, and G. I. Kurochkina, Dokl. Akad. Nauk SSSR, 140, 122 (1961).
6. F. Mayo and C. Walling, Chem. Revs, 27, 351 (1940).
7. I. N. Rozhkov and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 199, 614 (1971).
8. R. E. Lyle, E. J. DeWitt, and N. M. Nichols, J. Amer. Chem. Soc., 75, 5959 (1953).
9. M. F. Shostakovskii and N. A. Gershtein, Zh. Obshch. Khim., 16, 977 (1946).
10. L. Claisen, Ber., 31, 1020 (1898).
11. S. S. Yufim and V. F. Kucherov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2183 (1961).
12. E. E. van Tamelen and I. L. Burkoth, J. Amer. Chem. Soc., 89, 151 (1967).
13. T. Sakakibara, S. Nichimura, K. Kimura, S. Fujoka, and G. Odaira, Tetrahedron Letters, 4719 (1971).
14. H. Adkins and G. J. Pfeifer, J. Amer. Chem. Soc., 53, 1048 (1931).
15. K. von Auwers, Ber., 44, 3521 (1911).