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Studies on Nitrile Salts. IV.[1] Trimerization of Nitriles to 1,3,5-Triazines by the Combined Catalyst PCl_5-HCl

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The combined catalyst PCl_5–HCl shows effective catalysis in the trimerization of some aromatic nitriles or trichloroacetonitrile to *s*-triazines (III). The scope and limitation of the trimerization, in comparison with other Lewis acids, and its mechanism were studied. It was confirmed that PCl_5 is effective both in the formation of an intermediate, nitrile–HCl 2: 2 adduct, and in the reaction of the 2: 2 adduct with another nitrile to *s*-triazine.

According to U.S. patents[2,3] aromatic nitriles can be trimerized to produce 2,4,6-triaryl-*s*-triazines (III) by heating at *ca.* 200—500°C in the presence of metal halides or the combined catalyst, $AlCl_3$–HCl. Wakabayashi *et al.* reported that 2-substituted-4,6-bis(trichloromethyl)-*s*-triazines are obtainable by the cotrimerization of trichloroacetonitrile with some nitriles in the presence of the combined catalyst, Lewis acids–HCl.[4] However, they did not study the combined catalyst PCl_5–HCl.

While reports have been made concerning the reactions of PCl_5 with some cyano compounds under various conditions, no reactions with aromatic nitriles have been studied yet.[5,6]

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[1] Part III: S. Yanagida, T. Fujita, M. Ohoka, I. Katagiri, M. Miyake, and S. Komori, This Bulletin, **46**, 303 (1972).

[2] W. G. Toland, U. S. 360179 (1962).

[3] J. Sandner and W. L. Fierce, U. S. 3071586 (1963).

[4] K. Wakabayashi, M. Tsunoda, and Y. Suzuki, This Bulletin, **42**, 2924, 2931 (1969).

[5] F. C. Schaefer, "The Chemistry of the Cyano Group," ed. by Z. Rapoport, Interscience Publishers, New York, N. Y. (1970), p. 253.

[6] a) V. I. Schevchenko, N. K. Kulibaba, and A. V. Kirsanov, *J. Gen. Chem. USSR*, **38**, 328, 814 (1968); V. I. Shevchenko, N. K. Kulibaba, and A. V. Kirsanov, *ibid.*, **39**, 1656 (1969). b) H. P. Latscha, W. Weber, and M. Becke-Goehring, *Z. Anorg, Allg. Chem.*, **367**, 40 (1969).

In the course of our studies on the reactions of nitriles in the presence of HCl, it has been found that the combined catalyst PCl_5–HCl is quite effective in the trimerization of aromatic nitriles to *s*-triazines (III) under mild reaction conditions.

In the preceding paper[1] we reported that some aromatic nitriles (I) react with HCl in a sealed tube to afford the 2: 2 adducts (II). Our desire to find an explanation for the trimerization of nitriles (I) prompted us to investigate the reaction of the 2: 2 adducts (II) with aromatic nitriles (I) in the presence of PCl_5.

This paper reports the scope and limitation of catalysis of the PCl_5–HCl system in the trimerization of nitriles (I), in comparison with other Lewis acid–HCl systems, and a possible mechanism.

Results and Discussion

When benzonitrile (Ia) was allowed to react with PCl_5 in the presence of HCl in a sealed glass tube at 100—105°C, the reaction mixture solidified in 24 hr. The resulting solid product was identified as 2,4,6-triphenyl-*s*-triazine (IIIa) on the basis of its IR spectrum and elemental analysis. No product containing phosphorus atom was formed.

In order to know the role of PCl_5 in this reaction, we have studied the effect of varying the molar ratios of PCl_5 to benzonitrile from 0: 10 to 3: 10 on the yield under comparable conditions. An almost quantitative yield was obtained with a ratio 1: 10 or greater. A ratio 1: 50 was also effective, giving 60% yield of *s*-triazine (IIIa). In the absence of PCl_5, only a trace amount of IIIa was formed. When HCl was not used in the reaction,[7] 40% yield of IIIa was obtained after a period of 240 hr.

It is well-known that some Lewis acids catalyze the trimerization of aromatic nitriles.[2,3,8] However, the effectiveness of the combined catalyst Lewis acid–HCl has not been fully studied yet. From this point of view, some Lewis acid–HCl systems were examined.

