Dediazoniation of Arenediazonium Ions in Homogeneous Solution. 7.[1] On the Intermediacy of the Phenyl Cation

Robert G. Bergstrom, Robin G. M. Landells, George H. Wahl, Jr.,[2] and H. Zollinger*

Contribution from the Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule, CH-8006 Zürich, Switzerland. Received September 17, 1975

Abstract: The thermal decomposition (dediazoniation) of ^{15}N-labeled benzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol (TFE) proceeds with a significant accompanying amount (~8%) of isotopic rearrangement. When the reaction is conducted under 300 atm of unlabeled nitrogen, 2.46 ± 0.40% of "external" nitrogen is incorporated in the residual diazonium ion at 70% dediazoniation. Under 320 atm of carbon monoxide, a 5.2% yield of 2',2',2'-trifluoroethyl benzoate is obtained along with the "normal" products, fluorobenzene and 2',2',2'-trifluoroethyl phenyl ether. These results are interpreted in terms of a "molecular-ion" pair and a phenyl cation intermediate. The reverse step of the formation of the phenyl cation and N_2 is the first evidence for a reaction of nitrogen molecules with a purely organic reagent in solution. The relatively small influence of substituents (p-OCH_3, p-CH_3, p-NO_2) on the amount of isotopic rearrangement and exchange with external nitrogen indicates that these reactions are mechanistically of the same type as the solvolysis, namely additions of a nucleophile (N_2) to the phenyl cation.

The effect of structure on the stability of carbocations has been actively explored and is now generally understood. There is a great preference for a planar structure such that the "charge" resides in a vacant p orbital. This minimizes the interaction with the positively charged nucleus. Based on such reasoning it has long been felt that those carbocations in which the positive charge "resides" in an orbital of significant "s character" (e.g., sp^2 or sp) would be prohibitively unstable and thus nonobservable.

Within the last decade, convincing evidence for the intervention of vinyl cations (sp^2 carbocations) in solvolysis reactions has been assembled.[3,4] Similarly, only very recently has persuasive evidence for the intermediacy of the phenyl cation (I) in dediazoniation[5] been published.[6-11] In this paper we describe additional kinetic evidence for the intermediacy of I and for the reversibility of eq 1 during dediazoniation in

$$\text{(1)}$$
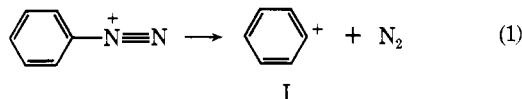
2,2,2-trifluoroethanol (TFE). TFE was chosen as a solvent since it is sufficiently polar to support ionic reactions yet almost non-nucleophilic. Considerable information is available on the characteristics of pure TFE and of TFE/H_2O mixtures.[12-14]

Experimental Section

Equipment Used. Uv, Beckman Acta III; ir, Beckman Acculab 4; NMR, Varian TL-60; MS, Hitachi-Perkin Elmer RMU-6; GLC, Varian Aerograph 1520.

Materials. Reagent grade (Fluka puriss.) 2,2,2-trifluoroethanol (TFE), trifluoroacetic acid (TFA), pyridine, and 2-naphthol were used without further purification. Sodium hydroxide and sulfuric acid solutions were prepared using Merck TITRISOL standard volumetric solutions. Phosphoric acid (85%, Fluka puriss.) was titrated with 1 N NaOH to a phenolphthalein end point. Aniline was treated with a small amount of zinc powder and vacuum distilled [~70 °C (20 mm)] in the absence of light. The first 10% of distillate was discarded, and the aniline was used within 48 h of distillation. p-Nitroaniline was recrystallized from ethanol/water (mp 146 °C). p-Methoxyaniline was recrystallized from charcoal/water (mp 57-58 °C). p-Methylaniline was recrystallized from water (mp 43.5-44.5 °C). Sodium 2-naphthol-3,6-disulfonic acid (R-Salt) was recrystallized twice from ethanol/water or from charcoal in water. Aqueous solutions of R-Salt[15] were prepared by dissolving 15 g in 1 l. of distilled water and adjusting the pH to approximately 9 by addition of $NaHCO_3$.

Trifluoroethyl Benzoate. This compound was prepared from TFE according to the method of Bourne et al.[16] The product was purified by vacuum distillation [bp 83 °C (19 mm)]: NMR (CCl_4) 4.55 (q,

2 H, CH_2, J = 8.5 Hz), δ 7.03-8.03 (m, 5 H, ArH); ir ν_{max} 3020, 1740, 1590, 1575, 1485, 1440, 1397, 1290, 1155, 1100, 1070, 1010, 970, 890 cm^{-1}.

