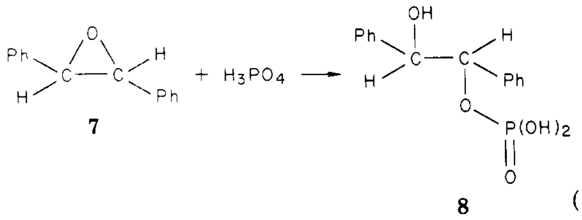
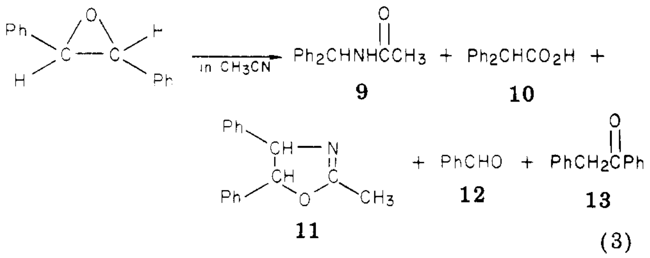
the basis of LC peak in comparison with that of the product from the reaction of *trans*-stilbene oxide with H_3PO_4.



(2)

Oxidation in Acetonitrile. When the reaction was carried out in acetonitrile, which is a considerably basic solvent, the further reactions of epoxide involving rearrangement, cleavage, and solvent participation were observed. The products and yields were *N*-diphenylmethylacetamide (**9**) (46.0%), diphenylacetic acid (**10**) (14.0%), 2-methyl-4,5-diphenyloxazoline (**11**) (12.2%), benzaldehyde (**12**) (5.3%), deoxybenzoin (**13**) (2.0%), and so on as shown in eq 3.



(3)

Virtually no *trans*-stilbene oxide remained in the products. Since *trans*-stilbene oxide gives the same products in the reaction with H_3PO_5 in acetonitrile, all of the products should be formed via *trans*-stilbene oxide.

The analogous reactions leading to oxazoline from ethylene oxide and nitriles[12,13] and the reaction leading to **9**[14] have been reported. The observed formation of 2-methyl-4,5-diphenyloxazoline by one step is of interest.

Experimental Section

Materials. *trans*-Stilbene, cyclohexene, styrene, and α-methylstyrene were of guaranteed grade and were used without further purification. Peroxymonophosphoric acid (2–2.5 M) was prepared by the method described in our previous paper.[3] *trans*-Stilbene oxide (mp 68 °C) was prepared by epoxidation of *trans*-stilbene with peroxyacetic acid.[6] *N*-Diphenylmethylacetamide (mp 156 °C) was prepared by the reaction of benzhydrol with acetonitrile.[14] Solvents were purified by distillation as described in the literature.

Products and Rates. Spectra were recorded on apparatuses described below: UV, a Hitachi 124 spectrophotometer; NMR, a Hitachi R-24B NMR spectrometer; GC–MS, a Shimadzu GCMS 7000 gas chromatograph–mass spectrometer (Silicone OV-17, 5% Shimalite W, 2.5 mm × 1.1 m); GLC, a Yanaco G 180 gas chromatograph (Silicone DCQF-1, 5% Chromosorb W, 2.5 mm × 0.75 m; PEG 20 M, 10% Chromosorb WAW, 2.5 mm × 0.75 m); and LC, a Yanagimoto L-1030 liquid-chromatograph (Yanapac DMS column, 2 mm × 0.25 m). Products were identified and estimated by means of GC–MS, GLC, and LC in comparison with those of the authentic samples. Mass spectral data of *N*-(diphenylmethyl)acetamide (**9**) and 2-methyl-4,5-diphenyloxazoline (**11**) were as follows. **9**: 225, 182, 167, 166, 148, 106, 104, **11**: 237, 195, 170, 166, 94, 78. The yields were measured by GLC using diphenyl as an internal standard. The rates were determined mainly by UV spectrophotometry of the remaining *trans*-stilbene (λ_{max} 306 nm, ϵ 27 200 in methanol) along with the iodometry[15] of remaining H_3PO_5.

Acidity Function.[3,16] The acidity function of dioxane–acetonitrile solvent was measured by means of UV spectrophotometry using *p*-nitroaniline as an indicator and by means of the following equation: $H_0 = \log K_B - \log I$, where $I = (\epsilon_N - \epsilon_A)/(\epsilon_A - \epsilon_S)$. This solvent has $\log K_B = 0.651$, $\lambda_N = 358$ nm, and $\epsilon_N = 15400$. The H_2SO_4 concentration in N and acidity function (H_0) of the solution were as follows: 0.10 N, 1.48; 0.05 N, 1.55; 0.04 N, 1.72; 0.02 N, 1.86; 0.015 N, 1.97; 0.01 N, 2.05.

Registry No. 3, 13598-52-2; **5**, 103-30-0; **7**, 1439-07-2; **9**, 5267-35-6; **10**, 117-34-0; **11**, 70369-11-8; **12**, 100-52-7; **13**, 451-40-1; acetonitrile, 75-05-8; cyclohexene, 110-83-8; styrene, 100-42-5; α-methylstyrene, 98-83-9; phenylacetic acid, 103-82-2; 2-phenylpropionic acid, 492-37-5.

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(12) R. Oda, M. Okano, S. Tokiura, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **35**, 1219 (1962).

(13) Y. Hayashi, S. Ueda, and R. Oda, *Nippon Kagaku Zasshi*, **90**, 946 (1969).

(14) B. Projsnar, *Chem. Anal. (Warsaw)*, 8, 255 (1963); *Chem. Abstr.*, **59**, 14581d (1963).

(15) D. Swern, *Org. React.*, 7, 392 (1953).

