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	$Arin(OOOF_8)_2 \longrightarrow Arno$		
Registry no.	Product ^a	Registry no. ²	$\mathbf{Yield},\ \%$
1516-21-8	4-Nitrosoanisole	28688-23-5	59 ^b
586-96-9	Nitrosobenzene	23586-54-1	43°
932-98-9	4-Nitrosochlorobenzene	23586-58-5	50ª
38899-21-7	Nitrosodurene	38899-26-2	93*
1196-12-9	Nitrosomesitylene	23586-57-4	931
22955-65-3	4-Nitrosoethylbenzene	35322-30-6	889
623-11-0	4-Nitrosotoluene	23586-55-2	88^{h}
38899-22-8	4-Nitroso-1,2-dimethylbenzene	23586-56-3	91^{i}
38974-06-0	4-Nitroso-1,3-dimethylbenzene	34202-98-7	90 <i>i</i>
17075-25-1	2-Nitroso-1.4-dimethylbenzene	34202-99-8	93*

TABLE 1				
SYNTHESIS OF	ARYLNITROSO	Compounds from	ARYLTHALLIUM	DITRIFLUOROACETATES
		ArTI(OOCCE _a) _a -	\rightarrow ArNO	

17 ^a The use of isomerically pure arylthallium ditrifluoroacetates led to the formation of isomerically pure arylnitroso compounds; otherwise, mixtures of isomeric arylnitroso compounds were obtained whose isomeric distribution matched that of the starting material (see Experimental Section). ^b A. Baeyer and E. Knorr, Ber., **35**, 3034 (1902); mp 32-34°. ^c 'Organic Syntheses,' Collect. Vol. III, Wiley, New York, N. Y., 1955, p 668; mp 64-67°. ^d R. E. Lutz and M. R. Lytton, J. Org. Chem., **2**, 68 (1937); mp 89.5°. ^e L. I. Smith and F. L. Taylor, J. Amer. Chem. Soc., **57**, 2460 (1935); mp 160° dec. ^f E. Bamberger and A. Rising, Ber., **33**, 3623 (1900); mp 122°. ^g See footnote d; mp 22°. ^h E. Bamberger, Ber., **28**, 245 (1895); mp 48.5°. ⁱ E. Bamberger and A. Rising, Justus Liebigs Ann. Chem., **316**, 257 (1901); mp 44-45°. ^j See footnote i; mp 41.5°. ^k See footnote i; mp 101.5°. ⁱ Of starting material.

TlCl₃). The chloroform extract was dried (MgSO₄) and evaporated to give the crude arylnitroso compound, which was purified by Kugelrohr distillation (in vacuo).

Glc analysis of the arylnitroso compounds was frustrated by poor separation and, as a consequence, isomer distributions were determined by oxidation with pertrifluoroacetic acid to the arylnitro compounds, which were then satisfactorily analyzed by glc. As expected, the use as substrates of arylthallium ditrifluoroacetates which had not been recrystallized to isomeric purity led to a mixture of isomeric arylnitroso compounds whose isomeric distribution matched precisely that of the precursor arylthallium ditrifluoroacetates. Thus in this reaction, as in all previously investigated conversions of ArTlX2 compounds to substituted aromatics, the new substituent group enters the ring at the position to which the thallium atom was originally attached.

Kinetic Evidence for an Enamine Mechanism in the Acid-Catalyzed Cleavage of β -Amino Alcohols¹

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The reaction of α -aryl- β -amino alcohols with strong acids has been known for some time to cause cleavage to β -carbonyl compounds.²⁻⁴ Two mechanisms have been proposed to account for the cleavage, one involving a glycol intermediate^{2,3} and the other involving



(1) The receipt of an NSF and a Lafayette summer fellowship and a grant from Merck Sharpe and Dohme, Inc., in support of this research is gratefully acknowledged.



an enamine intermediate.^{2,4} The details of these mechanisms have been reviewed recently.⁵ In general there has been little convincing experimental evidence in favor of either mechanism, although recent work⁵ has ruled out a glycol mechanism for the reaction of one amino alcohol with acid.

We have examined the acid-catalyzed reaction rates of 2-(N,N-diethylamino)-1-phenylethanol derivatives having from zero to three methyl groups on the aromatic rings. A large excess of 4 N hydrochloric acid at 100° was employed as the reaction medium, conditions which led to pseudo-first-order kinetics. Ultraviolet spectroscopy was used to monitor the disappearance of amino alcohols. The pseudo-first-order rate constants and relative rates are summarized in Table I.

