aqueous phase by neutralizing the solution with *tert*-octylamine to pH 7.5 and adding benzaldehyde (0.7 ml).

Anal. Calcd for $C_{31}H_{42}N_4O_4S$: S, 5.65; N, 9.9. Found: S, 5.36; N, 9.7.

The Schiff base **16** (3.2 g) was washed with toluene (5 ml) and dissolved in a mixture of H_2O (7 ml) and methyl isobutyl ketone (7 ml), then the pH was adjusted to 1.5 with HCl. The pH was adjusted once more to 4.9 with NaOH, and the precipitate was collected by filtration and air dried to afford **7c** (950 mg, as its trihydrate). The ir and nmr spectra were identical with those of an authentic sample.

Acknowledgment. The authors thank Mrs. B. Toeplitz for the ir spectra, Dr. P. Funke for the mass spectra, and Mr. J. Alicino and his staff for microanalyses.

Registry No.—**6a**, 53059-76-0; **6b**, 37628-54-9; **6c**, 53059-78-2; **7a**, 87-08-1; **7b**, 20109-75-5; **7c**, 69-53-4; **8**, 13114-23-3; **9**, 3412-73-5; **10**, 53059-79-3; **11**, 53059-80-6; **13**, 40216-77-1; **14**, 53128-97-5; **15**, 53059-81-7; **16**, 53129-37-6; **17**, 53176-74-2; phenoxyacetyl chloride, 701-99-5; L-phenylalanine methyl ester hydrochloride, 7524-50-7; benzaldehyde, 100-52-7.

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The Stieglitz Rearrangement with Lead Tetraacetate and Triarylmethylamines

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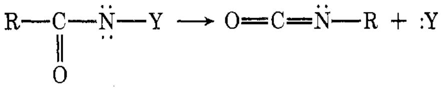
The results of the lead tetraacetate induced Stieglitz rearrangement with various mono-*para*-substituted triarylmethylamines are presented. Migratory aptitudes have been determined. In addition the results of trapping experiments are also given. A concerted mechanism is postulated consistent with all the data.

A common feature of the Curtius–Hofmann–Lossen and the lead tetraacetate-induced rearrangement of carboxylic acid amides is the migration of a group to a potentially electron-deficient nitrogen to yield an isocyanate (eq 1).[1]



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\cdot\cdot}{\ddot{N}}{-}Y \longrightarrow O{=}C{=}\ddot{N}{-}R + {:}Y} \tag{1}$$

$$Y = N_2,\ Cl^-,\ {}^-O_2CR,\ Pb(OAc)_2$$

The four rearrangements differ in their departing groups. The similarity to the Stieglitz rearrangement and its variations[2] with N-substituted amines is striking (eq 2). A recent preliminary paper[3] extended the likeness when a lead tetraacetate induced Stieglitz rearrangement was reported on triphenylmethylamine (eq 2, Y = $Pb(OAc)_2$) (eq 3).

$$\mathrm{R_3C{-}\underset{\cdot\cdot}{\ddot{N}}{-}Y \longrightarrow R_2C{=}\ddot{N}{-}R + Y{:}} \tag{2}$$

$$Y = N_2,\ Cl^-,\ O{=}PCl_3$$

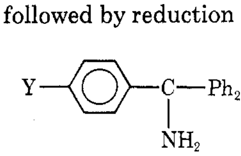
$$\underset{(85\text{–}90\%)}{\mathrm{Ph_3CNH_2}} \xrightarrow[\Delta]{\mathrm{LTA,\ C_6H_6}} \mathrm{PhN{=}CPh_2 + HOAc + Pb(OAc)_2} \tag{3}$$

On the basis of trapping experiments, electronic properties of the migrating group and kinetic isotope effects a concerted mechanism is strongly indicated[4] for the former rearrangements (eq 1). With respect to the Stieglitz rearrangements the situation is less clear. Migratory aptitudes spanning a range of 9 for the *p*-anisyl group to 0.4 for the *p*-nitrophenyl group argued in favor of a concerted pathway for the phosphorus pentachloride induced rearrangement of mono-para-substituted trityl-*N*-hydroxylamines.[5] Solely as a result of the statistical distribution of products obtained from phenyl and *p*-halophenyl migration in the base-induced Stieglitz rearrangement with *p*-halotrityl-*N*-haloamines, and the lack of rearrangement of *N*-methyl-*N*-chlorotritylamine, Stieglitz proposed a nitrene intermediate. Abramovitch[6] offers evidence that the thermolysis of tertiary alkyl azides gives rise to a singlet nitrene and their photochemical decomposition does not involve nitrenes.[7] Both conclusions are in opposition to those of Saunders.[8]

This paper attempts to elucidate the intermediate in the lead tetraacetate induced Stieglitz rearrangement from the results of migratory aptitude studies and trapping experiments.