(16) E. A. Braude, *J. Chem. Soc.*, 1971 (1948).

Oxidation of Amines with Sulfonyl Peroxides. 4. The Stieglitz Rearrangement of Tritylamines, Benzhydrylamines, and Benzylamines Induced by *p*-Nitrobenzenesulfonyl Peroxide[1]

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Received February 12, 1979

The Stieglitz rearrangement of tritylamines, **2a–g**, benzhydrylamines, **3a–g**, and benzylamines, **4b,c**, is induced by reaction with *p*-nitrobenzenesulfonyl peroxide. Migratory aptitudes for substituted aromatic groups indicate that a concerted cationic aryl migration in the *O*-sulfonylhydroxylamine intermediate obtains. The results are compared with other Stieglitz rearrangements, and they suggest that the charge development on the migrating aryl group is structure and leaving-group dependent.

There are a variety of reactions which involve the migration of an aryl group from carbon to nitrogen.[2a] One example of such a reaction is the Stieglitz rearrangement of N-substituted amines (eq 1).[2] Of considerable interest

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$$\underset{\mathbf{1}}{R_3CNHY} \rightarrow R_2C{=}NR + HY \qquad (1)$$

$$Y = -OPCl_4, -Br, -Cl, -Pb(OAc)_3, -N_2, -OSO_2Ar$$

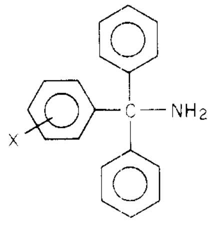
in this rearrangement is the electronic character of the nitrogen migration terminus. Stieglitz proposed a nitrene intermediate for these rearrangements based on statistical migration of phenyl and *p*-chlorophenyl in the base-induced rearrangement of substituted *N*-chlorotritylamines and the lack of such rearrangement in *N*-methyl-*N*-chlorotritylamines.

More recent studies on the Stieglitz rearrangement of *N*-tritylhydroxylamines with phosphorus pentachloride[3,4] and of *N*-chlorotritylamines with sodium methoxide[5] have shown that there is, in fact, a migratory preference for aryl groups. Migration is favored for aryl groups bearing electron-donating substituents, and these data have been used to support a concerted cationic migration for the Stieglitz rearrangement.[6,7]

We observed earlier that sulfonyl peroxides promote the Stieglitz rearrangement in *p*-methoxybenzylamine, benzhydrylamine, and tritylamine.[8] Aryl migration from carbon to nitrogen occurs in the *O*-sulfonylhydroxylamine (1, Y = $OSO_2C_6H_4NO_2$) which is produced initially in the reaction between amines and arylsulfonyl peroxides.[9] We wish to present migratory aptitude studies which characterize the transition states for these rearrangements.

Results

Monosubstituted tritylamines, **2a–g**, were prepared via the carbinol and carbinyl chloride followed by ammonolysis. Monosubstituted benzhydrylamines **3a–g** were prepared from the corresponding benzophenone by reduction of its oxime (see Experimental Section). Benzylamines **4b** and **4c** were purchased.



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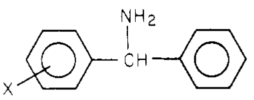

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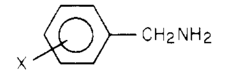


4

a, X = H; b, X = *p*-OCH_3; c, X = *p*-CH_3; d, X = *m*-CH_3; e, X = *p*-Cl; f, X = *m*-Cl; g, X = *m*-CF_3

Table I. Migratory Aptitudes for Aryl Groups in the Stieglitz Rearrangement of Tritylamines 2a–g Promoted by *p*-NBSP

amine	aryl substituent	MA[a]	% yield[b]
2a	H	1[c]	55
2b	*p*-OCH_3	22	20
2c	*p*-CH_3	4.5	38
2d	*m*-CH_3	1.5	39
2e	*p*-Cl	1.2	48
2f	*m*-Cl	0.47	49
2g	*m*-CF_3	0.30	51

[a] Migratory aptitudes (MA) defined by 2 × mol of benzophenone/mol of substituted benzophenone (±5%). [b] Total yield of benzophenones. [c] Migratory atptitude of -C_6H_5 is defined as 1.

Table II. Migratory Aptitudes for Aryl Groups in the Stieglitz Rearrangement of Benzhydrylamines 3a–g Promoted by *p*-NBSP

amine	aryl substituent	MA[a]	% yield of rearrang[b]	% yield of elim[c]
3a	H	1[d]	30.7	27.5
3b	*p*-OCH_3	373	44.7	1.3
3c	*p*-CH_3	12.6	78.1	21.7
3d	*m*-CH_3	1.7	71.3	23.9
3e	*p*-Cl	0.3	53.5	36.5
3f	*m*-Cl	0.03	52.7	33.7
3g	*m*-CF_3	0.009	70.3	25.7

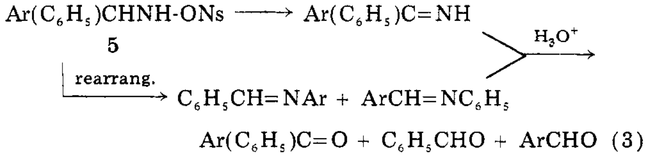
[a] Migratory aptitudes (MA) defined by mol of benzaldehyde/mol of substituted benzaldehyde (±5%). [b] Total yield of benzaldehyde products. [c] Yield of benzophenone. [d] Migratory aptitude of -C_6H_5 is defined as 1.