TABLE	I
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Graphi Cons Amino A	CALLY DETERMINED PSEUDO FANTS AND RELATIVE RATES ALCOHOLS WITH 4 N Hydrod	D-FIRST-ORDER S FOR REACTION CHLORIC ACID A	Rate n of at 100°
Registry			Relative
no.	Amino alcohol	k, sec ⁻¹	rate
4249-64-3	$C_6H_5CHOHCH_2NEt_2$	$2.63 imes 10^{-7}$	1.00
39008-11-2	p-CH ₂ C ₆ H ₄ CHOHCH ₂ - NEt ₂	$2.19 imes 10^{-6}$	8.33
39008-12-3	2,4-di-CH ₃ C ₆ H ₃ CHOH- CH ₂ NEt ₂	$1.61 imes 10^{-5}$	61.2
39008-13-4	2,4,6-tri-CH ₃ C ₆ H ₂ CHOH- CH ₂ NEt ₂	$8.14 imes 10^{-5}$	309

The rate constants are seen to increase with increasing methyl substitution on the ring, each increase by one methyl group leading to an increase in rate by a factor varying from approximately 5 to 8. A mech-

(5) S. A. Fine and R. L. Stern, J. Org. Chem., 35, 1857 (1970).

 ⁽²⁾ F. Kröhnke and A. Schulze, Chem. Ber., 75, 1154 (1942).
 (3) H. Auterhoff and H. J. Roth, Arch. Pharm. (Weinheim), 289, 470 (1956).

⁽⁴⁾ P. T. Sou, Bull. Fac. Sci. Univ. Fr-Chin. Peiping, 5, 1 (1935); Chem. Abstr., 30, 4463 (1936),

anism involving glycol intermediacy has a rate-determining step involving nucleophilic attack at the carbon atom bearing the diethylamino group,⁵ whereas an enamine mechanism involves a rate-determining dehydration with consequent carbonium ion formation. The rate data are consistent with the latter process and follow a trend noted by previous workers in the solvolysis of 1-phenylethyl chlorides. Thus, at 0°, the relative rates of ethanolysis of 1-phenylethyl chloride, 1-o-tolylethyl chloride, and 1-mesitylethyl chloride were approximately 1:34:3500,6 while at 25° the ratio was 1:22:1980.6 Although the p-methyl compound was not included in the solvolvsis study, the rate-enhancing effect of a *p*-methyl group on typical solvolysis reactions of benzylic compounds varies from fourfold to 80-fold, depending on the specific compound and reaction conditions.⁷ In the case of σ -methyl groups two competing effects operate: an inductive effect which stabilizes the carbonium ion, and a steric effect which destabilizes the ion by hindering coplanarity of the ion with the aromatic ring. It has been suggested that ions of the type $o-CH_3C_6H_4CHR^+$ suffer no significant steric inhibition of resonance but when two σ -methyl groups are present inhibition does occur, but is surpassed by stabilizing inductive effects.⁶ Our rate data also shows a greatly enhanced rate of reaction for the mesityl compound, but the increase in reactivity of the mesityl compound compared to the 2.4dimethyl compound is smaller than the increase in reactivity of the 2,4-dimethyl compound compared to the *p*-methyl compound and of the *p*-methyl compound compared to the unsubstituted amino alcohol.

Additional evidence is provided by a comparison of our rate data with rate data for the acid-catalyzed dehydrations of other 1-phenylethanol derivatives. Thus, ρ for the reaction of the amino alcohols is approximately -3.1 (σ^+ para) compared with typical values in the -3 to -4 range for reactions of the latter type.^{8,9}

In contrast, a bimolecular rate-determining step is not consistent with the present results.¹⁰ Even for compounds in which the group being displaced is on a benzylic carbon, there is always less than a twofold difference in the rates of *p*-tolyl *vs*. phenyl in typical SN2 reactions.¹¹

Experimental Section¹²

Synthesis of Amino Alcohols.—2-(N,N-Dimethylamino)-1-phenylethanol was prepared by a previously published proce-

(6) G. Baddeley and J. Chadwick, J. Chem. Soc., 368 (1951).

(7) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N.Y., 1962, p 76.

