

Studies of Trifluoroacetic Acid. Part XI. The Reactions of Diazonium Trifluoroacetates with Aromatic Compounds to give Diaryls.*

By M. R. PETTIT and J. C. TATLOW.

[Reprint Order No. 5073.]

N-Acetylarylamines react with alkyl nitrites in trifluoroacetic anhydride, and from the resultant mixtures the *N*-nitroso-derivatives are precipitated when water is added, whilst diphenyls are formed by treatment with benzene. Solutions of *N*-trifluoroacetylarylamines in the nitrosating agents, aqueous diazonium trifluoroacetates, solid diazonium acid trifluoroacetates (cf. *J.*, 1953, 3081), and aqueous solutions of diazonium chlorides containing added trifluoroacetate ions, all also give diphenyl derivatives when treated with aromatic compounds. Diazonium salts of other perhalogeno-carboxylic acids behave similarly.

THERE have been recently many investigations of the production of diaryl compounds by homolytic aromatic substitution (see, *inter al.*, Hey, *J.*, 1952, 1974; Waters, *Ann. Reports*, 1952, 49, 118; Hey, Nechvatal, and Robinson, *J.*, 1951, 2892; Huisgen and Horeld, *Annalen*, 1949, 562, 137; Bachmann and Hoffman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, 1944, p. 224). Among the important arylating agents are acylarylnitrosamines (Fischer, *Ber.*, 1876, 9, 463; Bamberger, *Ber.*, 1897, 30, 366) which have been made from acylarylamines by nitrosation with nitrous fumes (Haworth and Hey, *J.*, 1940, 361) or with nitrosyl chloride (France, Heilbron, and Hey, *ibid.*, p. 369).

* Part X, *J. Amer. Chem. Soc.*, in the press.

The present work began with the application, to the nitrosation of acylarylamines, of mixtures of trifluoroacetic anhydride and alkyl nitrites. Such mixtures give diazonium salts with reactive aromatic compounds; this reaction presumably proceeds by nitrosation to give nitroso-compounds, which then react further with nitric oxide present in the mixture (Bourne, Stacey, Tatlow, and Tedder, *J.*, 1952, 1695). It was found that solutions of a number of *para*-substituted acetanilides in ethyl or amyl nitrite-trifluoroacetic anhydride reacted with benzene under conditions similar to those usually employed with nitrosoacetanilides, to give the corresponding diphenyl derivatives (see Table 1). If a solution of the anilide in the nitrosating mixture was poured into water the *N*-nitrosoacetanilide derivative was precipitated, and in the one case tried, addition of alkaline β -naphthol gave the corresponding coupling product. Sodium nitrite can be used instead of an alkyl nitrite in the process.

Attempts were made next to extend the earlier work on acylarylamines by nitrosating *N*-trifluoroacetylarylamines (Bourne, Henry, Tatlow, and Tatlow, *J.*, 1952, 4014). Nitrosation of trifluoroacetanilide in trifluoroacetic acid solution with nitrous fumes was slow. No *N*-nitroso-derivative was precipitated when water was added to the solution, though unchanged anilide was obtained. However, after a relatively long time, addition of β -naphthol in alkali to the aqueous phase precipitated some azo- β -naphthol derivative (Table 2). Trifluoroacetanilide and its analogues reacted with trifluoroacetic anhydride-ethyl nitrite, but no precipitate was formed when water was added, though addition of β -naphthol in alkali gave the analogous azo- β -naphthol coupling derivative in good yield. Also, a solution of a trifluoroacetanilide in the nitrosating medium gave with benzene the expected unsymmetrical diphenyl (see Table 1). In general, the reactions were carried out for about 24 hours at 10–15° and then the benzene was evaporated at up to 100°. In one case a significant yield of diphenyl was obtained when the mixture was merely refluxed for 1 hour. Nitrosations, with trifluoroacetic anhydride-nitrite, of *N*-acetyl and -trifluoroacetyl derivatives of amines containing certain groups such as nitro or trifluoromethyl were more difficult than with other types of anilides, and in one case, that of 4-nitro-3-trifluoromethyltrifluoroacetanilide, no reaction was detected.