An ethyl acetate solution of tritylamines **2a–g** (3 equiv) was treated with *p*-nitrobenzenesulfonyl peroxide (*p*-NBSP) at −78 °C and stored at −20 °C overnight. Since direct analysis of the imine products is not reliable,[4,5,7] acid hydrolysis of the product mixture followed by steam distillation gave a mixture of benzophenones which was analyzed by GLC after addition of a suitable standard (eq 2). Control experiments showed that the hydrolysis was

$$Ar(C_6H_5)_2CNH_2 + (p\text{-}NO_2C_6H_4SO_2O)_2 \rightarrow$$
$$(C_6H_5)_2C{=}NAr + Ar(C_6H_5)C{=}NC_6H_5 \xrightarrow{H_3O^+}$$
$$(C_6H_5)_2C{=}O + Ar(C_6H_5)C{=}O \qquad (2)$$

essentially quantitative and that the recovery of individual benzophenones was identical (~90%). The ratio of product benzophenones was corrected statistically to yield the migration aptitudes (MA) found in Table I. When the reaction mixture from the oxidation of tritylamine was hydrolyzed with aqueous hydrochloric acid (2.5 M) at room temperature, extraction and chromatography led to the isolation of a small amount of trityl alcohol.

The oxidation of benzhydrylamines **3a–g** with *p*-NBSP in the same manner yielded, after hydrolysis, a product mixture consisting of a substituted benzophenone and a mixture of benzaldehydes (eq 3). The benzophenone



$$\underset{\mathbf{5}}{Ar(C_6H_5)CHNH\text{-}ONs} \xrightarrow{\text{elim.}} Ar(C_6H_5)C{=}NH$$
$$\xrightarrow{\text{rearrang.}} C_6H_5CH{=}NAr + ArCH{=}NC_6H_5 \xrightarrow{H_3O^+}$$
$$Ar(C_6H_5)C{=}O + C_6H_5CHO + ArCHO \qquad (3)$$

results from base-catalyzed elimination in the *O*-sulfonylhydroxylamine intermediate **5**,[9] and the benzaldehydes result from Stieglitz rearrangement of this adduct. The

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(1) (a) Taken in part from the M.S. Thesis of D. J. Poelker, New Mexico State University, 1978; (b) for part 3, see ref 9

(2) (a) Smith, P. A. S. In "Molecular Rearrangements", P. deMayo, Ed., Part 1; Interscience: New York, 1963; pp 480–567; (b) Stieglitz, J. *J. Am. Chem. Soc.* **1896**, *18*, 751; **1914**, *36*, 272; (c) Stieglitz, J.; Leech, P. N. *Chem. Ber.* **1913**, *46*, 2147; (d) Stieglitz, J.; Vosburgh, I. *ibid*, **1913**, *46*, 2151; (e) Senior, J. K. *J. Am. Chem. Soc.* **1916**, *38*, 2718.

(3) Newman, M. S.; Hay, P. M. *J. Am. Chem. Soc.* **1953**, *75*, 2322.

(4) Valint, P. L., Jr., Ph.D Thesis, Seton Hall University, 1966.

(5) Bochis, R. J., Ph.D. Thesis, Seton Hall University, 1966.

(6) The sodium methoxide promoted rearrangement of *N*-chlorotritylamines[5] may alternatively involve a concerted nitrenoid mechanism (eq i). Although the author argues against such a mechanism,

$$(C_6H_5)_2ArCNHCl + NaOCH_3 \rightarrow (C_6H_5)_2ArCN^{-}Cl \rightarrow$$
$$(C_6H_5)_2C{=}NAr + Cl^{-} \quad (i)$$

the data are well accomodated by such a pathway.

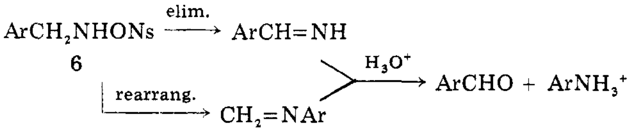
(7) (a) Sisti, A. J. *Chem. Commun.* **1968**, 1272; (b) Sisti, A. J.; Milstein, S. R. *J. Org. Chem.* **1974**, *39*, 3932.

(8) Hoffman, R. V.; Cadena, R.; Poelker, D. J. *Tetrahedron Lett.* **1978**, 203.

(9) (a) Hoffman, R. V. *J. Am. Chem. Soc.* **1976**, *98*, 6702; (b) Hoffman, R. V.; Cadena, R. *ibid.* **1977**, *99*, 8226.

products were measured by GLC after addition of a weighed standard, and the ratio of benzaldehydes determined the migration aptitudes given in Table II.

The oxidation of *p*-methoxybenzylamine **4b** with *p*-NBSP was undertaken analogously and after hydrolysis gave *p*-methoxybenzaldehyde (12%) and *p*-anisidine (40%) (eq 4). The benzaldehyde comes from elimination



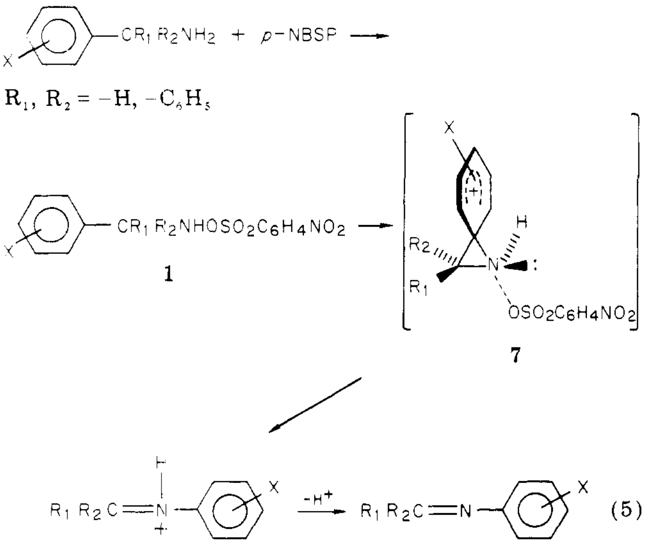
(4)

in the adduct **6** while the aniline results from Stieglitz rearrangement of this adduct. A similar experiment with *p*-methylbenzylamine **4c** gave *p*-methylbenzaldehyde (70%) and *p*-toluidine (<1%). Using the yields of rearranged products as a crude measure of the rearrangement efficiency, the *p*-anisyl to *p*-tolyl migration ratio is >40. Assuming a value of 8 from Tables I and II for the migratory aptitude of the *p*-tolyl group, an estimate of the migratory aptitude of the *p*-anisyl group is >320 for the Stieglitz rearrangement of benzylamines.

