Ionic Decomposition of Phenylazotriphenylmethane in Trifluoroacetic Acid[1]

Nobumasa KAMIGATA, Michio KOBAYASHI, and Hiroshi MINATO

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya, Tokyo

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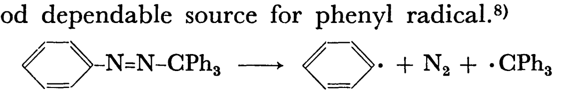
Acid-catalyzed decomposition of phenylazotriphenylmethane was studied in mixtures of benzene and large excess concentration of trifluoroacetic acid. The decomposition was of first order and the rate was much faster than that in pure aromatic solvents. The values of activation energy (E_a=22.3 kcal/mol) and activation entropy ($\Delta S^{\neq}=-5.2$ e.u.) fit the isokinetic relationship established for the ionic decomposition of benzenediazonium tetrafluoroborate in aprotic polar solvents and of phenylazo *p*-tolyl sulfone in mixtures of benzene and trifluoroacetic acid. The reaction products were benzene, biphenyl, benzophenone, triphenylmethane, triphenylmethyl alcohol and nitrogen. Orientations and partial rate factors for the phenylation of monosubstituted benzenes indicated that not phenyl radical but phenyl cation was produced as an intermediate. Further, the UV spectrum of PAT in benzene and trifluoroacetic acid shows λ_{max} at 403 mμ (log ε 4.48) and λ_{max} at 427 mμ (log ε 4.48). However, the UV spectrum of PAT in benzene and in the absence of trifluoroacetic acid has no absorption in this range. The formation of triphenylmethyl alcohol and the UV spectra of PAT in acid solution indicate that triphenylmethyl cation was formed as an intermediate. A plausible mechanism was discussed.

Benzenediazonium salts in aprotic polar solvents spontaneously decompose, yielding phenyl cation;[2] but they can generate phenyl radical when nitrite ion,[3] hydroxide ion[4] or pyridine[5] are added.

Phenylazo *p*-tolyl sulfone decomposes homolytically when such basic agents as pyridine, quinoline, and magnesium oxide are present,[6] but in the absence of such basic agents autocatalytic ionic decomposition takes place, yielding phenyl cation.[7]

However, there have been no papers reporting on the heterolytic decomposition of phenylazotriphenylmethane (PAT), which has been considered to be a good dependable source for phenyl radical.[8]



More recently, Takeuchi, Nagai, and Tokura reported that triphenylmethyl radical generated from PAT was converted to triphenylmethyl cation when SO_2 and O_2 were present in the reaction system.[9]

During a systematic investigation on the decomposition of arylazo compounds in our laboratories, it has been found that PAT decomposes quite rapidly with evolution of nitrogen under strongly acidic conditions. In order to determine whether this fast decomposition is homolytic or heterolytic, products of the decomposition have been analyzed and isomer distributions for phenylation of substituted benzenes have been studied.

In this papar, the results of this investigation will be described, and the mechanism of the reaction will be discussed.

Results and Discussion

Kinetic Studies. When a solution of PAT (1.00 g) in benzene (15.6 g) was mixed with trifluoroacetic acid (35.0 g), rapid evolution of nitrogen took place. The decomposition was of first order in PAT as shown in Fig. 1. The rate constants determined were compared with those for the decomposition of PAT in pure benzene,[10] and the results are summarized in Table 1. The values of the activation parameters were calculated (E_a=22.3 kcal/mol, $\Delta S^{\neq}=-5.2$ e.u.). These

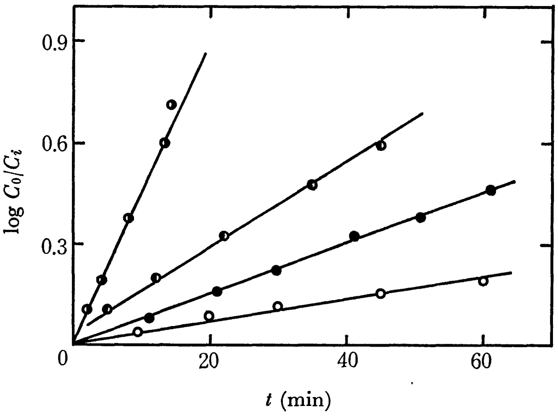


Fig. 1. First order rate plots for the decomposition of PAT in C_6H_6–CF_3CO_2H.
◑ 50.0°C, ◐ 40.0°C, ● 35.0°C, ○ 30.0°C

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[1] Cationic Arylation. IV.