Results

The mono-para-substituted triphenylmethylamines **1a–c** were prepared from the corresponding alcohols by converting them to the azides followed by lithium aluminum hydride ($LiAlH_4$) reduction. The amines **1d** and **1e** were synthesized by ammonolysis of the corresponding halides. The amine **2** was prepared from the alcohol by conversion to the azide followed by reduction with $LiAlH_4$.



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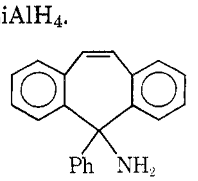


2

a, Y = H; b, Y = Cl; c, Y = CH_3;
d, Y = OCH_3; e, Y = NO_2

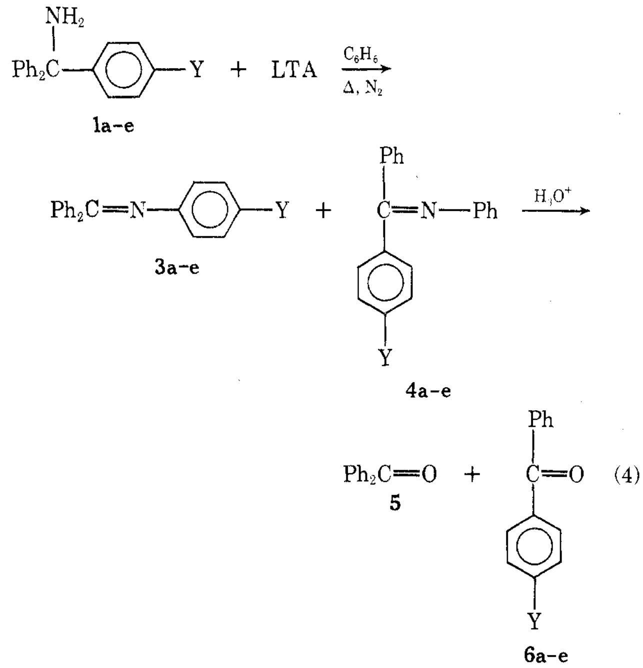
Treatment of the amines **1a–e** with acetic acid free lead tetraacetate (LTA) in refluxing benzene under nitrogen led to a rapid consumption of LTA (15–20 min as monitored by starch–iodide test paper). The product mixture in each case was obtained in close to quantitative yield (90–95%).

Table I
Reaction of LTA with Triarylmethylamines (Eq 4)

Amine 1	Overall % yield[a]	Relative % yield[b]			MA
			3	4	
a H	90	a	100		1.0[c]
b p-Cl	95[e]	b	38.6	41.4	1.86
c p-CH_3	92	c	84.4	15.6	10.9
d p-OCH_3	93	d	98.7	1.3	152[d]
e p-NO_2	92	e	16.3	83.7	0.39

[a] Average crude yields of product isolated after removal of solvent *via* rotary evaporator followed by vacuum pump; duplicate determinations. [b] Triplicate determination by glpc using biphenyl as internal standard. [c] Migratory aptitude (MA) = 2(% benzophenone)/% p-Y-benzophenone; phenyl taken as relative standard with migratory aptitude set equal to one by definition. [d] The migratory aptitude calculated should be viewed as the minimum value for the p-anisyl group (see ref 32). [e] Approximately a 10% yield of what is believed to be the acetamide of amine **1b** was also isolated.

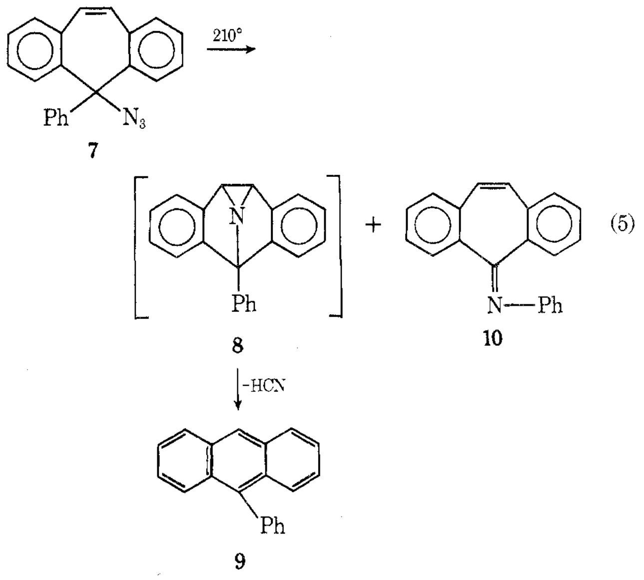
Infrared and nmr spectroscopy indicated that they were essentially mixtures of isomeric imines (eq 4). Separation of the isomeric imines by column chromatography has been reported to be fruitless.[8] Quantitative analysis was therefore performed indirectly by glpc procedures on the corresponding benzophenones (**5** and **6a–e**) derived from the acid hydrolyses of the isomeric imine mixtures.[9]



Based upon the product distributions observed and the statistical preference factor of 2 for the phenyl migration *vs.* the para-substituted phenyl, migratory aptitudes were calculated. The results are presented in Table I.