TABLE 1. CATALYSIS OF LEWIS ACID–HCl IN THE TRIMERIZATION OF BENZONITRILE[a]

Catalyst[b]	Yield (%)
PCl_5–HCl	98
$SbCl_5$–HCl	62
PBr_3–HCl	20
$AlCl_3$–HCl	18
$SnCl_4$–HCl	21
$ZnCl_2$–HCl	13
$FeCl_3$–HCl	13

a) Reaction conditions: Procedure A (see Experimental), reaction temp. 24 hr.
b) Molar ratio of benzonitrile to Lewis acid, 10: 1.

We see from Table 1 that superior catalysis of PCl_5–HCl system was established. $SbCl_5$–HCl was also found effective, but the resulting *s*-triazine was contaminated with considerable amounts of further chlorinated *s*-triazines and required purification. Compared with the results of the U.S. patent using the combined catalyst $AlCl_3$–HCl,[3] the procedure using a closed vessel under milder reaction conditions is favorable for an increase in the yield.

The reaction using the combined catalyst PCl_5–HCl was extended to several other aromatic nitriles. When nitriles were solid, nitrobenzene was used as a solvent. Most nitriles trimerized to give the corresponding *s*-triazines (III) in satisfactory yields (Table 2). In the cases of *s*-triazines from *m*-tolunitrile and *β*-naphthonitrile, their mass spectra showed molecular ion peaks corresponding to *s*-triazines having one chlorine atom, indicating that the contamination with small amounts of monochlorinated *s*-triazines resulted from chlorination by PCl_5.

In the cases of *o*-tolunitrile, *α*-naphthonitrile and phthalonitrile, the expected triazines were not isolated; the former two were recovered unchanged, and when the reaction mixture from phthalonitrile was treated with water, only phthalimide was isolated.

The reaction was further extended to trichloroacetonitrile and 1,1,2-trichloropropionitrile, which have

TABLE 2. SYNTHESIS OF 2,4,6-TRIARYL-*s*-TRIAZINES (III) FROM AROMATIC NITRILES (I)

III	Ar	Procedure[a]	Reaction time (hr)	Yield (%)	Mp (°C)	IR (KBr) (cm^{-1})	Mass[b] (M^+)
IIIa	C_6H_5–	A	24	98	242—243[c]	1527, 1372	309
IIIb	*p*-$CH_3C_6H_4$–	A	90	60	278—280[d]	1514, 1391	351
IIIc	*m*-$CH_3C_6H_4$–	A	120	63	142—147[e]	1530, 1370	351
IIId	*p*-$NO_2C_6H_4$–[f]	B	120	62(16)[g]	300[h]	1530, 1350	—
IIIe	*p*-CNC_6H_4–	B	120	34(26)[g]	350[i]	1515, 1370	—
IIIf	*β*-Naphthyl–	B	120	22	293—300[j]	1523, 1380	459
IIIg	*p*-$CH_3OC_6H_4$–	B	120	8	217—222[k]	1510	—
IIIh	CCl_3–	A[l]	240	82	92— 93	1540	—

a) See Experimental. b) 70 eV. c) Lit,[9] 231—232. d) Lit,[9] 278—279. e) Lit,[9] 152—153. f) Anal: Found: C; 56.73, H; 2.52, N; 18.66%. Calcd: C; 56.76, H; 2.72, N; 18.91. g) The yield when $AlCl_3$ was used instead of PCl_5. h) Lit,[10] 360. i) Lit,[3] 504. j) Lit,[11] 290. k) Lit,[12] 224. l) Reaction temp., room temp. m) Lit,[5] 93.

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[7] Strictly speaking, the presence of HCl can not be neglected since PCl_5 reacts with moisture giving HCl.

[8] E. M. Smolin and L. Rapoport, "*s*-Triazins and Derivatives," Interscience Publishers, New York, N. Y. (1959), p. 147.

[9] A. Cook and D. Jones, *J. Chem. Soc.*, **1941**, 278.

[10] O. Davis, *ibid.*, **87**, 1831 (1905).

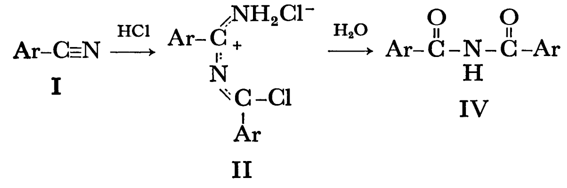
[11] M. Kunz, K. Koeberle, and E. Berthold, U. S. 1989042 (1935).