[2] a) R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc.*, *B*, **1968**, 497; M. Kobayashi, H. Minato, E. Yamada, and N. Kobori, This Bulletin, **43**, 215 (1970).

[3] M. Kobayashi, H. Minato, N. Kobori, and E. Yamada, *ibid.*, **43**, 1131 (1970).

[4] N. Kamigata, T. Kurihara, H. Minato, and M. Kobayashi, *ibid.*, **44**, 3152 (1971).

[5] R. A. Abramovitch and J. G. Saha, *Tetrahedron*, **21**, 3297 (1965).

[6] M. Kobayashi, H. Minato, M. Kojima, and N. Kamigata, This Bulletin, **44**, 2501 (1971); C. G. Overberger and A. J. Rosenthal, *J. Amer. Chem. Soc.*, **82**, 108, 117 (1960).

[7] M. Kobayashi, H. Minato, and N. Kobori, This Bulletin, **43**, 219 (1970).

[8] For exsample: D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, **1955**, 3963; D. H. Hey, M. J. Perkins, and G. H. Williams, *ibid.*, **1965**, 110; W. A. Pryor, J. F. Echols, Jr., and K. Smith, *J. Amer. Chem. Soc.*, **89**, 1189 (1967); C. M. Camaggi, R. Leardimi, M. Tiecco, and A. Tundo, *J. Chem. Soc.*, *B*, **1969**, 1251; M. Harada, R. Ito, T. Migita, and O. Simamura, *Kogyo Kagaku Zasshi*, **69**, 962 (1966).

[9] H. Takeuchi, T. Nagai, and N. Tokura, This Bulletin, **43**, 1747 (1970).

[10] S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **75**, 5504 (1953); T. Yamamoto, *Nippon Kagaku Zasshi*, **83**, 844 (1962); T. Yamamoto, *ibid.*, **85**, 691 (1964).

Table 1. First order rate constants for the decomposition of PAT in C_6H_6–CF_3CO_2H

T (°C)	$k_1 \times 10^4$ (sec^{-1})	
	C_6H_6–CF_3CO_2H	C_6H_6
30.0	0.92	
35.0	1.82	
40.0	4.04	
50.0	8.09	
43.30		0.60[9]
53.35		2.25[9]

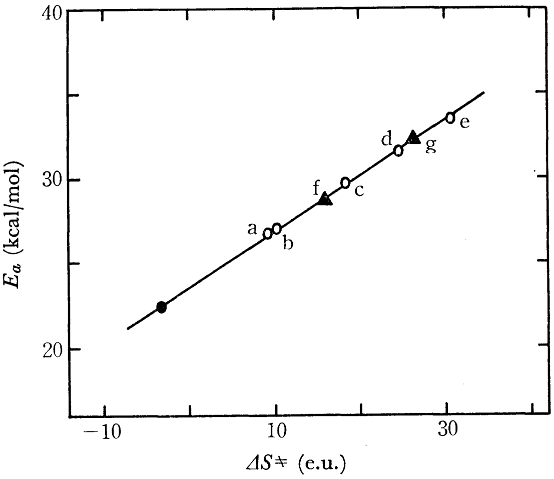

Fig. 2. Isokinetic relationship for the decomposition of PAT, PhN_2BF_4 and p-TsN_2Ph.
●: Decomposition of PAT in C_6H_6–CF_3CO_2H
○: Decomposition of PhN_2BF_4 in aprotic polar solvents[10]
(a: in $Me_2C{=}O$, b: in DMSO, c: in CH_3CN, d: in DMF, e: in CH_3NO_2)
▲: Decomposition of p-TsN_2Ph in C_6H_6–CF_3CO_2H[6]
(f: p-$TsN_2Ph/CF_3CO_2H=5.89$ mol/mol,
g: p-$TsN_2Ph/CF_3CO_2H=2.95$ mol/mol)