(8) N. C. Deno, F. A. Kish, and H. J. Peterson, J. Amer. Chem. Soc., 87, 2157 (1965).

(9) D. S. Noyce, D. R. Hartler, and F. B. Miles, J. Amer. Chem. Soc., 90, 3794 (1968).

(10) The reaction of PhCHOHCH₂OH with 1.78 M sulfurie acid is at least 70% complete in 1 hr: T. Matsuda and M. Sugishita, *Bull. Chem. Soc. Jap.*, **35**, 1446 (1962). Under our (similar) conditions PhCHOHCH₂NEt₂ required several days for half-reaction; hence, although diols dehydrate via a carbonium ion mechanism, the reaction of the diols to form carbonium ions could not be rate determining for the amino alcohols in this investigation if a diol mechanism were involved.

(11) Reference 7, p 18.

(12) Ketone starting materials were obtained commercially and were distilled before use. Melting points were taken on a Fisher-Johns block and are uncorrected. Infrared spectra were recorded on a Beckman IR-10 instrument. Ultraviolet spectra were recorded on a Beckman DK-2A spectrophotometer; reactions were monitored on a Beckman DU instrument. Elemental microanalyses were performed by Dr. George I. Robertson, Jr., Florham Park, N.J. dure.¹³ All other amino alcohols were prepared via the following general procedure. A solution of Br_2 (32 g, 0.20 mol) in CCl₄ (125 ml) was added at a slow dropwise rate¹⁴ to a vigorously stirred solution of the appropriate ketone (0.20 mol) in CCl₄ (175 ml). The solution was stirred for 20 min and approximately 75% of the solvent was evaporated under reduced pressure. The concentrated solution was cooled to 0° and the bromo ketone was collected, washed with cold hexane, and air dried.

The bromo ketone (10 g) was added in small portions to a large excess (35 ml) of vigorously stirred diethylamine at 0°. After stirring for 2 hr at 0° the reaction mixture was kept under N₂ at 30° for 24 hr. Excess Et₂NH was removed under reduced pressure and the residue was extracted with ether and filtered from Et₂NH · HBr. The ether layer was extracted with two 50-ml portions of cold 2 N HCl and the aqueous extract was then neutralized (NaOH). The crude product was reextracted with ether, solvent was removed under reduced pressure, and the amino ketone was vacuum distilled.

A solution of the amino ketone (0.03 mol) in anhydrous ether was added dropwise to a stirred mixture of LiAlH₄ (0.013 mol)in anhydrous ether. After addition was complete the mixture was refluxed for 30 min. Water-saturated ether was added cautiously to destroy excess LiAlH₄. The ether layer was separated and washed with water, sodium carbonate, and water. Drying of the ether solution (MgSO₄) followed by evaporation of solvent under reduced pressure gave the amino alcohol, which was purified by vacuum distillation. Overall yields of the amino alcohols were generally 30-40%. The results of these prepartions are summarized in Table II.

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л.	ADLL	T T

SUMMARY OF PHYSICAL AND SPECTRAL PROPERTIES OF AMINO Alcohols^a Synthesized by the Procedure Below

 $\operatorname{ArCOCH_3} \xrightarrow{\operatorname{Br_2}} \operatorname{ArCOCH_2Br} \xrightarrow{\operatorname{Et_2NH}} \operatorname{ArCOCH_2NEt_2} \xrightarrow{\operatorname{LiAlH_4}} \rightarrow$

		ArCH	OHCH₂NEt	
Compd	Bp, °C (mm)	Ir, ^b cm ⁻¹	Uv, ^c nm	
C ₆ H ₅ CHOHCH ₂ NEt ₂			$\lambda_{\max} 256$ (e 192)	
p-CH ₈ C ₆ H ₄ CHOHCH ₂ NEt ₂	135 (5) ^d	3380 (m, OH)	λ _{max} 261.5 (ε 331)	
$2,4\text{-}di\text{-}CH_{\$}C_{\$}H_{\$}CHOHCH_{2}NEt_{2}$	145 (5)	3410 (m, OH)	λ _{max} 264.5 (ε 334)	
$2,4,6-\text{tri-CH}_{8}C_{6}H_{2}CHOHCH_{2}NEt_{2}$	153 (5) ^e	3390 (m, OH)	λ _{max} 267 (ε 330)	

^a Satisfactory elementary microanalyses were obtained for all new amino alcohols. ^b Spectra were determined on neat liquids; no absorption in the C=O region was present in any of the amino alcohol spectra. ^c Ultaviolet spectra were determined as dilute HCl solutions. ^d Lit.¹⁰ bp 102-104° (0.2 mm). ^e Solidified on standing, mp 57-58°.