[12] P. Robin, *Ann. Chem.*, (Paris), (**9**), 16, 117 (1923).

no α-hydrogen susceptible to chlorination by PCl_5. Only trichloroacetonitrile gave 82% yield of 2,4,6-tris(trichloromethyl)-*s*-triazine by the reaction at room temperature for 240 hr.[13]

Mechanism. Some mechanisms for the trimerization of nitriles to *s*-triazines in the presence of acidic reagents have been proposed, but they still lack concrete evidences.[14]

Recently we found that some aromatic nitriles react with HCl, giving *N*-(α-chloroarylmethylidene)arylamidine hydrochlorides (II), and that their hydrolysis affords diaroylamines (IV) as follows;[1]



$$\underset{\mathrm{I}}{\mathrm{Ar{-}C{\equiv}N}} \xrightarrow{\mathrm{HCl}} \underset{\mathrm{II}}{\mathrm{Ar{-}\overset{+}{C}(NH_2Cl^-){=}N{-}C(Cl){-}Ar}} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{IV}}{\mathrm{Ar{-}C(=O){-}NH{-}C(=O){-}Ar}}$$

On treatment of the reaction mixture obtained in the trimerization of benzonitrile using the combined catalyst PCl_5–HCl with water, dibenzoylamine (IVa) was formed. The yield of IVa was much greater than that in the absence of PCl_5 (Table 3). When $AlCl_3$ or $SnCl_4$ was used instead of PCl_5, dibenzoylamine (IVa) could also be isolated in the same way. The results indicate that the 2: 2 adduct (II) is an intermediate to *s*-triazine (III) and that PCl_5 is effective in the dimerization of nitriles to II in the presence of HCl.

TABLE 3. EFFECT OF LEWIS ACIDS–HCl ON THE YIELDS OF DIBENZOYLAMINE (IVa) AND THE *s*-TRIAZINE IIIa[a)]

Lewis acid	Yield of IVa (%)	Yield of IIIa (%)
None	12(18[b)])	0
PCl_5	45	11
$AlCl_3$	24[c)]	3
$SnCl_4$	11[c)]	3

a) Reaction conditions: molar ratios, PhC≡N: HCl: PCl_5=1: 0.9: 0.1; reaction temp., 30°C; reaction time, 110 hr.
b) The yield of IIa.
c) Reaction time: 140 hr.

We observed that the pyrolysis of adducts (II) gives 2,4,6-triphenyl-*s*-triazines (III).[1] In order to estimate the sequence of this pyrolysis, differential thermal analysis of *N*-(α-chlorobenzylidene)benzamidine hydrochloride (IIa) was carried out (Fig. 1). On the basis of the decrease in weight and the analysis of the products, we estimated that two moles of amidine IIa reacts at 123°C, giving one mole of *s*-triazine IIIa, one mole of benzonitrile and four moles of HCl presumably through the following sequence;

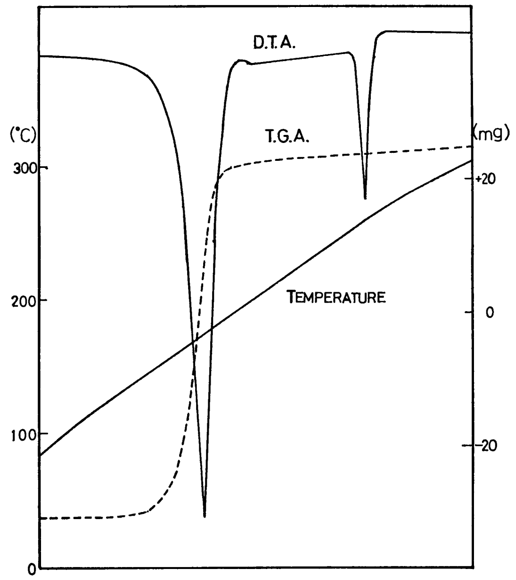
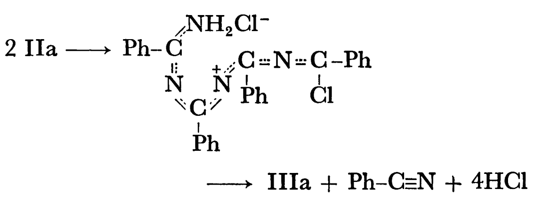