activation parameters fit surprisingly well the isokinetic relationship established for the decomposition of benzenediazonium tetrafluoroborate in various aprotic polar solvents[11] and for the decomposition of phenylazo p-tolyl sulfone in a mixture of benzene and trifluoroacetic acid,[7] as shown in Fig. 2 ($\beta=311$°K). The activation parameters are quite different from those reported[10] for the homolytic decomposition of PAT ($E_a=27$ kcal/mol, $\Delta S^{\neq}=5$ e.u.). These findings suggest that the decomposition of PAT in this medium is not homolysis but heterolysis. The fact that the activation parameters found fit the isokinetic relationship established for the decomposition of benzenediazonium ions suggests that benzenediazonium ion is an intermedate in this system and the rate-determining step is the decomposition of the diazonium ion.

$$\text{Ph-N=N-CPh}_3 \xrightarrow{CF_3CO_2H} \text{PhN}_2^+ \xrightarrow{\text{rate-determining step}} \text{Ph}^+ + \text{N}_2$$

Table 2. Decomposition products of PAT (40°C)

Products (mol/mol of PAT)	in $C_6H_6+CF_3CO_2H$[a]	in CF_3CO_2H[b]
N_2	0.93	0.95
PhH	—	0.74
Ph_2	0.16	0
Ph_3CH	0.24	0.26
Ph_3COH	0.53	0.57
PhCOPh	trace	trace

a) PAT (1.51g) was dissolved in C_6H_6 (23.5g) and CF_3CO_2H (50.0g): (Expt. 1).
b) PAT (1.42g) was dissolved in CF_3CO_2H (44.2g): (Expt. 2).

Products Studies. PAT was decomposed in a mixture of benzene and trifluoroacetic acid at 40°C and the reaction products are summarized in Table 2. Evolution of nitrogen was almost quantitative (93—95%) and the yield of benzene was high in contrast to low yield of biphenyl and triphenylmethane; these results are quite different from those reported for homolysis of PAT.[8] In addition, a trace of benzophenone and a considerable amount of triphenylmethyl alcohol were produced, but no triphenylmethyl peroxide was found though the reaction was carried out under air. The formation of triphenylmethyl alcohol suggests that triphenylmethyl cation was produced as the intermediate, and then converted to triphenylmethyl alcohol.

$$\text{Ph-N=N-CPh}_3 \xrightarrow{CF_3CO_2H} \text{Ph}_3\text{C}^+ \xrightarrow{H_2O} \text{Ph}_3\text{COH}$$

Kinetic studies and product studies described above show that benzenediazonium ion and triphenylmethyl cation were formed as the intermediates from PAT. These results are abnormal and very surprising.

$$\text{Ph-N=N-CPh}_3 \longrightarrow \text{Ph}^+ + \text{N}_2 + \text{Ph}_3\text{C}^+$$

UV Spectra of PAT in Benzene and Trifluoroacetic Acid. In order to ascertain the formation of trityl cation in this medium, the UV spectrum of PAT was measured in benzene and trifluoroacetic acid at room temperature. The spectrum is shown in Fig. 3. The values of log ε at 403 mμ and 427 mμ were 4.48; no absorptions were observed in this range, when trifluoroacetic acid was absent. The UV absorptions reported for trityl cation are as follows:

Trityl chloride:[12] $\lambda_{max}^{98\%H_2SO_4}$ 430 mμ (log ε 4.58)
Gomberg's trityl:[13] $\lambda_{max}^{H_3PO_4}$ 400 mμ and 440 mμ(log ε 4.5)
Gomberg's trityl:[13] $\lambda_{max}^{POCl_3}$ 420 mμ and 440 mμ(log ε 4.2)