Discussion

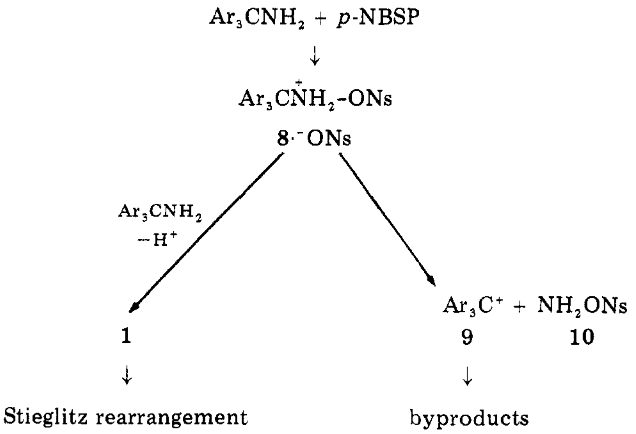
The migratory aptitudes determined for the (*p*-nitrobenzene)sulfonyl peroxide induced Stieglitz rearrangement of the amine series **2a–g**, **3a–g**, and **4b,c** change significantly with substituent. This indicates that aryl migration is quite sensitive to the electronic nature of the aryl substituent (electron donating or withdrawing) and that the transition state for aryl migration is similar for the three amine series studied. Hammett plots of the migratory aptitude data for **2a–g** and **3a–g** vs. σ^+ constants[10] gave $\rho = -1.57$ ($r = 0.992$) and $\rho = -3.97$ ($r = 0.994$), respectively. A much poorer fit was obtained with σ constants. The negative ρ values show that significant electron deficiency is built up on the migrating aryl group.

The migratory aptitudes and ρ values determined for the *p*-NBSP-induced Stieglitz rearrangement are clearly consistent with a cationic transition state **7** in which aryl migration is concerted with loss of the arylsulfonate leaving group, eq 5. These values are similar to those obtained by Sisti and Milstein for the lead tetraacetate promoted Stieglitz rearrangement of tritylamine (eq 1, Y = $Pb(OAc)_3$, $\rho = -1.7$)[7b] and by Tietz and McEwen for the Schmidt rearrangement of benzhydrol (eq 1, Y = N_2, $\rho = -2.03$).[11] Both of these reactions are thought to proceed via a concerted cationic rearrangement. The migratory aptitudes are also similar to those obtained for the acid-catalyzed pinacol rearrangement (*p*-OCH_3, 500; *p*-CH_3, 15.7; *p*-Cl, 0.7) which proceeds by a concerted cationic aryl rearrangement.[12]



(5)

Scheme I



Mechanisms involving other nitrogen intermediates are not supported by our results. A nitrene intermediate is excluded due to the fact that aryl migrations to nitrenes show little migratory preference.[13] A nitrogen-centered free radical or radical cation can be excluded by similar reasoning[14] and also by noting that N–O bond homolysis in the *O*-sulfonylhydroxylamine **1** should present a much higher activation barrier for the reaction than is observed.[15] While discrete nitrenium ions are not ruled out by our results, the electronegativity of nitrogen should provide a significant driving force for concerted rearrangement which minimizes charge buildup on nitrogen.[11]

Although aryl migration probably takes place by a concerted cationic mechanism in all three systems studied, several differences were noted for the oxidation of the tritylamine and benzhydrylamine series by *p*-NBSP. In the first place, the yields of rearrangement in the tritylamine series are only moderate (Table I) while the benzhydrylamine series gives excellent yields of oxidation

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[10] Taken from Gordon, A.; Ford, R. "The Chemist's Companion: A Handbook of Practical Data, Techniques, and References", Wiley-Interscience: New York, 1972; pp 152–153.

[11] Tietz, R. F.; McEwen, W. E. *J. Am. Chem. Soc.* **1955**, *77*, 4007.

[12] Bachmann, W. E.; Ferguson, J. W. *ibid.* **1934**, *56*, 2081.

[13] (a) Saunders, W. H., Jr.; Caress, E. A. *J. Am. Chem. Soc.*, **1964**, *86*, 861; (b) Saunders, W. H., Jr.; Ware, J. C. *ibid.* **1958**, *80*, 3328; (c) Abramovitch, R. A.; Kyba, E. P. *ibid.* **1974**, *96*, 480.

[14] Goerner, R. N.; Cote, P. N.; Vittimberga, B. M. *J. Org. Chem.* **1977**, *42*, 19, provides an excellent discussion of these rearrangements.

[15] (a) The activation energy for N–O bond homolysis should approach the N–O bond energy of about 30 kcal/mol for such a substituted hydroxylamine. Assuming an *A* factor of 10^{16} for a homolytic unimolecular dissociation,[16] the calculated half-life at −20 °C is >200 years. Since the observed rearrangement is complete in 12 h (probably less) at −20 °C, N–O bond homolysis is an unlikely mechanistic alternative. (b) The O–O bond energy in hydrogen peroxide (51 kcal/mol)[17] is similar to the N–O bond energy in hydroxylamine (53 kcal/mol).[18] A single alkyl substituent lowers the O–O bond energy by about 8 kcal/mol[16] and a arylsulfonyl substituent lowers the O–O bond energy by approximately 13 kcal/mol.[19] If these substituents cause similar changes in the hydroxylamine system, then the N–O bond energy in an *N*-alkylhydroxylamine *O*-arylsulfonate is estimated to be about 32 kcal/mol.