Fig. 1. Differential thermal and thermal gravimetrical analysis of *N*-(α-chlorobenzylidene)benzamidine hydrochloride (IIa).
Conditions for measurement: standard sample, α-Al_2O_3; amount of sample, 103.1 mg; sensitivity of gravimetry, ±50 mg; sensitivity of thermocouple, ±50 μV; heating rate, 2.5°C/min; circumstance, N_2: thermocouple, Pt–PtRh (13%); decrease of the weight (between 123—179°C), 52.0 mg (50.4%).



$$2\,\mathrm{IIa} \longrightarrow \mathrm{Ph{-}C(NH_2Cl^-){=}N{-}C(Ph){=}\overset{+}{N}{-}C(Ph){=}N{-}C(Cl){-}Ph} \longrightarrow \mathrm{IIIa} + \mathrm{Ph{-}C{\equiv}N} + 4\mathrm{HCl} \quad (1)$$

For the purpose of obtaining further proof for the catalysis of PCl_5, the reaction of the 2: 2 adducts (II) with other aromatic nitriles was effected under various conditions. In view of the pyrolysis of the adduct II, all the reactions were made at 30°C for 12 days.

The reaction of the 2: 2 adduct IIa from benzonitrile with *p*-tolunitrile in the presence of PCl_5 and HCl gave, although in low conversion, a mixture of *s*-triazines consisting of 2,4-diphenyl-6-*p*-tolyl-*s*-triazine (IIIa′) and 2,4,6-tris(*p*-tolyl)-*s*-triazine (IIIb) as major products, and 2,4,6-triphenyl-*s*-triazine (IIIa) and 2-phenyl-4,6-bis(*p*-tolyl)-*s*-triazine (IIIb′) as minor products. Without PCl_5, however, only traces were obtained even at 60°C for 5 days. Analogous treatment of the 2: 2 adduct IIb from *p*-tolunitrile with benzonitrile resulted in the major formation of IIIb′ and IIIa as expected.

Formation of IIIa and IIIb in these reactions apparently results from homotrimerization of benzonitrile and *p*-tolunitrile, respectively. In order to suppress the homotrimerization, the 2: 2 adduct IIa was made to react with *p*-tolunitrile only in the presence of PCl_5, giving IIIa′ exclusively, although in a low conversion.

PCl_5 is believed to have an ionic character on the basis of X-ray analysis and its IR spectra in solution, no complexes of PCl_5 with nitriles being re-

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[13] Kornuta *et al.* reported that trichloroacetonitrile reacts with PCl_5 at 140—145°C giving pentachloroethylphosphorimidic trichloride. P. P. Kornuta, V. I. Schevchenko, and A. V. Kirsanov, *J. Gen. Chem. USSR.*, **37**, 2657 (1967).

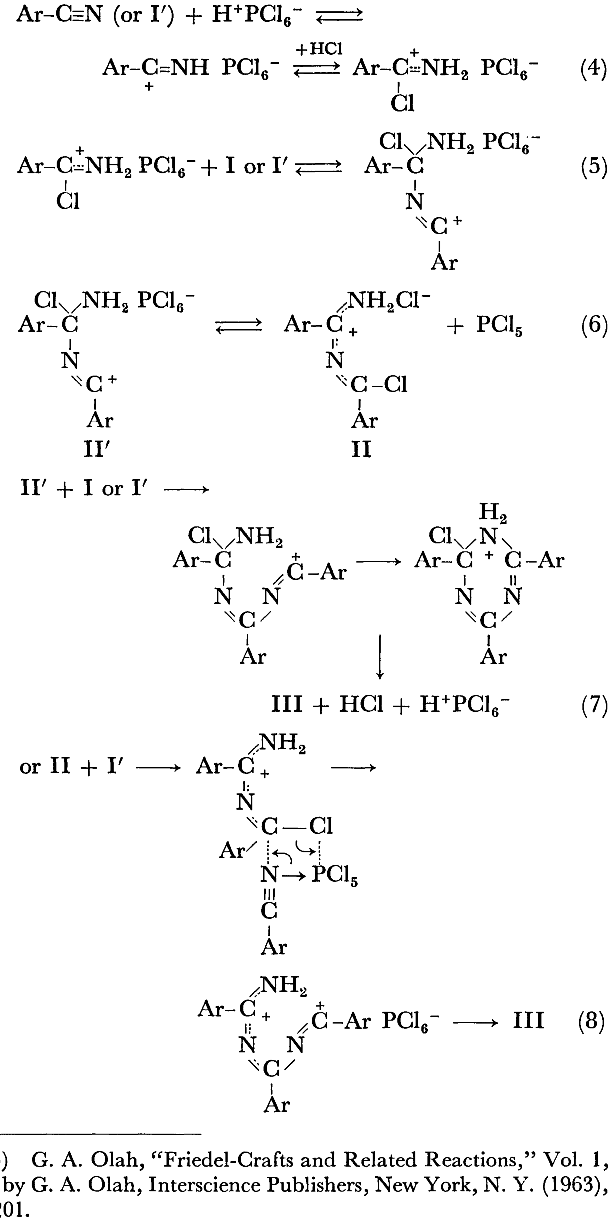
[14] a) M. Lora-tamayo and R. Madronero, "1,4-Cycloaddition Reactions", ed. by J. Hamer, Academic Press, New York, N. Y. (1967), p. 132. b) A. I. Meyers and J. G. Sircar, "The Chemistry of the Cyano Groups," ed. by Z. Rapoport, Interscience Publishers, New York, N. Y. (1970), p. 341.