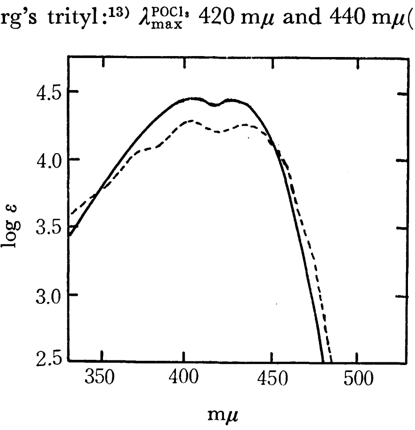

Fig. 3. The absorption spectrum of PAT in C_6H_6–CF_3CO_2H
—— PAT in C_6H_6–CF_3CO_2H
- - - Gomberg's trityl in liq. SO_2–O_2[9]

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[11] K. Ishida, N. Kobori, M. Kobayashi, and H. Minato, This Bulletin, **43**, 285 (1970).

[12] A. G. Evans, J. A. G. Jones, and G. O. Osborne, *J. Chem. Soc.*, **1954**, 3803.

[13] T. L. Chu and S. I. Weissman, *J. Chem. Phys.*, **22**, 21 (1954).

Therefore, the peaks at 403 mμ and 427 mμ in trifluoroacetic acid are ascribable to the presence of trityl cation in this medium. The values of log ε in our experiments are quite similar to the value reported[12] (log ε 4.58), and this means that PAT in trifluoroacetic acid is transformed to trityl cation to the same extent as the trityl chloride in 98% sulfuric acid.

TABLE 3. ORIENTATION (%) AND PARTIAL RATE FACTORS FOR THE PHENYLATION OF PhX WITH PAT IN CF_3CO_2H AT 40°C

X in PhX	Orientation (%)			Partial rate factors		
	o-,	*m*-,	*p*-,	k_o/k	k_m/k	k_p/k
OMe	57.6	10.9	31.5	1.52	0.28	1.66
Et	31.5	16.1	52.4	1.80	0.92	5.99
Cl	69.1	12.4	18.5	0.89	0.16	0.48
NO_2	33.7	63.1	3.2	0.18	0.34	0.03

Phenylation of Substituted Benzenes with PAT in Trifluoroacetic Acid. Isomer distributions and partial rate factors for the phenylation of substituted benzenes with PAT in trifluoroacetic acid were determined at 40°C. The results are summarized in Table 3. The MeO, Et, and Cl groups behaved as *o,p*-directors and accelerated the phenylation, whereas the NO_2 group behaved as a *m*-director, and retarded the phenylation. These results are quite different from the results of phenylation with phenyl radicals generated from benzoyl peroxide[14] or *N*-nitrosoacetanilide[15] but similar to the phenylation with phenyl cations generated from benzenediazonium tetrafluoroborate in aprotic polar solvents[2] and phenylazo *p*-tolyl sulfone in trifluoroacetic acid.[7] Figure 4 is the Hammett plots for the phenylation *versus* σ^+, which followed a good straight line except for the points for *p*-OMe and *m*-NO_2 groups. In the case of the phenylation of PhX with phenyl cation generated from benzenediazonium tetrafluoroborate, the points for *p*-OMe and *m*-NO_2 also deviated from a straight line in the Hammett plots.[2] The ρ value (ρ = −2.1) is a larger negative value than those obtained for the phenylation with benzenediazonium tetrafluoroborate (ρ = −0.82)[1] or phenylazo *p*-tolyl sulfone (ρ = −0.10).[7] This means that the decomposition of benzenediazonium ion in trifluoroacetic acid is more sensitive to the electron supply of substituents. Brown and Wirkkala reported that the relative rate of bromination of toluene and benzene (k_T/k_B) was 605 in 85% CH_3CO_2H and 2580 in CF_3CO_2H.[16]

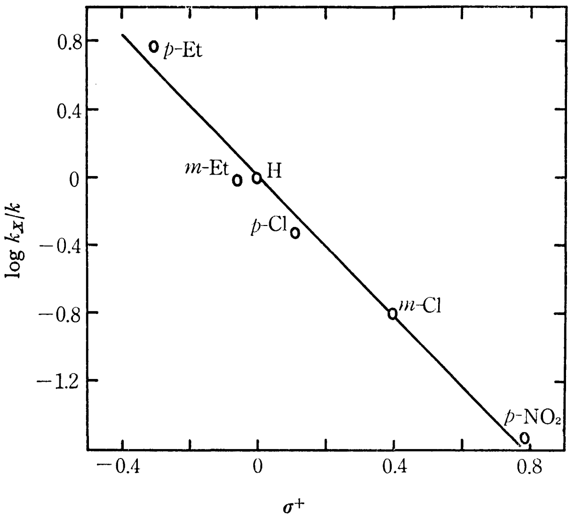
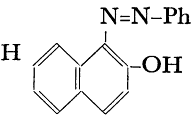