Thus, it was shown that trifluoroacetic anhydride-nitrite mixtures are effective for the *N*-nitrosation of acylarylamines, though, as frequently occurs, the yields obtained in the diaryl synthesis were not high—they did not often exceed 40%. Mechanisms which may be advanced to explain the reactions of trifluoroacetic anhydride-oxy-acid mixtures (Bourne, Randles, Stacey, Tatlow, and Tedder, unpublished work) and involve the formation, first, of the appropriate unsymmetric anhydride derived from trifluoroacetic acid and the oxy-acid, appear to be in accord with these nitrosations.

The experiments described above suggested that, though nitrosation of trifluoroacetylated arylamines occurred, the products might well be trifluoroacetates and not *N*-nitroso-derivatives. Accordingly, aromatic amines were diazotized in trifluoroacetic acid, and the diazonium solutions were treated with benzene in attempts to promote the diaryl synthesis. Aniline was diazotised in benzene with ethyl nitrite-trifluoroacetic acid in the absence of water and, after 24 hours at room temperature, a significant yield of diphenyl was isolated. Further, several *para*-substituted aromatic amines were diazotized with sodium nitrite in aqueous trifluoroacetic acid, and the aqueous solutions were stirred with benzene: again the corresponding unsymmetrical diphenyls were obtained (see Table 3), though the yields generally were not high (10–25%). As was expected with a heterogeneous reaction of this type, stirring was necessary, a very poor yield otherwise resulting. When aqueous benzenediazonium chloride or aqueous *p*-chlorobenzenediazonium chloride was stirred with benzene under similar conditions no diaryl was found in the products, nor was it if acetic acid was added to the former mixture. However, when trifluoroacetic acid or sodium trifluoroacetate was added to the aqueous diazonium chloride-benzene systems, the corresponding diphenyl was formed in moderate yield (10–20%) (see Table 4). As would be expected, these yields fell as the aqueous phase was made more dilute.

Earlier work (Pettit, Stacey, and Tatlow, *J.*, 1953, 3081) has shown that diazotizations of certain aromatic amines in trifluoroacetic or other perhalogenocarboxylic acids give solid diazonium acid salts, $\text{Ar}\cdot\text{N}_2^+\}\text{R}\cdot\text{CO}_2^-, \text{R}\cdot\text{CO}_2\text{H}$, which are sparingly soluble in water.

Such solid salts have now been found to react with benzene, and, after either many hours at *ca.* 15° or a short time at higher temperatures, diphenyls were isolated (Table 5). Salts derived from trifluoroacetic, heptafluorobutyric, and trichloroacetic acid were all used successfully in reactions of this type. Also, in analogous reactions, aqueous diazonium salts derived from the two last acids gave diphenyls if treated with benzene.

In all the reactions described so far, the diazonium, or related, components were treated with benzene to avoid the formation of isomeric diphenyls and so to enable a ready assessment to be made of the scope of the process. In other cases, however, benzene derivatives were treated with diazonium salts. Toluene-*p*-diazonium acid trifluoroacetate was treated at 100° with methyl benzoate and with toluene, and its aqueous solution was treated with the same liquids at 25°. In all cases it appeared that mixtures of isomers were formed and, from these, very small yields of the *p*-substituted products, 4-carbomethoxy-4'-methyl- and 4 : 4'-dimethyl-diphenyl, respectively, were obtained. Though only the *para*-isomers could be isolated, these particular products would almost certainly crystallise most readily from such mixtures so that little information on directing effects is provided by these experiments.