[16] Harris, J. M.; Wamser, C. C. "Fundamentals of Organic Reaction Mechanisms", Wiley: New York, 1976; p 110.

[17] Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

[18] Pimentel, G. C.; Spratley, R. D. "Chemical Bonding Clarified Through Quantum Mechanics", Holden-Day: San Francisco, Calif., 1969; p 314.

[19] Yokoyama, Y.; Yada, H.; Kobayashi, M.; and Minato, H. *Bull. Chem. Soc., Jpn.* **1971**, *44*, 2479.

[20] Sargeant, P. B.; Shechter, H. *Tetrahedron Lett.* **1964**, 3457.

products (elimination plus migration, Table II). It was found that small amounts of trityl alcohol were produced from the oxidation of **2a** with *p*-NBSP. This finding suggests that carbon–nitrogen bond cleavage in the amine–peroxide adduct may be competitive with Stieglitz rearrangement in tritylamines but not in the benzhydrylamine series.

Initial attack by the amine on the peroxide bond gives a protonated hydroxylamine *O*-arylsulfonate, **8**, which is deprotonated to **1** (Scheme I). Deprotonation of **8** to **1** is required for rearrangement since ionization of the nosyl group from the already positively charged nitrogen of **8** is unlikely. An alternative reaction channel available to **8** is carbon–nitrogen bond ionization to a trityl cation **9**. Reaction of **9** with traces of water gives the observed trityl alcohol. The *p*-nitrobenzenesulfonylhydroxylamine **10** is not expected to survive the reaction.[21]

The yields shown in Table I support this interpretation. There is a gradual decrease in the yield of the Stieglitz products as the electron-donating ability of the tritylamine substituent increases. A better electron donor should stabilize ion **9** and its formation should be favored. Thus less Stieglitz rearrangement is predicted in accord with the observed yields. Furthermore, if more of the amine substrate is used, increased deprotonation of **8** should raise the yield of rearranged products. Indeed, when 9 equiv of tritylamine were oxidized, instead of the normal 3 equiv, the yield of rearrangement increased from 55 to 61%.

A second difference between the *p*-NBSP oxidation of tritylamines **2a–g** and benzhydrylamines **3a–g** is the magnitude of the ρ value of rearrangement, $\rho = -1.57$ for the former and $\rho = -3.97$ for the latter. For **3a–g** there is significantly greater electron deficiency generated in the migrating aryl group than for **2a–g**. One possible origin of this difference is that the tritylamines contain considerable B strain relative to benzhydrylamines.[22] The release of this strain by rearrangement produces an earlier transition state with less charge development on the migrating group and hence a lower ρ value.

A second explanation for the differing ρ values between **2a–g** and **3a–g** comes from an examination of the transition state for aryl rearrangement **7**. During migration in **3a–g** ($R_1 = C_6H_5$, $R_2 = H$), the nonmigrating phenyl group can achieve a periplanar conformation with the developing aziridenyl ring which allows for delocalization of these strained ring bonds and hence a greater electron deficiency. Such cyclopropyl-type delocalization is well known.[23] However, for **2a–g** ($R_1 = R_2 = C_6H_5$), such a conformation is sterically unfavorable.[24]

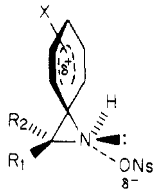

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Table III. ρ Values for Various Stieglitz Rearrangements of Tritylamine Derivatives, Ar_3CNHY

leaving group Y	ρ	ref
$-N_2$	-0.63^a	13
	-0.0336^b	13
$-OPCl_4$	-0.89	3
-Cl	-1.52	5
-ONs	-1.57	this work
$-Pb(OAc)_3$	-1.70	7b

[a] Pyrolysis of trityl azides. [b] Photolysis of trityl azides.

These data further support Sisti's contention that the position of the transition state for aryl migration in the Stieglitz rearrangement varies as a function of the leaving group (eq 2). Table III is a comparison of the present data with other studies for tritylamine derivatives.

It is necessary, however, to use caution in comparing these data. It is quite likely that the rearrangements of tritylazides (Table III, $Y = N_2$)[13] and perhaps the base-promoted rearrangement of *N*-chlorotritylamines (Table III, Y = Cl)[5,6] are of nitrene–nitrenoid character and thus are not justly comparable to a cationic rearangement.

It is more instructive to select particular systems for comparison. The lead tetraacetate induced Stieglitz rearrangement of tritylamines ($Y = Pb(OAc)_3$)[7b] and the *p*-NBSP-induced reaction (Y = ONs) are mechanistically similar and have similar but different ρ values (Table III). In the benzhydryl series, the Schmidt rearrangement of benzhydrols (eq 1, $Y = N_2$, $\rho = -2.03$)[11] and the *p*-NBSP-induced Stieglitz rearrangement of benzhydrylamines (Y = ONs, $\rho = -3.97$) are mechanistically similar and have ρ values of quite different magnitudes. These comparisons more clearly illustrate that charge development on the migrating aryl group is indeed influenced by the leaving group.