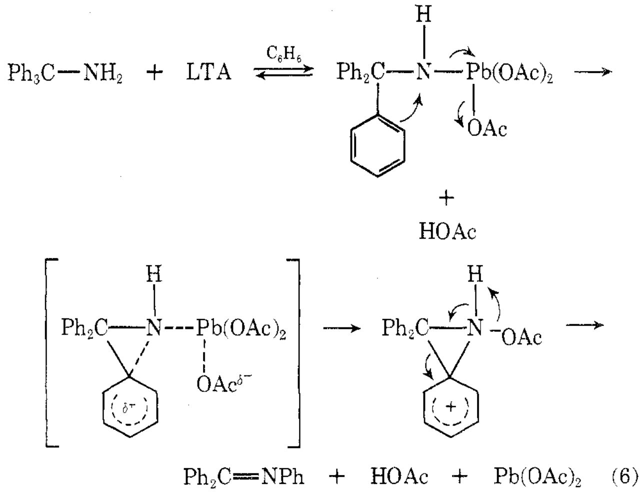
The LTA-induced rearrangement of triphenylmethylamine was also conducted in cyclohexene–benzene[3] and in pure cyclohexene in an attempt to trap a possible nitrene intermediate. However, no decrease in yield of benzophenone anil (**3a**) was noted nor was any spectral evidence[10] obtained which would indicate the presence of an aziridine. The only other expected material present was identified as 3-acetoxycyclohexene from its boiling point and ir spectrum.

Looker[11] has recently succeeded in trapping a possible nitrene (eq 5) with a suitably disposed double bond in **7**. Accordingly, **2** was treated with LTA in benzene and the *only* product isolated was **10** (85%).



Discussion

Bartlett[12] has observed that one of the best criteria for the operation of a cationic mechanism in 1,2-rearrangements should be the experimental finding of relative migratory aptitudes similar to those characteristic of the Wagner–Meerwein, pinacol, and related rearrangements and different from those prevailing in reactions of a known free radical type. Such a distinction should be readily made as it is generally well known that the migratory aptitudes observed in free radical migrations have been considerably less selective electronically[13] than those observed in the corresponding cationic migrations. More recently, the use of aromatic migratory aptitudes in order to determine the nature of the migrating terminus has been extended to include 1,2 shifts from carbon to oxygen[12,14,15] and nitrogen[5,8,16] as well as from carbon to carbon. The values of the migratory aptitudes accumulated (spanning p-anisyl, 152, to p-nitrophenyl, 0.39) (Table I) argue against either a free radical mechanism or a nitrene[8] mechanism. Rather the pathway involving a concerted migration of the aryl group with the departure of the lead acetate or its triacetoxyplumbate anion precursor seems most consistent with the data (eq 6). The results, however, do not preclude a nitrenium ion rationale from consideration; however, arguments[17] have been presented that a nitrenium ion should be of considerably higher energy than its carbonium ion analog owing to the higher electronegativity of nitrogen. Thus, a greater driving force should exist for a rearrange-



ment to be synchronous in systems which could also potentially proceed *via* a nitrenium ion.

Since migratory aptitudes indirectly reflect rates of phenyl *vs.* para-substituted phenyl migration, a modified Hammett equation can be employed to analyze such data (eq 7). Such a quantitative treatment has been employed

$$\log \mathrm{MA} = \rho\sigma^{+}$$

$$\mathrm{MA} \propto 2k_{p\text{-Y}}/k_{\mathrm{H}} \qquad (7)$$

by McEwen[17] and more recently by Starnes.[18] A plot our data employing the modified Hammett equation gave a good straight line whose slope, ρ, was -1.70 ($r = -0.903$, $s = 0.54$, $n = 5$). The result is consistent with a transition state in which a partial positive charge is generated in the migrating aryl group (eq 6). Analogous linear plots were obtained using the data of Saunders[8,16] (triarylmethyl azides, pyrolytic and photolytic decompositions) and Newman[5] (triarylmethylhydroxylamines with phosphorus pentachloride) yielding ρ values of -0.63, -0.036, and -0.89, respectively. One tentative conclusion which may be drawn is that in the several variations of the Stieglitz rearrangement it cannot be strictly said that there is one mechanism operative. More accurately, there are several mechanisms involving a spectrum of transition states differing in the degree of aryl participation invoked by the departure of the particular leaving group. The formation of a discrete nitrene intermediate could be said to constitute a limiting case.