cognized.[5,6,15,16] However, it was reported that its homologue $SbCl_5$ reacts with nitriles giving the 1:1 adduct $R-C\equiv N\cdot SbCl_5$, which readily reacts with HCl or alkyl chlorides to give nitrilium salts.[17,18] Accordingly PCl_5 can be expected to act as a weak Lewis acid.[15] Lewis acids are known to polarize the cyano group and to increase not only the electrophilic character of carbon but also the nucleophilic character of nitrogen.[14a,19]

In view of these facts and the proposed mechanism for the dimerization of nitriles,[1] the trimerization can be explained as involving the following sequences.

$$\underset{\text{I}}{\text{Ar-C}\equiv\text{N}} + PCl_5 \rightleftharpoons \underset{\text{I}'}{\text{Ar-C}\equiv\text{N } PCl_5} \qquad (2)$$

$$HCl + PCl_5 \rightleftharpoons H^+PCl_6^- \qquad (3)$$



At a high reaction temperature, sequence 1 (pyrolysis of II) can not be neglected. The failure of *o*-tolunitrile, phthalonitrile and α-naphthonitrile to trimerize is probably due to the steric hindrance of *ortho* groups in the sequences 4 and 7 or 8. Formation of phthalimide implies the exclusive intramolecular dimerization of the two cyano groups induced by the combined catalyst PCl_5–HCl.[20]

To our knowledge, the trimerization reported here is the first example of the catalysis of PCl_5 as a Lewis acid.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and were corrected. The IR spectra were recorded with a Japan Electroscopic IR-E spectrophotometer, and the mass spectra with a Hitachi mass spectrometer Model RMU-6E. Thermal gravimetrical and differential analyses were carried out with a Rigaku Denki Thermoflex, and glpc analysis with a Yanagimoto G-8 apparatus.

General Procedure. *A. Without Solvent*: Aromatic nitrile (30—50 mmol) and Lewis acid (3—5 mmol) (molar ratio 10:1) were placed in a 30 ml glass tube. Dry HCl (15—25 mmol) was bubbled into the mixture under cooling. The tube was stoppered, cooled in Dry Ice–acetone, sealed carefully and heated to 100—105°C in an oil bath for an appropriate time. After the end of the reaction, the tube was chilled in Dry Ice–acetone and opened. The reaction mixture was poured into water and insoluble *s*-triazine was filtered with suction and dried. The *s*-triazine was recrystallized from a suitable solvent (acetone, nitrobenzene or acetic acid) when necessary for analysis.[8] The analytical results are summarized in Tables 1 and 2.

B. In Nitrobenzene: Into a mixture of aromatic nitrile (20—30 mmol), PCl_5 (3.3—3.8 mmol) (Molar ratio 10:1) and nitrobenzene (5—10 g), was bubbled dry HCl (12—18 mmol). The tube was sealed and heated to 100—105°C for an appropriate time. When the tube was opened and the reaction mixture was degassed on standing, a precipitate was formed except for the case of *p*-methoxybenzonitrile. The resulting precipitate was filtered with suction, washed with some appropriate solvents having low solubility for *s*-triazine (ether, alcohol and acetone), and dried. In the case of *p*-methoxybenzonitrile, the mixture was condensed under reduced pressure and the residue was treated with water and extracted with ether. The extract was evaporated, giving *s*-triazine IIIg.