It must be emphasised that the work described in this paper was of an introductory nature only, and that no systematic attempts have been made to find the best reaction conditions, to obtain optimum yields, to identify by-products, or to study the reactions in a detailed quantitative fashion. The preliminary results indicate, however, that the nitrosating activity of trifluoroacetic anhydride-nitrite mixtures may find useful applications, and also that diazonium trifluoroacetates, and diazonium salts of other perhalogeno-carboxylic acids, possess interesting properties. In general, diaryls are formed from the reactions of aromatic derivatives with diazo-compounds derived from strong acids, (*a*) in aqueous alkali (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; Gomberg and Pernert, *ibid.*, 1926, **48**, 1372), (*b*) in aqueous sodium acetate (Elks, Haworth, and Hey, *J.*, 1940, 1284), or (*c*) when they are stabilised with sulphonic acids or metallic chlorides and in the presence of acetic acid-sodium acetate or sodium carbonate (Hodgson and Marsden, *J.*, 1940, 208). Dry solid aromatic diazonium chlorides can decompose in a homolytic manner (Waters, *J.*, 1939, 864, and papers quoted therein) and with anhydrous aluminium chloride and aromatic compounds give diaryls (Möhlau and Berger, *Ber.*, 1893, **26**, 1196, 1994), but there seem to be few reports of the production of unsymmetric diaryls from aromatic compounds and acidic aqueous solutions of diazonium salts of strong acids other than the early experiments of Hirsch (*Ber.*, 1890, **23**, 3705; 1892, **25**, 1973). Though aqueous diazonium salts and pyridine give phenylpyridines an excess of the base is apparently necessary (Haworth, Heilbron, and Hey, *J.*, 1940, 349). Diazonium salts of perhalogeno-carboxylic acids thus seem to occupy a unique position. Their aqueous solutions exhibit typical reactions of diazonium salts of strong acids [*i.e.*, they undergo simple replacement and coupling reactions (Pettit, Stacey, and Tatlow, *loc. cit.*)] and yet these solutions, as well as the solid acid salts, and non-aqueous systems containing diazonium perhalogeno-carboxylates, can all react with aromatic nuclei to give diaryls, even under acidic conditions. In this they resemble the diazoacetates, even though the conditions of reaction of the two species in the diaryl synthesis may differ considerably.

Current ideas on the decomposition of nitrosoacetanilides and diazoacetates (Huisgen and his co-workers, *Annalen*, 1949, **562**, 137; 1951, **573**, 163, 181; **574**, 157, 171, 184; DeTar, *J. Amer. Chem. Soc.*, 1951, **73**, 1446; Hey, Stuart-Webb, and Williams, *J.*, 1952, 4657, and papers mentioned therein) may well explain the reactions of diazonium perhalogeno-carboxylates also. Although the latter are probably ionised to a considerable extent in aqueous acid, the alternative hypothesis of Hodgson (*J.*, 1948, 348) does not appear to give a satisfactory explanation of their reactions, in particular of the effect of addition of trifluoroacetate ions to diazonium chlorides. We suggest tentatively that it is more likely that, in these compounds, there can exist an equilibrium between ionic and some type of covalent structure and that the latter can react with aromatic compounds in substitutions of the homolytic type. If such an equilibrium does exist there is, probably, only a small concentration of covalent-type material, since diazonium acid trifluoroacetates appear to be largely dissociated in dilute aqueous solutions (Pettit, Stacey, and Tatlow, *loc. cit.*).

EXPERIMENTAL

Nitrosations of Acetylaminines with Amyl Nitrite-Trifluoroacetic Anhydride and Conversions into Diphenyls.—Trifluoroacetic anhydride was added slowly to amyl nitrite at -10° . After 5 min., the anilide was added slowly and with shaking, and after a further 20 min. solution was stirred with benzene (25 c.c.) for 24 hr. at 15° . The dark liquid was then evaporated *in vacuo*, finally at 100° , and the tarry residue was distilled in steam. The distillate was extracted with ether, the extracts were dried (MgSO_4), filtered, and evaporated, and the residue was recrystallised from aqueous ethyl alcohol to give the diphenyl. The results of these experiments are given in Table 1.

Diphenyl from Acetanilide Nitrosated by Sodium Nitrite-Trifluoroacetic Anhydride.—Trifluoroacetic anhydride (4.95 g.) was added slowly to sodium nitrite (1.52 g.) at -10° , and then acetanilide (2.72 g.) was introduced. After 30 min. the mixture was stirred with benzene (30 c.c.) for 24 hr. at 15° . Diphenyl (0.90 g.), m. p. and mixed m. p. 69° , was isolated as before.