Experimental Section

General. All melting points were obtained on a Gallenkamp apparatus and are corrected. Proton magnetic resonance spectra were recorded on a Varian A-60-A spectrometer in deuteriochloroform using tetramethylsilane as an internal reference. Mass spectra were obtained on a Hitachi RMU-6E mass spectrometer. Gas chromatographic analyses were performed on either an Aerograph A-90-P3 instrument or a Varian 920 instrument with thermal conductivity detectors. Standard product mixtures were used to calibrate the detector response for all products. Thin-layer chromatography was performed on Eastman silica gel sheets. All yields and migratory aptitudes reported are the result of at least duplicate determinations (usually triplicate).

Triarylmethylamines 2a–g. The tritylamines used in this study were prepared by the same general route. A substituted benzoic acid was converted to its methyl ester, either directly[25] or via its acid chlodride.[26,27] Reaction of the ester with phenylmagnesium bromide in dry ether gave a substituted triarylcarbinol[28] which was converted to the triarylchloromethane with acetyl chloride.[29] Purification was effected at this stage since the triarylmethyl chloride could usually be crystallized from the reaction mixture. (If not, the crude chloride was carried on as obtained.) Ammonolysis of the chloride was accomplished by treatment with liquid ammonia.[30] The amines **2a–g** thus obtained were purified by conversion to their hydrochloride salt in ether. The salt was filtered and washed copiously with ether, suspended

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(21) Tamura, Y.; Minamikawa, J.; Ikeda, M. *Synthesis* **1977**, 1.

(22) (a) March, J. "Advanced Organic Chemistry: Reactions, Mechanism and Structure", 2nd ed.; McGraw-Hill: New York, 1977; pp 153, 249; (b) Deno, N. C.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3051.

(23) Reference 22a, p 141.

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in benzene, and treated with ammonia to furnish the pure tritylamine as a benzene solution.[5] The solvent was removed under vacuum to furnish the pure amine which was homogeneous by thin-layer chromatography and gave the correct ^{1}H NMR spectrum and melting point (when possible).

(*m*-Tolyl)diphenylmethylamine (2d). Amine **2d** was prepared by the above method, but it does not appear to have been characterized in the literature. **2d** is a clear oil whose ^{1}H NMR spectrum consisted of two singlets at δ 7.2 (14 H, aromatic H) and 2.25 (5 H, accidental equivalence of $-CH_3$ and $-NH_2$ protons). The mass spectrum gave no parent ion but did give an ion at m/e 182 (P − 91) indicating loss of the tolyl group from the parent ion. Anal. for the hydrochloride salt of **2d**. Calcd: C, 77.52; H, 6.52. Found: C, 77.55; H, 6.65.

(*m*-(Trifluoromethyl)phenyl)diphenylmethylamine (2d). Benzophenone (54.6 g, 0.3 mol) in dry ether (150 mL) was added dropwise to a stirred solution of *m*-(trifluoromethyl)phenylmagnesium bromide, prepared from *m*-(trifluoromethyl)bromobenzene (67.5 g, 0.3 mol) and magnesium turnings (Grignard type, 7.3 g, 0.3 mol) in dry ether (300 mL). The mixture was maintained at reflux during the addition and stored at room temperature overnight. The reaction mixture poured onto ice (500 g) and sulfuric acid (500 mL, 6 M) and extracted with ether (3 × 100 mL). The ether extracts were dried ($MgSO_4$), and the ether was removed by rotary evaporation to yield the crude (*m*-(trifluoromethyl)phenyl)diphenylcarbinol as a viscous oil. The crude carbinol was placed in a 500-mL flask fitted with a reflux condenser and treated with acetyl chloride (58.9 g, 0.75 mol) in hexane (200 mL). After the solution was cooled, the solvent was removed in vacuo, and the residue was distilled to yield (*m*-(trifluoromethyl)phenyl)diphenylmethyl chloride (62.4 g, 0.18 mol, 60%) with bp 115–125 °C (0.15 mmHg).

The above chloride (60 g, 0.17 mol) was stirred in refluxing liquid ammonia (6 h), and the ammonia was allowed to evaporate overnight. The residue was triturated with ether (300 mL) and filtered to remove ammonium chloride. The ether extract was washed with saturated sodium bicarbonate and then saturated brine, dried with magnesium sulfate, and treated with gaseous HCl to give the tritylammonium hydrochloride salt as a white precipitate (27.3 g, 0.078 mol, 26% yield). Anal. Calcd for $C_{20}H_{17}NClF_3$: C, 66.02; H, 4.72. Found: C, 65.93; H, 4.65.

The salt was dissolved in benzene and treated with anhydrous ammonia. Filtration followed by solvent evaporation yielded a clear oil **2g** which slowly solidified, mp 63–64.5 °C. The spectral properties were in accord with the assigned structure.

Diarylmethylamines 3a–g. The substituted benzhydrylamines **3a–g** were all prepared by the same general route (the preparation of **3g** will be detailed later). A substituted benzaldehyde was added to a solution of phenylmagnesium bromide in ether to give, after hydrolysis, the substituted diarylcarbinol.[31] The carbinol was oxidized to the corresponding benzophenone with Jones reagent[32] which was purified by distillation under reduced pressure. The pure ketone was refluxed with hydroxylamine in alcohol to give the oxime[33] which was reduced with zinc and concentrated ammonium hydroxide to the substituted diarylmethylamine **3a–g**.[34] An ether solution of the crude amine was treated with gaseous hydrogen chloride to give the flocculent hydrochloride salt which was filtered and washed copiously with ether. The free amine was regenerated by treatment of a benzene suspension with ammonia. Filtration followed by solvent removal gave the pure amine which was stored under nitrogen to prevent carbamate formation.