The chief difficulty inherent in a successful intermolecular trap of an alkyl nitrene has been attributed to their extremely brief lifetime[19] and relatively high reactivity.[20] Therefore the negative intermolecular trapping results cannot be viewed as further evidence against a nitrene (and indirectly favoring the concerted mechanism) but must be viewed as inconclusive. However, greater success[11,21] has been reported in trapping alkyl nitrenes on an intramolecular basis. Thus, the reported[11] successful intramolecular trapping of the alkyl nitrene derived from **7** (eq 5) becomes significant with respect to the present study in that the negative[22] trapping result from the reaction of LTA with **2** lends indirect support for the concerted mechanism.

Experimental Section[23,24]

Triphenylmethylamine (1a). Method A. Into a dry three-necked round-bottom flask equipped with a reflux condenser, addition funnel, drying tubes, and magnetic stirrer were placed 2.0 g (0.052 mol) of $LiAlH_4$ and 100 ml of anhydrous ether. A solution of 10 g (0.035 mol) of triphenylmethyl azide[8] in 50 ml of ether was slowly added dropwise. The mixture was refluxed for 2 hr and decomposed.[25] The mixture was filtered and washed with ether, and the combined ether extracts were dried ($MgSO_4$). The solvent was distilled off and the residual solid was recrystallized from absolute ethanol, yielding 7.7 g (85%) of a white solid: mp 97–100° (lit.[26] mp 99–100°); ir 3300, 3370 cm^{-1} (NH_2); nmr τ 2.75 (s, 15 H, phenyl), 7.75 (s, 2 H, NH_2).

Method B. The procedure of Vosburgh[27] was followed employing a 250 ml benzene solution of trityl chloride (5.6 g, 0.02 mol) and soda-lime-dried NH_3 gas. The solid was recrystallized from absolute ethanol to yield 2.3 g (44%) of a white solid, mp 97–100°, identical in all properties with the material prepared by method A.

***p*-Chlorophenyldiphenylmethylamine (1b)** was prepared according to method A using 9.5 g (0.030 mol) of azide,[8] 4.0 g (0.104 mol) of $LiAlH_4$, and 175 ml of ether. There was obtained 8.2 g (0.028 mol) (94%) of amine **1b** as a colorless viscous gum:[27] ir (neat) 3370, 3305 cm^{-1} (NH_2); nmr τ 2.6–3.2 (m, 14 H, aromatic), 7.75 (broad s, 2 H, NH_2).

The acetamide of amine **1b** was prepared and recrystallized from benzene–cyclohexane: mp 205–208°; ir (KBr) 3260, 1660 cm^{-1}.

Anal. Calcd for $C_{21}H_{18}NOCl$: C, 75.11; H, 5.40; N, 4.17. Found: C, 74.95; H, 5.67; N, 4.30.

Diphenyl-*p*-tolylmethylamine (1c) was prepared according to method A employing 9 g (0.030 mol) of azide,[8] 2.0 g of $LiAlH_4$, and 175 ml of ether. Recrystallization (EtOH) yielded 6.9 g (0.025 mol) (83%) of **1c** as a white solid: mp 74.5–76°; ir (KBr) 3310, 3380 cm^{-1} (-NH_2); nmr ($CDCl_3$) τ 2.7 (s, 10 H, phenyl), 2.86 (s, 4 H, *p*-tolyl), 7.67 (s, 3 H, CH_3), and 7.88 (s, 2 H, NH_2).

Anal. Calcd for $C_{20}H_{19}N$: C, 87.89; H, 7.01; N, 5.12. Found: C, 87.73; H, 7.01; N, 5.22.

***p*-Anisyldiphenylmethylamine (1d)** was prepared according to method B using 6.08 g (0.020 mol) of chloride[28] in 250 ml of benzene. The crude amine was chromatographed on neutral alumina (80–200 mesh). Elution with benzene and 50% ether–benzene afforded 5.3 g (0.018 mol) (91%) of **1d** as a colorless, viscous gum: ir (neat) 3300, 3370 cm^{-1} (–NH_2); nmr τ 2.55–3.45 (m, 14 H, aromatic), 6.4 (s, 3 H, OCH_3), 7.95 (broad s, 2 H, NH_2).

Anal. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.99; H, 6.42; N, 4.84.

The acetamide of amine **1d** was prepared and recrystallized from 50% aqueous ethanol and then cyclohexane: mp 178–180°; ir (KBr) 3270, 1660 cm^{-1}.

Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.56; H, 6.56; N, 4.32.

Diphenyl-*p*-nitrophenylmethylamine (1e) was prepared according to method B using 10 g (0.027 mol) of bromide[8,18] in 250 ml of benzene. The initially obtained gum was dissolved in hot CCl_4 and allowed to stand overnight at −10°. The resulting solid was recrystallized (EtOH) to yield 4.25 g (0.014 mol, 51%) of a white solid: mp 118–120°; ir (KBr) 3315, 3375 cm^{-1} (NH_2); nmr τ 1.85–2.6 (4 H, A_2B_2, $J = 8.3$ Hz, *p*-nitrophenyl), 2.78 (s, 14 H, phenyl), 7.85 (broad s, 2 H, -NH_2).

Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.97; H, 5.30; N, 9.20. Found: C, 75.01; H, 5.21; N, 9.31.

5-Amino-5-phenyl-5*H*-dibenzo[*a*,*d*]cycloheptene (2) was prepared according to method A using 7 g (0.023 mol) of the azide[11] and 2.2 g (0.058 mol) of $LiAlH_4$ in 200 ml of ether. Several recrystallizations from ethene–ligroin (bp 60–90°) afforded 4.8 g (0.017 mol) (73%) of **2**: mp 170–171.5°; ir (KBr) 3305, 3370 cm^{-1} (–NH_2); nmr τ 1.8–2.0 (m, 2 H, aromatic), 2.3–2.9 (m, 9 H, aromatic), 3.2–3.7 (m, 4 H, 2 vinyl, 2 aromatic), 7.9 (s, 2 H, NH_2).

Anal. Calcd for $C_{21}H_{17}N$: C, 88.99; H, 6.06; N, 4.94. Found: C, 89.02; H, 6.02; N, 4.89.

Reaction of LTA with Triphenylmethylamine (1a). Into a dry, three-necked, round-bottom flask equipped with a dropping funnel, reflux condenser, and magnetic stirrer was placed 4.9 g (0.01 mol) of LTA (under nitrogen). The flask was covered with aluminum foil and then evacuated on a vacuum pump (1 torr) for 2 hr after which 100 ml benzene was added. A solution of 2.6 g (0.01 mol) of **1a** in 100 ml of benzene was added dropwise, after which the reaction mixture was refluxed for 1 hr. The solution was cooled to room temperature, filtered, and washed successively with 10 ml of ethylene glycol, 10 ml of water, 25 ml of 10% Na_2CO_3 solution, and 10 ml of water. After drying ($MgSO_4$) the solvent was removed (rotary evaporator) and the residue recrystallized (EtOH) to yield 2.2 g (0.0085 mol) (85%) of **3a**: mp 111–113° (lit.[29] mp 113–114°); ir and nmr spectra of this material were superimposable on those derived from authentic[29] **3a**.

In a subsequent run the LTA was refluxed in benzene solution with 2 g of anhydrous $CaCO_3$ for 1 hr before admitting the solution of **1a**. The product isolated, 2.35 g (0.009 mol) (90%), **3a** was identical with that previously obtained.

In a third experiment, the reactants were refluxed for 1 hr in cyclohexene. There was isolated 2.66 g of crude material: ir 1740, 1240 ($OCOCH_3$), and 1620 cm^{-1} (C=N). A comparison of the relative intensities of these absorption bands with those derived from authentic mixtures of **3a** and 3-acetoxycyclohexene[30] of known composition allowed the ester's relative composition to be estimated at 15%. Recrystallizations (EtOH) yielded 2.25 g (0.0087 mol, 87%) of **3a**. From the filtrate there was obtained 3-acetoxycyclohexene, bp 71–72° (17 torr) [lit.[30] bp 68–71° (12 torr)].

Control Acid Hydrolysis of 3a. Into a 50-ml flask was placed 1.02 g (3.9 mmol) of **3a**, followed by 10 ml of glacial acetic acid, 30 drops of water, and 30 drops of concentrated hydrochloric acid. The mixture was kept at room temperature for 49 hr. Distilled water (10 ml) and 0.6 g (3.9 mmol) of biphenyl were added before extraction with ether. The ether solution was dried (Na_2SO_4), concentrated, and subjected to glpc analysis.[24a] Two peaks were observed corresponding to biphenyl and benzophenone (**5**), respectively. The area of each peak was determined.[24] The methods[24] gave relative yields of **5** of 98.6 and 93.8%. The peak for **5** was also collected: ir 1667 cm^{-1}.