Nitrosations of Acetylaminines with Ethyl Nitrite-Trifluoroacetic Anhydride and Conversions into Diphenyls.—(a) Trifluoroacetic anhydride (2.70 g.) was mixed with ethyl nitrite (0.85 g.) at -10° , and after 5 min. acetanilide (1.33 g.) was added slowly. After 20 min. at -10° the mixture was poured into an excess of alkaline β -naphthol, to give phenylazo- β -naphthol (from ethyl alcohol) (1.33 g.), m. p. and mixed m. p. $130-132^{\circ}$.

(b) Acetanilide was nitrosated as in (a), and the mixture was poured into ice-water. The precipitate was filtered off, washed with water, and dried; it was *N*-nitrosoacetanilide (0.86 g.), m. p. $44-48^{\circ}$ (decomp.), which decomposed vigorously when heated. Grieve and Hey (*J.*, 1934, 1797) gave m. p. $51-52^{\circ}$ (decomp.). Addition of alkaline β -naphthol to the filtrate and washings afforded phenylazo- β -naphthol (0.30 g.), m. p. and mixed m. p. 131° . *N*-Nitrosoanilides were obtained similarly from *p*-methylacetanilide and from *p*-chloroacetanilide.

(c) Various *N*-acetylaminines were nitrosated as in (a) and each mixture was stirred for 24 hr. at 15° with benzene (25 c.c.) and then worked up as before. The experiments are summarised in Table 1.

TABLE 1. *Diphenyls from N-acylaminines nitrosated by alkyl nitrite-trifluoroacetic anhydride mixtures.*

Reactants						Diphenyl products		
N-Acylamine $p\text{-X}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COR}$			Alkyl nitrite $\text{A}\cdot\text{O}\cdot\text{NO}$		$(\text{CF}_3\cdot\text{CO})_2\text{O}$ (g.)	$4\text{-X}\cdot\text{C}_6\text{H}_4\cdot\text{Ph}$		
X	R	g.	A	g.		X	Yield (g.)	M. p. and mixed m. p.
H	Me	1.35	Amyl	1.32	2.55	H	0.50	69°
Cl	"	1.77	"	"	"	Cl	0.34	$75-76$
Me	"	1.48	"	"	"	Me	0.35	$45-47$
NO_2^a	"	1.78	"	"	"	NO_2	0.27	$113-114$
H	"	1.36	Et	0.85	"	H	0.70	69
Me	"	1.49	"	0.81	3.00	Me	0.27	$45-46$
Cl	"	1.71	"	"	2.55	Cl	0.63	$75-76$
CF_3	"	1.48	"	0.85	2.70	CF_3	0.37	70^b
NO_2^a	"	1.84	"	0.81	2.55	NO_2	0.12	$113-114$
H	CF_3	1.71	"	0.85	"	H	0.68 ^c	$68-70$
" ^d	"	1.91	"	"	"	"	0.59	"
Me	"	1.01	"	0.54	1.50	Me	0.31	$46-47$
MeO	"	1.63	"	0.76	2.40	MeO	0.16	$87-89$
$\text{NO}_2^{a,e}$	"	1.94	"	1.30	3.90	NO_2	0.11	$113-114$

^a Complete solution of the anilide in the nitrosating mixture was not achieved. ^b Pettit and Tatlow, *J.*, 1954, 1071, gave m. p. 70° . ^c Found: C, 93.8; H, 6.5. Calc. for $\text{C}_{12}\text{H}_{10}$: C, 93.5; H, 6.5%. ^d In this experiment, after the addition of the benzene, the temperature of the mixture was raised progressively to 100° during 1 hr., gas evolution having then ceased. ^e Unchanged anilide (0.88 g.), m. p. and mixed m. p. $146-150^{\circ}$, and *p*-nitroaniline (0.15 g.), m. p. and mixed m. p. $143-145^{\circ}$, were isolated also.

Trifluoroacetyl Derivatives of Amines.—These were prepared as described previously (Bourne, Henry, Tatlow and Tatlow, *loc. cit.*). 4-Nitro-3-trifluoromethyltrifluoroacetanilide, m. p. $115-116.5^{\circ}$ (yield 90% after recrystallisation from benzene-light petroleum), was made similarly (Found: C, 36.0; H, 1.2; F, 37.7. $\text{C}_9\text{H}_4\text{O}_3\text{N}_2\text{F}_6$ requires C, 35.8; H, 1.3; F, 37.7%).