(*m*-(Trifluoromethyl)phenyl)phenylmethylamine (2d). Benzaldehyde (15.3 g, 0.14 mol) in dry ether (100 mL) was added dropwise to a stirred solution of *m*-(trifluoromethyl)phenylmagnesium bromide, prepared from *m*-(trifluoromethyl)bromobenzene (31.5 g, 0.14 mol) and magnesium turnings (Grignard grade, 3.4 g, 0.14 mol) in dry ether (150 mL). The mixture was maintained at reflux during the addition and allowed to stand at room temperature overnight. The reaction mixture was poured onto ice (250 g) and sulfuric acid (6 M, 250 mL) and steam distilled to remove unreacted benzaldehyde and *m*-(trifluoromethyl)bromobenzene. The residue was extracted with ether (3 × 100 mL), and the ether extracts were dried ($MgSO_4$) and evaporated to give (*m*-(trifluoromethyl)phenyl)phenylcarbinol as a brown oil. The crude carbinol was dissolved in acetone (250 mL), titrated with Jones reagent until an orange color persisted, and evaporated to a green residue. The residue was stirred with ether (200 mL), and the ether layer was washed with saturated sodium bicarbonate and saturated brine, dried over magnesium sulfate, and evaporated. The product was distilled (bp 113–137 °C (0.4 mmHg)) to give *m*-(trifluoromethyl)benzophenone (26.6 g, 0.11 mol, 76% yield). Recrystallization from hexane afforded a white solid, mp 52–53 °C.

To a solution of the ketone (25 g, 0.1 mol) and hydroxylamine hydrochloride (20 g 0.29 mol) in ethanol (225 mL) was added sodium hydroxide (20%, 150 mL), and the mixture was refluxed (1 h), poured onto ice (300 g), and acidified with dilute sulfuric acid to precipitate the white oxime. The crude oxime, dissolved in ethanol (200 mL), was added to a mixture of concentrated ammonium hydroxide (1 L), ammonium acetate (8 g), and granular zinc (60 g, 0.92 mol) and refluxed for 6 h. The reaction was cooled, filtered, and extracted with ether (2 × 100 mL). The ether extracts were washed with sodium hydroxide (50%, 40 mL), dried ($MgSO_4$), and evaporated to yield **3g**, a tan oil. A solution of the amine in ether was treated with hydrogen chloride to give the white hydrochloride salt which was filtered, washed with ether, and dried (8.6 g, 0.03 mol, 21.4% yield). Anal. Calcd for $C_{14}H_{13}NClF_3$: C, 58.44; H, 4.56. Found: C, 58.27; H, 4.46. A benzene solution of the salt was treated with gaseous ammonia to regenerate the free amine in benzene solution. After filtration, the benzene was removed to yield **3g** as a clear oil which was stored under nitrogen.

Oxidation of Tritylamines 2a–g with *p*-NBSP. A solution of *p*-NBSP[35] (0.404 g, 1 mmol) in ethyl acetate (115 mL) was cooled to −78 °C under a nitrogen atmosphere. A solution of the amine (3.1 mmol) in ethyl acetate (10 mL) was added to the cold peroxide solution by syringe. The mixture was stirred at −78 °C (3 h) and allowed to warm to −20 °C overnight in a freezer. The solvent was removed by rotary evaporation with a bath temperature of 25 °C. Hydrochloric acid (2.5 M, 200 mL) was added to the residue, and the mixture was immediately placed in a preheated oil bath and distilled until 125 mL of distillate was collected. The distillate was extracted with ether (4 × 10 mL), and the organic layers were combined and extracted with saturated sodium bicarbonate and saturate brine and dried ($MgSO_4$). A weighed standard, methyl *p*-anisate, was added and analyzed by GLC using a 5% QF-1 column (2.4 m × 0.63 cm aluminum, 160 °C, 70 cm^3/min He). Control experiments showed that the hydrolysis of diphenylmethylideneaniline to benzophenone was of high yield (>90%) and that the recovery of benzophenones by the steam distillation protocol was the same, regardless of substituent (>90%).

Tritylamine (9 mmol) was oxidized with *p*-NBSP as above and the yield of benzophenone increased from 55 to 61%.

In another experiment, **2a** was oxidized as above. After solvent removal, hydrochloric acid (2.5 M, 125 mL) was added, and the mixture was stirred for 1 h at room temperature. The mixture was extracted with ether (4 × 35 mL), and the organic fraction was washed with saturated sodium bicarbonate and saturated brine, dried ($MgSO_4$), concentrated, and chromatographed on silica gel using benzene–hexane (1:1) as eluant. Two components were obtained; the first was benzophenone (26%), and the second was identified as triphenylcarbinol (7 mg, 0.03 mmol, 3% yield) by its R_f value on thin-layer chromatography sheets and its ^{1}H NMR spectrum. No triphenylcarbinol was detected when tritylamine, without added *p*-NBSP, was carried through this procedure. This indicates that *p*-NBSP is required for carbinol formation from tritylamine.

Oxidation of Diphenylmethylamines 3a–g with *p*-NBSP. A procedure analogous to that used for **2a–g** was employed. The amine (3.0 mmol) was oxidized with *p*-NBSP (1 mmol). A point of departure came after the steam distillation step. The steam distillate (75 mL) was extracted with dichloromethane (3 × 10

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mL). The organic layers were combined and washed with saturated bicarbonate then brine and dried ($MgSO_4$). Addition of a weighed standard anisole was followed by GLC analysis of the benzaldehyde products (5% QF-1, 1.9 m × 0.63 cm, 80 °C, 60 cm^3/min He). Addition of a second weighed standard, methyl *p*-anisate, permitted GLC analysis of the benzophenone yield as above. We had shown earlier that substituted benzaldehydes are obtained nearly quantitatively by this isolation procedure[9b] so that the measured ratio of benzaldehydes is a true measure of the migratory aptitudes of substituted aromatic groups.

Acknowledgments. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, to whom we are extremely grateful.