Isolation of Phthalimide. The reaction mixture obtained from phthalonitrile according to procedure B was poured into aqueous acetone and allowed to stand at room temperature for 3 days. The mixture was then extracted with ether, and the extract was evaporated to give a small amount of precipitate, which was confirmed as phthalimide on the basis of the following analyses; mp 236—238°C (lit,[21] 238) IR (Nujol) 3230, 2775, 1745, 1312, 1055, and 715 cm^{-1}.

Isolation of Dibenzoylamine (IVa). The reaction mixture obtained from benzonitrile according to procedure A was poured into 50 ml of water. After filtration of the

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[15] G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. 1, ed. by G. A. Olah, Interscience Publishers, New York, N. Y. (1963), p. 201.

[16] I. R. Beattie and M. Webster, *J. Chem. Soc.*, **1963**, 38.

[17] I. Klages and W. Grill, *Ann. Chem.*, **592**, 21 (1951).

[18] E. Allenstein and A. Schmidt, *Spectrochim. Acta.*, **20**, 1451 (1964).

[19] H. Hover, "Problems in Organic Reaction Mechanism," Wiley-Interscience, London, (1970), p. 119.

[20] Some dicyano compounds can be cyclized intramolecularly in the presence of hydrogen halides, when the two cyano groups are situated close to each other at appropriate positions. However, the intramolecular cyclization of phthalonitrile in the presence of HCl has not been reported.

[21] W. N. Hartley and E. P. Hedley, *J. Chem. Soc.*, **91**, 317 (1907).

s-triazine IIIa, the filtrate was extracted with ether to remove unreacted benzonitrile. The resulting aqueous phase was left standing at room temperature overnight. The needle-like crystal formed was filtered, washed with water and dried under reduced pressure. The product was confirmed by direct comparison with an authentic sample.[1]

Reaction of II with Aromatic Nitriles in the Presence of PCl_5. A typical procedure is as follows. The 2:2 adduct IIa (1.02 g, 3.66 mmol), *p*-tolunitrile (4.10 g, 35 mmol) and PCl_5 (0.30 g, 1.44 mmol) were placed in a 30 ml glass tube. Dry HCl (0.68 g, 18.6 mmol) was bubbled into the mixture under cooling. The tube was sealed and placed in a thermostat at 30°C for 12 days. Ether was added to the reaction mixture, giving a crystalline product which was confirmed to be a mixture of IIa and IIb by IR spectrum analysis (1.78 g) The filtrate was mixed with water (30 ml) and extracted with 50 ml of ether. The extract was dried with $MgSO_4$ and evaporated, giving a precipitate. The viscous residue was triturated with methanol giving an additional precipitate. Both precipitates were combined together (0.2 g) and analyzed. IR and mass spectra indicated that the product is a mixture of 2,4-diphenyl-6-*p*-tolyl-*s*-triazine (IIIa′), 2,4,6-tris(*p*-tolyl)-*s*-triazine (IIIb), 2-phenyl-4,6-bis(*p*-tolyl)-*s*-triazine (IIIb′), and 2,4,6-triphenyl-*s*-triazine (IIIa). Their ratios were determined to be roughly 56:38:2:4 by glpc by assuming that the sensitivity is proportional to their weight percentages.

Glpc was performed with a column of silicon gum SE, 10% on Diasolid L (60—80 mesh, 3 mmϕ × 1 m column, 300°C, hydrogen carrier gas, 30 ml/min).

A similar reaction of the 2:2 adduct IIb from *p*-tolunitrile with benzonitrile in the presence of PCl_5–HCl gave a mixture of IIIb′, IIIa, IIIa′, and IIIb in an approximate ratio 22:74:trace:4.

The reaction of IIa (1.05 g) with *p*-tolunitrile (4.30 g) only in the presence of PCl_5 (0.30 g) yielded a mixture (0.27 g) of IIIa′, IIIb, IIIb′, and IIIa in an approximate ratio 88:4:2:6.