Fig. 4. The Hammett plots for the phenylation of PhX with PAT in CF_3CO_2H at 40°C.
ρ = −2.1

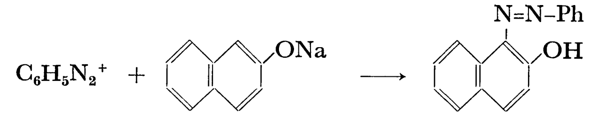
Plausible Reaction Mechanism. Since the formation of trityl cation was instantaneous and almost quantitative upon addition of trifluoroacetic acid, trityl ion must be present before the rate-determining step. The red color of trityl cation did not fade when such nucleophiles as water was absent in the medium. When water was added to the mixture, the red color disappeared instantaneously.

It is of interest to determine what kind of chemical species are present in the mixture when the mixture changed from yellow to red upon addition of trifluoroacetic acid. When water was added about 20 sec after addition of trifluoroacetic acid, the products isolated from the benzene layer contained more triphenylmethane and less triphenylcarbinol, whereas the main product was triphenylcarbinol when water was added about 60 sec after addition of trifluoroacetic acid. The results are shown in Table 4.

TABLE 4. PRODUCTS OF HYDROLYSIS OF $PAT–C_6H_6–CF_3CO_2H$ MIXTURE

	Time interval between addition of CF_3CO_2H and that of H_2O	Products (mol/100 mol PAT)		
		Ph_3CH	Ph_3COH	
Expt. 7	about 20 sec	58.9	30.9	45
Expt. 8	about 60 sec	2.9	86.0	54

When the aqueous layer was separated and added to a 10% sodium β-naphthoxide solution, the coupling product was produced in good yield, indicating the presence of benzenediazonium ion in the mixture.



A mechanism which is consistent with these results is shown below.

The mechanism shown requires that the reaction between phenyl cation and triphenylmethane produces benzene and triphenylmethyl cation. Taft[17] and Abramovitch[18] proposed that phenyl cation is in equi-

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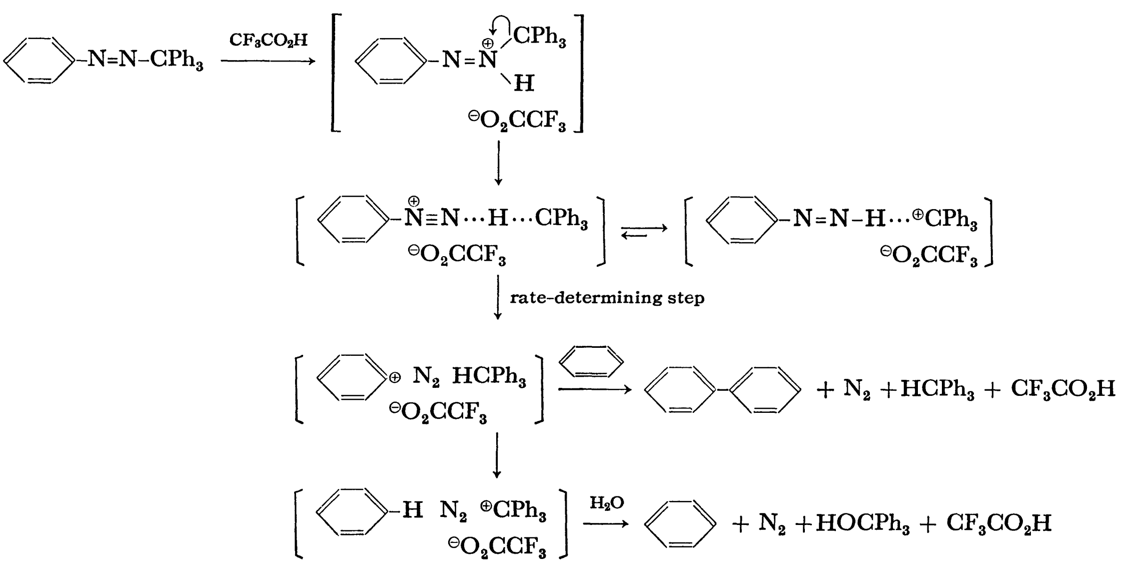
[14] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford (1960), p. 73.