Determination of Reaction Rates of Amino Alcohols with 4 NHydrochloric Acid. General Procedure.--A tightly stoppered 50-ml flask containing 35 ml of 4 N HCl and a Teflon-coated stirring bar was placed in a magnetically stirred oil bath maintained at 100° by means of an electronic temperature controller.15 After 1 hr the amino alcohol (300-500 mg) was introduced into the flask and timing was begun. At various times 1-ml aliquots were pipetted from the reaction mixture into a 25-ml volumetric flask containing 20 ml of cold water. The solution was washed four times with ether,¹⁶ the ether being removed each time by careful suction with a disposable pipette. The aqueous solution was diluted to 25 ml with water and the ultraviolet absorbance of the solution at λ_{max} was determined. The solutions obtained after 1-min reaction times were used for zero-point readings, the rate constants being such that the extents of reaction were usually negligible after 1 min. The reference blank consisted cf a sample of 4 N HCl, carried through the same procedure as the

(15) Cole-Parmer Versatherm Model 2156 proportional electronic temperature controller.

(16) The ether washes served to remove the aldehyde products, which might otherwise interfere with the uv measurements.

⁽¹³⁾ S. L. Shapiro, H. Soloway, and L. Freedman, J. Amer. Chem. Soc., **80**, 6060 (1958).

⁽¹⁴⁾ Addition was stopped as soon as a Br_2 color persisted.

Notes

The results of the experiments and a representative samples. run are tabulated in Tables I and III.

Тав	LE III	
Represent	TATIVE RUN.	
RAW KINETIC DATA 1	FROM THE REACTION OF	
2-(N,N-DIETHYLAMINO)-1-(2,4,6-TRIMETHYLPHENYL)ETHANOI		
with $4 N$	HCl at 100°	
Time,	Absorbance	

2 1110 j	
min	(at 267 nm)
0	0.547
19	0.432
37	0.346
58	0,282
79	0.225
98	0.184
118	0.152

Registry No.—ArCOCH₃ (Ar = C_6H_5), 98-86-2; ArCOCH₃ (Ar = p-CH₃C₆H₄), 122-00-9; ArCOCH₃ $(Ar = 2, 4-di-CH_3C_6H_3), 89-74-7; ArCOCH_3 (Ar = 2, 4-di-CH_3C_6H_3), 89-74-7; ArCOCH_3C_7H_3C_$ 2,4,6-tri-CH₃C₆H₂), 1667-01-2; ArCOCH₂Br (Ar = C_6H_5 , 70-11-1; ArCOCH₂Br (Ar = p-CH₃C₆H₄), 619-41-0; ArCOCH₂Br (Ar = 2,4-di-CH₃C₆H₃), 26346-85-0; $ArCOCH_2Br$ (Ar = 2,4,6-tri-CH₃C₆H₂), 4225-92-7; $ArCOCH_2NEt_2$ (Ar = C₆H₅), 4061-29-4; Ar- $COCH_2NEt_2$ (Ar = $p-CH_3C_6H_4$), 39008-15-6; Ar-COCH_2NEt_2 (Ar = 2,4-di-CH_3C_6H_8), 39008-16-7; Ar- $COCH_2NEt_2$ (Ar = 2,4,6-tri-CH₃C₆H₂), 39008-17-8; Br₂, 7726-95-6; LiAlH₄, 16853-85-3; diethylamine, 109-89-7.

An Improved Synthesis of 2-Chloro-2-fluoropropane

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2-Chloro-2-fluoropropane (1) was first prepared in 10-15% yield by the action of antimony trifluoride containing 5% bromine on 2,2-dichloropropane in 1937 by Henne.¹ Small yields of 1 can also be prepared² by heating $(CH_3)_2CCIN(O)$ = NF to 60° and by the action of chlorine in the liquid or gas phase on 2-fluoropropene.³⁻⁵ The free-radical chlorination of 2-fluoropropane gave 2-chloro-2-fluoropropane in 77% yield.6 Henne⁷ found that the reaction of 2-chloropropene with anhydrous fluoride (without solvent) yielded a mixture of 2,2-difluoropropane and 2,2-dichloropropane instead of the simple addition product 1. However, Chapman⁸

(1) A. L. Henne and M. W. Renoll, J. Amer. Chem. Soc., 59, 2424 (1937). (2) A. N. Medvedev, K. N. Smirnov, S. S. Dubov, and V. A. Ginsburg,

Zh. Obshch. Khim., 38, 2462 1968); Chem. Abstr., 70, 46737u (1969) (3) J. P. Henry and L. O. Moore, U. S. Patent 3,215,746 (1965); Chem. Abstr., 64, P6492e (1966).