Nitrosations of Trifluoroacetylaminines and Conversions into Diphenyls.—(a) To a mixture of ethyl nitrite (0.18 g.) and trifluoroacetic anhydride (0.52 g.) at -10° was added trifluoroacet-

anilide (0.30 g.). After being shaken for 20 min. the mixture, which was then homogeneous, was poured into alkaline β -naphthol. Recrystallised from ethyl alcohol the precipitate, phenylazo- β -naphthol (0.31 g.), had m. p. and mixed m. p. 130—132°.

(b) Trifluoroacetanilide was added in small portions to a mixture of ethyl nitrite and trifluoroacetic anhydride which was cooled to -5° . About 15 min. after the completion of the addition a spontaneous reaction occurred and the residual solid dissolved. Benzene (25 c.c.) was added and the mixture was stirred at 15° for 24 hr. (a small lower layer persisted throughout) and was then worked up as before. Experiments of this type are summarised in Table 1.

(c) A cooled solution of trifluoroacetanilide (1.81 g.) in benzene (25 c.c.) was added slowly and with shaking to a solution of ethyl nitrite (0.90 g.) in trifluoroacetic anhydride (3.0 g.) and the mixture was stirred for 24 hr. Diphenyl (0.48 g.), m. p. and mixed m. p. 69—70°, was obtained.

(d) When 4-nitro-3-trifluoromethyltrifluoroacetanilide was treated as described in expt. (b) no diphenyl derivative was detected; the anilide (81%) was recovered.

Nitrosations of Trifluoroacetanilide with Nitrous Fumes.—(a) A stream of nitrous fumes (made from concentrated aqueous sodium nitrite and dilute sulphuric acid) was passed into a solution of trifluoroacetanilide in trifluoroacetic acid at $5-10^\circ$. A dark colour had developed after *ca.* 30 min. The solution was poured into water, the colour disappearing, and a colourless precipitate of trifluoroacetanilide was formed. The aqueous filtrate was treated with alkaline β -naphthol. The results are given in Table 2.

(b) Nitrous fumes were passed into a solution of trifluoroacetanilide (0.53 g.) in glacial acetic acid (10.0 c.c.) at $5-10^\circ$ for $4\frac{1}{2}$ hr. The green liquid was then poured into water, and the

TABLE 2. *Nitrosations of trifluoroacetanilide with nitrous fumes.*

Ph·NH·CO·CF ₃ (g.)	CF ₃ ·CO ₂ H (c.c.)	Time of nitrosation (hr.)	Recovered Ph·NH·CO·CF ₃ (g.)	Phenylazo- β -naphthol (g.)	Total recovery (%)
1.20	14.0	0.5	0.94	—	78
1.01	5.0	2.5	0.56	0.07	60
0.47	3.0	5.0	0.12	0.17	53

TABLE 3. *Diphenyls from aqueous diazonium trifluoroacetates and benzene.*

Reactants						Diphenyl produced 4-X·C ₆ H ₄ ·Ph			
Amine 4-X·C ₆ H ₄ ·NH ₂		CF ₃ ·CO ₂ H	H ₂ O	NaNO ₂	H ₂ O	Benzene	X	Yield	M. p. and mixed m. p.
X	g.	(g.)	(c.c.)	(g.)	(c.c.)	(c.c.)		(g.)	
H	4.60	15.0	0	4.00	10.0	40	H	1.80	69°
Me ^a	1.07	3.4	7.0	0.89	2.0	25	Me	0.14	43—46
OMe	1.29	3.4	2.0	0.92	2.0	25	OMe	0.48	86—89
Cl ^a	1.22	3.7	5.0	0.82	2.0	20	Cl	0.21	74—76
NO ₂ ^b	1.37	4.0	1.0	0.75	1.5	25	NO ₂	0.21	112—113
CF ₃ ^b	1.80	3.7	1.0	0.85	1.5	25	CF ₃	0.41 ^d	68—70
H ^c	0.98	3.0	1.5	0.85	2.0	25	H	0.08	67—68

^a Some solid diazonium acid salt was present initially. ^b The nitrite was added rapidly to the amine to avoid the formation of diazoamino-compounds. ^c No stirring was applied in the reaction between the diazonium salt and the benzene. ^d Found: C, 70.1; H, 4.0. Calc. for C₁₃H₉F₃: C, 70.3; H, 4.1%.

precipitate was filtered off and recrystallised to give trifluoroacetanilide (0.24 g.), m. p. and mixed m. p. 88—89°. The aqueous filtrate gave no red precipitate when treated with alkaline β -naphthol.