Reaction of LTA with 1c. The reaction was carried out as described for **1a** employing 4.9 g (0.01 mol) of LTA and 2.73 g (0.01 mol) of **1c.** There was obtained 2.48 g (0.0092 mol, 92%) of a yellow-orange oil: ir (neat) 1620 cm^{-1} (C=N–); nmr τ 2.25–3.7 (m, 14 H, phenyl), 7.9 (s, 3 H, CH_3). The oil was subjected to the acid hydrolysis as described for **3a,** and the ether extract was analyzed by glpc[24a] (242°). The observed peaks corresponded to biphenyl, benzophenone (**5**), and *p*-methylbenzophenone (**6c**). The identity of each peak was confirmed by selective peak enhancement upon coinjection with the authentic material. The peaks were suitable for area measurement.[24] The value for the migratory aptitude for the *p*-tolyl group is given in Table I.

Reaction of LTA with 1d. The reaction was conducted as described for **1a** and **1c** with 4.9 g (0.01 mol) of LTA and 2.89 g (0.01 mol) of **1d.** Following the work-up, 2.63 g (0.0093 mol, 93%) of a yellow-orange oil was obtained: ir (neat) 1610 cm^{-1} (C=N–); nmr τ 2.6–3.5 (m, 14 H, aromatic), 6.3 (s, 3 H, OCH_3).

A portion of the oil was dissolved in hot ethanol and allowed to stand overnight at −10°. A yellow solid, **3d,** was isolated, mp 68–70° (lit.[31] mp 71°). Structure **3d** was also confirmed on the basis of the acid hydrolysis (below).

The remainder of the oil was hydrolyzed, the ether extract from which was analyzed by glpc.[24a] In addition to the biphenyl and benzophenone peaks, a very small peak corresponding to that of *p*-methoxybenzophenone (**6d**) was noted. The identity of this peak was confirmed by selective peak enhancement upon coinjection with authentic **6d.** The relative corrected areas[24] of these peaks were used in order to calculate the value for the migratory aptitude for the *p*-anisyl group[32] (Table I).

The aqueous acidic fraction of the hydrolysate was neutralized and extracted with ether. The ether was dried (Na_2SO_4), and evaporation of the ether left an oil which crystallized when cooled. Recrystallization (water) yielded only *p*-anisidine, mp 50–54° (lit.[33] mp 57°). The ir was superimposable upon that of an authentic sample.

Reaction of LTA with 1e. The same procedure was followed using 1.38 g (4.6 mmol) of **1e** and 2.44 g (5 mmol) of LTA. Following the work-up 1.3 g (4.2 mmol, 92%) of a yellow-orange oil was isolated. The major component of the oil **4e** was isolated by crystallization (EtOH): mp 125–127°; ir 1625 (C=N–), 1520, 1352 cm^{-1} (NO_2).

Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.49; H, 4.67; N, 9.27. Found: C, 75.26; H, 4.62; N, 9.31.

A 200-mg sample of **4e** was hydrolyzed by refluxing for 2 hr in 50 ml of 10% hydrochloric acid. The solution was extracted with benzene, the extracts were dried ($MgSO_4$), and the solvent was largely removed (rotary evaporator). Analysis by glpc procedures[24b] revealed a single peak corresponding to that of *p*-nitrobenzophenone (**6e**).

In a subsequent experiment the initial oil was subjected to acid hydrolysis (the extracting solvent was benzene). The concentrated benzene solution was analyzed by glpc procedures.[24b] Three peaks corresponding to biphenyl, benzophenone, and *p*-nitrobenzophenone (**6e**) were observed. The corrected relative areas[24] were used in order to calculate a value for the migratory aptitude of the *p*-nitrophenyl group (Table I).

Reaction of LTA with 1b was carried out with 2.93 g (0.01 mol) of **1b** and 4.9 g (0.01 mol) of LTA. After work-up there was obtained 2.74 g (0.0095 mol, 95%) of a yellow-orange oil: ir (film) 3450 (-NH), 1665 (C=O), 1618 cm^{-1} (C=N–); nmr τ 2.3–3.6 (m, 14 H, aromatic). Assuming the extraneous component to be the acetamide of **1b,** the relative abundance of the acetamide was estimated at 10% by comparison of the relative intensities of the carbonyl and imino ir absorption peaks of the oil with those of prepared mixtures with known compositions. Acid hydrolysis of the oil and glpc analysis were then performed.[24b] Peaks corresponding to biphenyl, benzophenone, and *p*-chlorobenzophenone (**6b**) were observed. The corrected relative areas measured[24] were used in order to obtain a value of the migratory aptitude for the *p*-chlorophenyl group (Table I).