(4) J. P. Henry and L. O. Moore, U. S. Patent 3,277,188 (1966); Chem. Abstr., 66, P10571x (1967)

(5) L. D. Moore, J. P. Henry, and J. W. Clark, J. Org. Chem., 35, 4201

(1970).
(6) L. G. Anello and C. Woolf, Belgian Patent 632,995 (1963); Chem.

(7) A. L. Henne and P. Plueddeman, J. Amer. Chem. Soc., 65, 1271 (1943).

did obtain a 47% yield of 1 by the stannic chloride catalyzed addition of anhydrous hydrogen fluoride to 2-chloropropene.

We have found that the simple addition of hydrogen fluoride to 2-chloropropene to produce 1 can be achieved very smoothly and in high yield (75%) when the reaction is carried out in nitrobenzene at 14° for 10 min, as shown in eq 1. The use of nitrobenzene moderated

$$CH_{2} = C + HF (excess) \xrightarrow{PhNO_{2}, 14^{\circ}} CH_{3}CCH_{3} \qquad (1)$$

$$CH_{3} = CH_{3} + CH_{3}CCH_{3} + CH_{3}C$$

the reactivity of hydrogen fluoride and permitted the clean addition of HF across the double bond without further reaction to produce 2,2-diffuoropropane (Scheme I) or the formation of tars. Reaction times greater



than 10 min led to a disproportionation, producing 2,2-difluoropropane (2) and 2,2-dichloropropane (3) as shown in Scheme I. The disproportionation products 2 and 3 were readily distinguished from 1 by their nmr spectrum. The methyl absorption of 2 was a triplet, of 3 was a singlet, and of 1 was a doublet.

The yield (75%) was based on isolated material. However, an nmr spectrum of the crude reaction mixture showed no products other than 1 and indicates, if allowances are made for recovered starting material and for evaporation (bp 35°) of product during work-up, that the addition is highly efficient.

Experimental Section

To 80 ml of nitrobenzene (dried, reagent) in a 125-ml Teflon bottle containing a Teflon-coated magnetic stirring bar was added 10.0 g (0.130 mol) of 2-chloropropene. Anhydrous hydrogen fluoride gas was rapidly added to the cooled (14°) mixture until 22 g (1.1 mol) had been absorbed. The mixture was allowed to stir for 10 min, and then rapidly added to cold water. Carbon tetrachloride (300 ml) was added, the organic layer was washed three times with water and dried (Na_2SO_4) , and the solution was distilled on a spinning band column to yield 10.7 g of liquid, bp $<50^{\circ}$ (mostly 35°). Integration of the pmr spectrum indicated that 13 mol % (11 wt %) of the isolated material was 2-chloropropene. Thus a yield of 75% and an efficiency of 89% were realized. The sample was redistilled on a spinning band column to obtain pure 2-chloro-2-fluoropropane: bp 33-35°; ir 824 and 604 cm⁻¹; pmr (CDCl₃) (60 MHz) δ 1.99 (d, J = 19.0 Hz); pmr (acetone- d_6) (100 MHz) δ 1.85 (d, J = 19.0 Hz); ¹⁹F nmr (acetone- d_6) (100 MHz) δ 10.42 upfield from external CF₆CO₂H (septet, J = 19.0 Hz); mass spectrum (70 eV) m/e (rel intensity) 96 (0), 83 (7), 81 (20), 61 (100), 59 (11), 45 (13), 41 (36), 39 (15), 33 (7), 27 (6).

Registry No.-1, 420-44-0; 2-chloropropene, 557-98-2; hydrogen fluoride, 7664-39-3.

(8) J. Chapman and R. Roberts, U. S. Patent 2,495,407 (1950); Chem. Abstr., 44, P4020c (1950).