When a solution of acetanilide in trifluoroacetic acid was treated similarly, *N*-nitrosoacetanilide (11%), m. p. 48—50° (decomp.), and phenylazo- β -naphthol (15%), m. p. and mixed m. p. 132°, were obtained.

Diphenyl Derivatives from Aqueous Diazonium Trifluoroacetate Solutions.—The amine, in trifluoroacetic acid, was treated at *ca.* 5° with aqueous sodium nitrite. Benzene was then added and the mixture was stirred at 23° for 24 hr. The organic layer was separated, washed with aqueous sodium hydroxide, then with water, and dried (MgSO₄). After filtration and evaporation the residue was distilled in steam, and the product was isolated from the distillate and crystallised in the normal way. The results of the experiments of this type are given in Table 3.

Diphenyl from the Reaction of Benzene with Aniline Diazotised in Trifluoroacetic Acid—Ethyl Nitrite.—Ethyl nitrite (4.5 g.), in benzene (15 c.c.), was added slowly to aniline (4.40 g.) and

trifluoroacetic acid (15.0 g.), in benzene (25 c.c.), at 5—8°. The mixture was stirred at 10—15° for 24 hr. The volatile constituents were then evaporated, and the residue was steam-distilled, etc., to give diphenyl (2.22 g.), m. p. and mixed m. p. 69—70°.

Diphenyl from Benzene and Aqueous Benzenediazonium Chloride-Trifluoroacetate.—The amine was diazotized in the normal manner with concentrated hydrochloric acid and aqueous sodium nitrite. The series of experiments summarised in Table 4 was carried out by treating such diazonium solutions, in the presence of the addenda described, with benzene at 23° for 24 hr. The diphenyl formed was isolated as usual. No diphenyl was detected in the product when no trifluoroacetate was present.

Reactions of Solid Diazonium Perhalogeno-carboxylates with Benzene.—Diazonium acid salts prepared as described previously (Pettit, Stacey, and Tatlow, *loc. cit.*) were treated with benzene under the conditions given in Table 5, the product being isolated in the normal manner.

Diphenyl from Aqueous Benzenediazonium Perhalogeno-carboxylates and Benzene.—(a) Aniline (0.98 g.) in heptafluorobutyric acid (6.6 g.) and water (2.1 c.c.) was diazotized with aqueous sodium nitrite. The solution was stirred at 25° for 24 hr. with benzene (50 c.c.), and, after isolation as usual, diphenyl (0.26 g.), m. p. and mixed m. p. 67—69°, was obtained.

TABLE 4. *Diphenyls from diazonium chlorides, trifluoroacetates, and benzene.*

Amine 4-X·C ₆ H ₄ ·NH ₂		Conc. HCl (c.c.)	NaNO ₂ (g.)	H ₂ O (c.c.)	Benzene (c.c.)	Addenda		Diphenyl 4-X·C ₆ H ₄ ·Ph	
X	g.					Formula	g.	g.	M. p. and mixed m. p.
H	4.50	11.0	4.00	15.0	40	—	—	—	—
H	0.96	3.0	0.78	4.0	20	CH ₃ ·CO ₂ H	1.8	—	—
H	0.91	3.0	0.81	13.0	20	CF ₃ ·CO ₂ Na	3.75	0.11 ^a	68—70°
H	1.91	5.6	1.60	6.0	30	"	7.24	0.60 ^a	"
H	1.95	6.0	1.59	8.0	20	CF ₃ ·CO ₂ H	6.60	0.45 ^a	"
H	4.00	13.0	3.20	11.0	50	"	0.69	0.20 ^a	67—69
Cl	8.00	20.0	5.00	20.0	100	"	—	—	—
Cl	1.40	5.0	1.00	5.0	50	CF ₃ ·CO ₂ H	3.00	0.20 ^b	74—76

^a X = H. ^b X = Cl.