[15] R. Ito, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

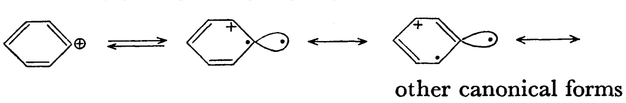
[16] H. C. Brown and R. A. Wirkkala, *J. Amer. Chem. Soc.*, **88**, 1447 (1966).

[17] R. W. Taft, *ibid.*, **83**, 3350 (1961).

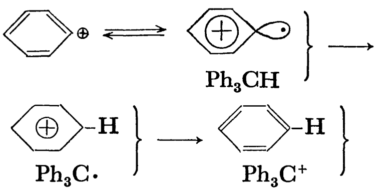
[18] R. A. Abramovitch and J. G. Saha, *Can. J. Chem.*, **43**, 3269 (1965); R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc.*, *B*, **1968**, 1497.



librium with a diradical cation.



The formation of triphenylmethyl cation from triphenylmethane would be better explained in terms of hydrogen abstraction by a diradical cation rather than hydride transfer.



In order to prove that phenyl cation can oxidize triphenylmethane to triphenylmethyl cation, the phenyl cation produced from another source, benzenediazonium tetrafluoroborate (Exp. 3) or phenylazo *p*-tolyl sulfone (Exp. 4), were let to react with triphenylmethane in benzene-trifluoroacetic acid. Triphenylmethyl alcohol was found indeed as one of the products, though its yield was not so high (0.023 and 0.027 mol per mol of the benzenediazonium tetrafluoroborate and phenylazo *p*-tolyl sulfone, respectively). The lower yield in comparison with the yield in the case of the PAT–CF_3CO_2H system can be ascribed to the occurrence of the reaction in cage in the case of the PAT–CF_3CO_2H system. The yield must have been lowered by the reaction between phenyl cation and benzene, which was used to dissolve the triphenylmethane.

In an attempt to produce a system which resembles a mixture of PAT and trifluoroacetic acid, benzenediazonium trifluoroacetate was synthesized and dissolved in benzene containing triphenylmethane and trifluoroacetic acid. However, only a trace amount of triphenylcarbinol was found as a product by glc. These findings show that the tertiary hydrogen of triphenylmethane is very efficiently abstracted by phenyl cation in a cage, but much less efficiently in a system formed by simply mixing a diazonium ion and triphenylmethane.

According to the mechanism proposed, the amount of diphenyl produced must be comparable to that of triphenylmethane, and the amount of triphenylcarbinol must be comparable to that of benzene. The results in Table 2 are approximately in agreement with this mechanism.

Experimental

Materials. Phenylazotriphenylmethane was prepared by the bromine-water oxidation of phenylhydrazotriphenylmethane,[19] which was synthesized from the reaction between phenylhydrazine and triphenylmethyl chloride in ether.[20] Crude PAT was recrystallized from benzene–ethanol, mp 111—112°C (decomp.). Benzenediazonium tetrafluoroborate,[21] phenylazo *p*-tolyl sulfone[22] and benzenediazonium trifluoroacetate[23] were prepared according to the method described in the literature. Benzene, ethylbenzene, and chlorobenzene were washed with concentrated sulfuric acid and water successively, dried over calcium chloride, and distilled. Boiling points were 80, 135.5, and 131°C, respectively. Anisole was washed with an aqueous sodium hydroxide solution and water, dried over calcium chloride, and then distilled; bp 153°C. Nitrobenzene was washed repeatedly with a potassium dichromate solution and water, dried over calcium chloride, and distilled; bp 95.5°C/18 mmHg. Trifluoroacetic acid of Wako Pure Chemical Industries Limited was used without further purification. Isomeric ethylbiphenyls, methoxybiphenyls, chlorobiphenyls, and nitrobiphenyls were prepared as the reference compounds by the methods described in the literature.[24] They were purified by elution chromatography, distillation or recrystallization, and their melting points and boiling points agreed with the values reported in the literature. Triphenylmethane was prepared by lithium aluminum hydride reduction of