Reaction of LTA with 2 was studied employing 2.83 g (0.01 mol) of **2** and 4.9 g (0.01 mol) of LTA as before except that the effluent gases from the reaction vessel passed through a gas-washing bottle containing 75 ml of distilled water to which four drops of 50% sodium hydroxide had been added. After the usual work-up, 75% of the benzene was removed and tlc plates were spotted with microspots of the reaction mixture, authentic **10,** and **9.** These plates were developed with 50% v/v benzene–ligroin (bp 60–90°) and then examined first under uv lamp (Burton Model 1910) and then after treatment in an iodine chamber. No fluorescent spot corresponding to **9** was observed, only one corresponding to **10.** An aliquot of the reaction mixture was also analyzed by glpc procedures[24c] with coinjected biphenyl. Peaks attributed to biphenyl and **10** were only observed. The remainder of the benzene was removed yielding an oil which when triturated with ligroin (bp 63–75°) crystallized. Two recrystallizations (methylcyclohexane) gave 2.4 g (0.0085 mol, 85%) of **10:** mp 122–124° (lit.[11] mp 122–123°); ir 1620 cm^{-1} (C=N–); nmr τ 1.8–2.0 (m, 2 H, aromatic), 2.3–2.9 (m, 9 H, aromatic), and 3.2–3.7 (m, 4 H, aromatic and vinyl). Acid hydrolysis of **10** (500 mg) for 1 hr (reflux) with 50 ml of 10% hydrochloric acid yielded after work-up and recrystallization (MeOH), 350 mg (95%) of 5*H*-dibenzo[*a,d*]cyclohepten-5-one, mp 86–88° (lit.[34] mp 89°); ir 1645 cm^{-1}.

The aqueous trap gave a negative test for cyanide ion.[35]

In another run the reaction mixture was chromatographed directly on 60 g of Florisil (Baker 60–80 mesh) employing the technique of Loev.[23] Elution with 50% (v/v) *n*-hexane–benzene (800 ml) and benzene (1000 ml) gave 2.12 g (0.0075 mol, 75%) of **10,** mp 122–124°.

Registry No.—**1a,** 5824-40-8; **1b,** 53060-10-9; **1b** acetamide, 53060-11-0; **1c,** 53060-12-1; **1d,** 53060-13-2; **1d** acetamide, 53060-14-3; **1e,** 53060-15-4; **2,** 53060-16-5; **3a,** 574-45-8; **3b,** 17273-16-4; **3c,** 24215-01-8; **3d,** 42834-19-5; **4b,** 53060-17-6; **4e,** 53060-18-7; **5,** 119-61-9; **10,** 27971-66-0; LTA, 546-67-8; triphenylmethyl azide, 14309-25-2; *p*-chlorophenyldiphenylmethyl azide, 13189-73-6; diphenyl-*p*-tolymethyl azide, 13189-72-5; 5-phenyl-5*H*-dibenzo[*a,d*]cyclohepten-5-yl azide, 27915-27-1.

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Since the reaction of LTA with ketonic Schiff bases (**3** and **4**) has received little attention, product stability was demonstrated when no change was observed when **3** and **4** were refluxed 0.5 hr in benzene containing a 50% excess of LTA.

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(22) Since the pyrolysis of **7** was performed at 210°, the possibility arose that the initially formed azasemibullvalene **8** might have decomposed at that elevated temperature (producing **9**) and yet been stable in the refluxing benzene used in our experiments. Accordingly, several aliquots of a concentrated benzene solution of the reaction products were injected directly onto a gas chromatograph whose injection port, column, and detector temperatures were all thermostated above 210°. No peak corresponding to 9-phenylanthracene (**9**) was detected.

(23) Melting points were determined on a Thomas-Hoover Unimelt apparatus. Infrared spectra were run as 20% solutions in CCl_4 unless otherwise specified. Nmr spectra were determined as 10% solutions in CCl_4 unless otherwise specified. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Column chromatography was carried out using the dry column method of B. Loev and M. M. Goodman, *Chem. Ind. (London)*, 2026 (1967). Analytical thin-layer chromatography was carried

out employing Eastman Kodak precoated silica gel chromatogram sheets. The benzene used in the LTA reactions was Baker spectrograde, dried over sodium and redistilled prior to use. All aryl halides used were freshly distilled prior to use. Lead tetraacetate, 10% moist with acetic acid, was obtained from Arapahoe. All other reagents were of the highest purity commercially available. All LTA reactions were run under nitrogen.