TABLE 5. *Diphenyls from benzene and diazonium acid salts.*

Diazonium acid salt			Benzene (c.c.)	Reaction conditions		Diphenyl produced		
Amine	Acid	g.		Time (hr.)	Temp.	Formula	g.	M. p. and mixed m. p.
<i>p</i> -C ₆ H ₄ Me·NH ₂	CF ₃ ·CO ₂ H	1.44	15	24	15°	4-Me·C ₆ H ₄ ·Ph	0.30	45—47°
<i>p</i> -C ₆ H ₄ Cl·NH ₂	CF ₃ ·CO ₂ H	4.36	50	2	80	4-Cl·C ₆ H ₄ ·Ph	0.41 ^a	75—76
"	C ₂ F ₅ ·CO ₂ H	6.50	50	2	80	"	0.66	"
"	CCl ₃ ·CO ₂ H	23.2 ^b	250	2	80	"	1.90	"

^a Found: C, 76.2; H, 4.9. Calc. for C₁₂H₉Cl: C, 76.4; H, 4.8%. ^b This acid salt had m. p. 90° (decomp.) (Found: C, 26.2; H, 1.2. C₁₀H₅O₄N₂Cl, requires C, 25.8; H, 1.1%).

(b) Aniline (5.0 g.), in trichloroacetic acid (26.0 g.) and water (20 c.c.), was diazotized as before. The solution was stirred for 24 hr. at 25° with benzene (250 c.c.) and afforded diphenyl (1.06 g.), m. p. and mixed m. p. 68—69°.

*Reaction of Toluene-*p*-diazonium Trifluoroacetate with Methyl Benzoate.*—(a) The acid salt (15.5 g.) was dissolved in methyl benzoate (140 c.c.). During ½ hr. the temperature was raised to 100° and after 2 hr. the excess of methyl benzoate was distilled off and the residue was distilled in steam. Part of the distillate solidified, and this was extracted and worked up in the usual way, to give *methyl 4-methyldiphenyl-4'-carboxylate* (0.13 g.), m. p. 115—116° (Found: C, 79.4; H, 6.3. C₁₆H₁₄O₂ requires C, 79.6; H, 6.2%). After hydrolysis with aqueous-alcoholic sodium hydroxide, there was obtained the free acid, m. p. 245—248° (Found: C, 79.3; H, 5.9. Calc. for C₁₄H₁₂O₂: C, 79.2; H, 5.7%), for which Carnelley (*J.*, 1877, 32, 653) gave m. p. 245° (decomp.).

(b) *p*-Toluidine (3.20 g.) was diazotized as usual in trifluoroacetic acid (10.0 g.) and water (10 c.c.), with saturated aqueous sodium nitrite solution. Some solid salt separated, but was not removed. The slurry was stirred at 25° for 24 hr. with methyl benzoate (100 c.c.). Isolation as before yielded *methyl 4-methyldiphenyl-4'-carboxylate* (0.042 g.) m. p. 115—116°, un-depressed on admixture with the material mentioned above.

*Reaction of Toluene-*p*-diazonium Trifluoroacetate with Toluene.*—(a) The acid salt (17.3 g.) and toluene (140 c.c.) were heated to 100° for 3 hr. After isolation as before, there was obtained 4 : 4'-dimethyldiphenyl (0.16 g.), m. p. 120—121° (Found : C, 92.4; H, 7.6. Calc. for C₁₄H₁₄ : C, 92.3; H, 7.7%), for which Zincke (*Ber.*, 1871, 4, 396) gave m. p. 121°.

(b) The suspension of toluene-*p*-diazonium acid trifluoroacetate obtained by diazotization with sodium nitrite of *p*-toluidine (2.14 g.) in trifluoroacetic acid (7.5 g.) and water (10 c.c. total) was stirred for 24 hr. at 25° with toluene (100 c.c.). 4 : 4'-Dimethyldiphenyl (0.045 g.), m. p. and mixed m. p. 119—121°, was obtained.

The authors thank Professor M. Stacey, F.R.S., for his interest, and the University of Birmingham for a grant from the Research Fund.

CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

[Received, January 23th, 1954.]