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19) M. Gomberg and H. W. Berger, *Ber.*, **36**, 1088 (1903).

20) C. R. Hauser and B. E. Hudson, Jr., "Organic Syntheses," Coll. Vol. III, p. 842 (1955).

21) E. B. Starkey, "Organic Syntheses," Coll. Vol. II, p. 225 (1943).

22) A. Hantzsch and M. Singer, *Ber.*, **30**, 312 (1897).

23) M. R. Pettit, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, **1953**, 3081.

24) R. Adams, "Organic Reactions," Coll. Vol. II, John Wiley and Sons, Inc., London (1957); P. E. Fanta, *Chem. Rev.*, **64**, 613 (1954).

triphenylmethyl chloride in ether and recrystallized from methanol, mp 92°C. Triphenylcarbinol was prepared by hydrolysis of triphenylmethyl chloride with an aqueous sodium hydroxide solution, and recrystallized from ethanol, mp 164°C.

Kinetic Measurements. PAT (1.00 g) was dissolved in benzene (15.6 g) and trifluoroacetic acid (35.0 g), and was decomposed in a water bath, the temperature of which was regulated within ±0.1°C. The rate of decomposition was followed by measuring the evolution of nitrogen gas by use of a gas burette, and the total yield of nitrogen was determined.

Products of Decomposition of PAT in C_6H_6-CF_3COOH. *Experiment 1*: PAT (1.51 g) was decomposed in benzene (23.5 g) and trifluoroacetic acid (50.0 g) at 40°C. After the decomposition was over, the reaction mixture was washed successively with water, a 5% sodium hydrogen carbonate solution and water, and then dried over anhydrous magnesium sulfate. The nitrogen gas evolved was identified by gas chromatography with a Shimadzu GC-3AH (Molecular Sieve 5A 1m Column). The amounts of diphenyl, benzophenone, and triphenylmethane produced were determined by a Hitachi Gas Chromatograph K-53 on a column packed with 10% Apiezon L on Chromosorb W, on the basis of the comparison with the gas chromatograms of authentic samples. Triphenylmethyl alcohol was isolated by elution chromatography (alumina–benzene), identified by means of its IR spectrum and its melting point (164°C), and the weight was determined.

Products of Decomposition of PAT in CF_3COOH. *Experiment 2*: PAT (1.42 g) was decomposed in trifluoroacetic acid (44.2 g) at 40°C. The amount of benzene produced was determined by gas chromatography. The amounts of benzophenone, triphenylmethane and triphenylmethyl alcohol were determined according to the methods described above.

Phenylation of Monosubstituted Benzenes with PAT. PAT (1.00 g) was dissolved in an equimolar mixture of benzene and a substituted benzene (total aromatics, 50 mol per mol of PAT), and trifluoroacetic acid (35.0 g) was added to this solution. The flask containing the solution was placed in a bath at 40±0.1°C, and the decomposition was followed by measuring the rate of evolution of nitrogen. After the evolution of nitrogen ceased, the reaction mixture was washed with water, a 5% sodium hydrogen carbonate solution and water, and dried over anhydrous magnesium sulfate, and then the amounts of substituted biphenyl isomers were determined by a Hitachi Gas Chromatograph K-53 (Apiezon L 10% on Chromosorb W).

Since the presence of a great quantity of a substituted benzene made the gas chromatographic determination of substituted biphenyls unreliable due to the tailing, the determination was made after about 70% of aromatic solvents were evaporated. Biphenyl isomers were identified by comparison of their retention times with those of the authentic samples.