Registry No. 2a, 5824-40-8; **2b**, 53060-13-2; **2c**, 53060-12-1; **2d**, 70428-89-6; **2e**, 53060-10-9; **2f**, 70428-90-9; **2g**, 70428-91-0; **3a**, 91-00-9; **3b**, 2538-34-3; **3c**, 55095-21-1; **3d**, 55095-20-0; **3e**, 28022-43-7; **3f**, 55095-14-2; **3g**, 70428-92-1; **3g** hydrochloride, 49703-61-9; **4b**, 2393-23-9; **4c**, 104-84-7; *p*-$OCH_3C_6H_4(C_6H_5)CO$, 611-94-9; *p*-$CH_3C_6H_4(C_6H_5)CO$, 134-84-9; *m*-$CH_3C_6H_4(C_6H_5)CO$, 643-65-2; *p*-$ClC_6H_4(C_6H_5)CO$, 134-85-0; *m*-$ClC_6H_4(C_6H_5)CO$, 1016-78-0; *m*-(trifluoromethyl)benzophenone, 728-81-4; *p*-anisidine, 104-94-9; *p*-$OCH_3C_6H_4CHO$, 123-11-5; *p*-$CH_3C_6H_4CHO$, 104-87-0; *m*-$CH_3C_6H_4CHO$, 620-23-5; *p*-ClC_6H_4CHO, 104-88-1; *m*-ClC_6H_4CHO, 587-04-2; *m*-$CF_3C_6H_4CHO$, 454-89-7; benzophenone, 119-61-9; benzaldehyde, 100-52-7; *p*-toluidine, 106-49-0; *m*-(trifluoromethyl)phenyl bromide, 401-78-5; (*m*-(trifluoromethyl)phenyl)diphenylcarbinol, 742-91-6; (*m*-(trifluoromethyl)phenyl)diphenylmethyl chloride, 57381-92-7; (*m*-(trifluoromethyl)phenyl)phenylcarbinol, 728-80-3; *p*-NBSP, 6209-72-9; triphenylcarbinol, 76-84-6.

S_N2 Displacements and Reductive Coupling of Ketones with Olefins in *N,N*-Diethylacetamide and *N*-Ethylpyrrolidone

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Received March 8, 1979

N,N-Diethylacetamide (DEA) and *N*-ethylpyrrolidone (NEP) are complementary to hexamethylphosphoric triamide (HMPA), dimethylformamide, and dimethyl sulfoxide as solvents in which to carry out several reactions commonly conducted in polar, aprotic media. Reaction of neopentyl tosylates with lithium halides in DEA and NEP gives good yields of neopentyl halides. Ketones and terminal olefins are reductively coupled to tertiary alcohols in fair to good yields in mixtures containing NEP, sodium, and *tert*-butyl alcohol; 1-hepten-6-one and 1-octen-7-one are cleanly cyclized to five- and six-membered rings, respectively, in good yield by this same mixture. Terminal olefins are reduced to alkanes in fair yield by DEA–sodium–*tert*-butyl alcohol mixtures; di- and tetrasubstituted olefins are resistant to reduction by this mixture.

Hexamethylphosphoric triamide (HMPA) is a dipolar aprotic solvent[1,2] that is particularly valuable for such reactions as S_N2 displacement with anionic nucleophiles[3,4] and dissolving-metal reductions.[5] The routine use of HMPA has been discouraged by the announcement that it may be carcinogenic.[6] In the course of other studies, we required quantities of several neopentyl halides. Compounds of this type had proved in previous work to be most rapidly prepared by displacement of tosylate ion by halide ion using HMPA as solvent.[3,7] A recent paper by Young and Dewald reported that *N,N*-diethylacetamide (DEA) and other tertiary amide solvents dissolved sodium metal and gave blue solutions containing solvated electrons and metal anions.[8] Young and Dewald suggested in passing that the high sodium cation solvating ability and chemical stability indicated by this observation might find application in other types of reactions.[8] Here we describe experiments confirming that DEA and *N*-ethylpyrrolidone (NEP) are comparable to HMPA as solvents for displacement reactions and that they are of significant, but more limited value than HMPA for dissolving-metal reduction of olefins. In addition, we describe a useful new reaction which occurs in NEP (but not in HMPA) by which ketones and terminal olefins are reductively coupled to tertiary alcohols by sodium–*tert*-butyl alcohol mixtures.

Results and Discussion

Bimolecular Substitution in DEA and NEP. Table I lists the yields of alkyl halides detected following the treatment of neopentyl and cyclohexyl tosylates with ca. 2 equiv of lithium halide in various solvents. DEA, NEP, and *N*-acetylpyrrolidine (NAcP) afford marginally higher yields of neopentyl chloride than HMPA and significantly improved yields compared with yields obtained with the common dipolar aprotic solvents *N,N*-dimethylacetamide (DMA), DMF, and Me_2SO. Several analogues of DEA listed in this table proved to be less effective solvents for displacement than their parent structure. Although DEA is comparable to HMPA as a solvent for nucleophilic substitutions involving neopentyl tosylate and 2,2-dimethylpropanediyl 1,3-ditosylate, it is notably poorer than HMPA for nucleophilic displacement of tosylate from 2,2,3,3-tetramethylbutanediyl 1,4-ditosylate with lithium chloride: in addition to lower yields, NEP and DEA appear to give products contaminated by monohalogenated materials (ca. 10–15%); DMF and Me_2SO are again much less effective. The practical utility of DEA as a solvent for displacements at neopentyl centers is indicated by the isolation of good yields of neopentyl chloride, 1-chloro-2,2-diethylbutane, 1,4-dibromo-2,2-dimethylpropane, and pentaerythrityl tetrabromide from preparative-scale reactions. The experimental procedures followed in DEA

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