(24) Gas chromatographic analyses were performed on an F&M Scientific Model 720 dual column temperature programmed gas chromatograph. Quantitative analysis of the reaction products in a given mixture was performed by internal standardization method with relative percentages being assessed *via* cutting and weighing or triangulation methods. These methods generally gave answers within 5% of one another. The columns employed were as follows. (a) Column A: 4 ft × 0.25 in Apiezon L on Chromosorb P (60–80 mesh); 40 psi of He (60 ml/min); 230–245°; temperature programmed to 280° in order to elute *p*-methoxybenzophenone with minimum tailing. (b) Column B: 2 ft × 0.25 in. 19% Silicone gum rubber (UC-bw98) on Chromosorb P (60–90 mesh); 40 psi of He (60 ml/min); 200°. (c) Column C: 4 ft × 0.25 in. 20% Silicone gum rubber (SE-30) on Chromosorb W; 40 psi of He (60 ml/min); 210°.

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Notes

Trifluoroacetic Acid as a Medium for Aromatic Nitration Using Sodium Nitrate

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The nitration of aromatic systems is one of the most thoroughly studied of all organic reactions, and the central role of the nitronium ion, NO_2^+, in these processes has been well established.[2] Trifluoroacetic acid (TFA) has occasionally been used as a medium for electrophilic aromatic substitutions[3] and, in particular, Brown and Wirkkala used neat TFA and anhydrous nitric acid to nitrate benzene and toluene.[4] Some of our work on the use of TFA as a medium for the permanganate oxidation of hydrocarbons[5] involved cryoscopic measurements in TFA and these results indicated that nitronium and nitrosonium ions could be conveniently generated in TFA using sodium nitrate and sodium nitrite, respectively. We report herein the results obtained for nitration of benzene, toluene, and phenol, using these reagents.

The data presented in Table I show that nitration is almost quantitative after 4 hr of reaction with sodium nitrate. The mixture of isomers resulting from the nitration of toluene is similar to that reported by Brown and Wirkkala (ortho, meta, para = 61.6%, 2.6%, 35.8%).[4]

Trace amounts of phenolic substances were detected in the reaction products.[6] Such products may result either from oxygen attack by the ambident nitronium ion, followed by solvolysis and rapid nitration to produce nitrophenols, or by an addition–elimination mechanism[7] to give phenyl trifluoroacetate which then undergoes solvolysis and nitration.[8]

Attempts to use this medium for nitrosations were unsuccessful, as the data in Table I illustrate, even though cryoscopic and spectroscopic measurements indicated that up to 50% of the nitrite salt was converted to nitrosonium ion. Complex formation between nitrosonium ion and the arene was observed, as had been previously reported.[9] The small amount of nitration that occurs under these conditions is presumably the result of disproportionation[10] or oxidation[11] of nitrogen(III).

Table I

Reactants	Products	% yield[a]	% Conversion[b]
Benzene and $NaNO_3$	Nitrobenzene	99.9	100
	Phenolic products[c]	$\sim$0.05	
Toluene and $NaNO_3$	*p*-Nitrotoluene[d]	30.0	95
	o-Nitrotoluene	63.7	
	m-Nitrotoluene	1.2	
Phenol and $NaNO_3$	Tar[e]		
Benzene and $NaNO_2$	Nitrobenzene	3	3
Toluene and $NaNO_2$	Nitrotoluene mixture	$\sim$2	$\sim$2

[a] Based on quantities of starting materials used. [b] Based on quantities of starting materials consumed. [c] Indicated by the reversible changes in spectra of the product mixture produced by acidification and basification: λ_{max} 415, 366 nm in base and 320 nm (sh) in acid; a 1:1 mixture of *o*- and *p*-nitrophenols has λ_{max} at 415 nm in base and 330 nm in acid. [d] The mixture of nitrotoluenes was analyzed by vpc on a 10% silicon GS-SF-96 firebrick 60/80, 0.25-in. × 10-ft column at 162° and with 40 cm³/min of helium; it was then matched against known samples. Retention times were as follows: *o*-nitrotoluene, 8.5 min; *p*-nitrotoluene, 11.1 min., *m*-nitrotoluene, 10.5 min; toluene, 1.5 min. [e] Rapid, exothermic reaction occurred; could be hazardous.

Experimental Section

In a typical experiment 0.01 mol of sodium nitrate or sodium nitrite was added to 25 ml of neat TFA and then 0.01 mol of the arene was added while the mixture was stirred magnetically. The reaction was allowed to continue for 4 hr at room temperature, after which it was quenched by the addition of 20 ml water and by the addition of enough sodium hydroxide (either as 6 *M* solution or as pellets) to achieve a pH ≥10. The resulting solution was saturated with sodium chloride and successively extracted with three 50-ml portions of ether. The ether extracts were combined and dried over anhydrous magnesium sulfate and then reduced to 50 ml by flash evaporation. The concentrates were weighed and analyzed by vpc.

If TFA recovery is important, the sodium chloride saturation step can be omitted; then, after the ether extraction, the aqueous