Not benzene but chlorobenzene was used as the standard for the competitive phenylation, since unsubstituted biphenyl easily sublimes during the evaporation of substituted benzenes. The reactivity of each position of substituted benzenes was calculated relative to the reactivity of the *ortho* position of chlorobenzene. The partial rate factor of the *ortho* position of chlorobenzene was determined by an experiment carried out without evaporation of aromatic solvents. The partial rate factors of various substituted benzenes were calculated by the following equation.

$$k_x/k = (k_x/k_{o\text{-Cl}}) \times (k_{o\text{-Cl}}/k)$$

where,

k_x/k: partial rate factor for phenylation of PhX at the x (*o*-, *m*-, or *p*-) position
$k_x/k_{o\text{-Cl}}$: relative rate of phenylation at the x position of PhX against the *ortho* position of chlorobenzene
$k_{o\text{-Cl}}/k$: partial rate factor for phenylation at the *ortho* position of chlorobenzene

Spectra Measurements. UV and IR spectra were recorded with a Hitachi EPS-3T and Hitachi EPU-S2 spectrophotometer, respectively.

Decomposition of Benzenediazonium Tetrafluoroborate in the Presence of Triphenylmethane. *Experiment 3*: Benzenediazonium tetrafluoroborate (1.866 g) and triphenylmethane (0.650 g) were dissolved in a mixture of benzene (20 g) and trifluoroacetic acid (30 g). The diazonium salt was decomposed at 40°C overnight. The reaction mixture was washed successively with water, a 5% aqueous sodium carbonate solution and water. Triphenylmethyl alcohol was determined by gas chromatography (SE 30 on Chromosorb W). Yield, 58 mg (0.023 mol per mol of the diazonium salt).

Decomposition of Phenylazo p-*Tolyl Sulfone in the Presence of Triphenylmethane.* *Experiment 4*: Phenylazo *p*-tolyl sulfone (1.16 g) and triphenylmethane (0.94 g) were dissolved in a mixture of benzene (25 g) and trifluoroacetic acid (30 g). The azosulfone was decomposed for 20 hr in a water bath regulated at 40°C. The reaction mixture was washed successively with water, a 5% aqueous sodium carbonate solution and water. Triphenylmethyl alcohol was isolated by elution chromatography and identified by comparison of its IR spectrum with that of an authentic sample. Yield, 32 mg (0.027 mol per mol of the azosulfone).

Decomposition of Benzenediazonium Trifluoroacetate in the Presence of Triphenylmethane. *Experiment 5*: Benzenediazonium trifluoroacetate (2.0 g) and triphenylmethane (0.576 g) were dissolved in benzene (10 g) and trifluoroacetic acid (13 g) and stirred vigorously. The diazonium acetate was decomposed at room temperature overnight. The reaction mixture was treated in the manner described in Expt. 1, and triphenylmethyl alcohol was analyzed by glc; a trace of triphenylmethyl alcohol was detected.

Experiment 6: Benzenediazonium trifluoroacetate (2.0 g) and triphenylmethane (0.618 g) were dissolved in benzene (11 g), and stirred vigorously. The diazonium acetate was decomposed at room temperature overnight. The reaction mixture was treated in the manner described in Expt 2, and triphenylmethyl alcohol was analyzed quantitatively by glc; a trace of triphenylmethyl alcohol was detected.

Products of Hydrolysis of PAT–C_6H_6–CF_3CO_2H Mixture. *Experiment 7*: About 20 sec after the addition of CF_3CO_2H (30 g) to a benzene (20 g) solution of PAT (1.69 g), ice water was added. The aqueous layer was added to a 10% NaOH solution containing *β*-naphthol (1.4 g), and *α*-phenylazo-*β*-naphthol formed was filtered and dried; 0.508 g (45%).

The organic layer was treated in the manner described in Expt. 1, and the amounts of triphenylmethane and triphenylmethanol were determined by glc. Results are shown in Table 4.

Experiment 8: About 60 sec after the addition of CF_3CO_2H (30 g) to a benzene (20 g) solution of PAT (1.55 g), ice water was added. Evolution of nitrogen before addition of water was very little. The mixture was treated in the manner described in Expt 7. Results are shown in Table 4.