Benzenediazonium-β-^{15}N tetrafluoroborate ($C_6H_5N^+\equiv{}^{15}N$ BF_4^-) was prepared according to the method of Starkey.[17] Fluoroboric acid (4 ml) was added to 0.69 ml (0.0073 mol) of aniline. The solution was cooled in an ice-salt bath, and 0.5 g (0.0073 mol) of $NaNO_2$ (99.2% nitrogen-15, Stohler Isotope Chemicals) in 1 ml of water was added slowly with vigorous stirring. The precipitate was collected by filtration and washed with cold fluoroboric acid, water, ethanol, and ether. The white powder was dried in vacuo at room temperature, recrystallized from acetonitrile/ether, and stored in the dark. The purity was determined by coupling with R-Salt and comparing the observed extinction coefficient at 490 nm with the literature value[15] (ϵ = 2.2 × 10^4). The [15]N p-nitro, p-methoxy, and p-methyl diazonium salts were prepared by the same method.

Aniline-2,4,6,N,N-d_5 was prepared according to the procedure of Best and Wilson.[18] Aniline hydrochloride (6.0 g, 0.046 mol) was dissolved in 30 ml of D_2O and refluxed under dry nitrogen for 24 h. The D_2O was removed by vacuum distillation and the procedure twice repeated with fresh D_2O. The solution was then neutralized with anhydrous Na_2CO_3 and extracted with three 15-ml portions of ether. After removal of the ether, a small amount of Zn powder was added and the aniline vacuum distilled [bp 65 °C (20 mm)]: NMR (CCl_4) δ 7.00 (s, ArH); ir ν_{max} 3415, 3030, 3010, 2980, 2600, 2540, 2490, 2440, 2260, 1830, 1570, 1450, 1390, 1355, 1290, 1235, 1160, 1075, 960, 918, 835, 680 cm^{-1}.

Benzenediazonium-β-^{15}N-2,4,6-d_3 tetrafluoroborate was prepared as described above using 0.69 ml of aniline-2,4,6,N,N-d_5.

Dediazoniation of Labeled Diazonium Salts. A typical dediazoniation[15] was carried out as follows. Approximately 300 mg of labeled benzenediazonium salt was dissolved with magnetic stirring in 20 ml of TFE in a jacketed three-neck reaction vessel thermostated at 30 ± 0.1 °C. Before addition of the salt, the TFE was deoxygenated using dry nitrogen. The reaction vessel was covered with aluminum foil to exclude light. A 0.3-ml sample of the solution was taken and quenched in R-Salt as soon as possible after addition of the salt. After the appropriate time for approximately 70% reaction (calculated from the first-order rate constant), another 0.3-ml aliquot was taken and quenched. These samples were used to determine the exact extent of reaction. The entire reaction solution was then quenched by pouring it into 25 ml of 1 N sodium hydroxide containing 0.3 g of 2-naphthol. The precipitated 1-phenylazo-2-naphthol was filtered and dried (mp 130 °C).

Reduction of 1-Phenylazo-2-naphthol. The azo dye was reduced to aniline and 1-amino-2-naphthol according to the procedure of Swan and Kelley.[19] Approximately 0.1 g of the red azo dye (obtained from the quenching reaction) was refluxed with 0.25 g sodium dithionite in a mixture of 3 ml of water, 7 ml of ethanol, and 0.1 ml of 40% sodium hydroxide solution until the color was discharged. Then a few drops of 1 N sodium hydroxide was added to bring the pH to about 8.5. The mixture was steam distilled and the aniline containing dis-

Table I. Isotopic Rearrangement of Substituted Benzenediazonium-β-^{15}N Tetrafluoroborate in the Dark

Conditions	Substituent	P (%)^a	k_r/k_s^{b}	$10^4 k_s$ (s^{-1})^c	$10^6 k_r$ (s^{-1})	N_{BS}^{d}	Y^d
H$_2$O, 30 °C	H	1.89	0.016	0.927	1.48	−0.26	3.493
70 wt% TFE, 30 °C	H	7.14	0.064	1.581	10.1	−1.09	1.66
85 wt% TFE, 30 °C	H	7.65	0.069	1.642	11.3	−1.83	1.35
97 wt% TFE, 30 °C	H	8.16	0.074	1.607	11.9	−2.59	1.15
TFE, 30 °C	H	7.96	0.072	1.590	11.4	−3.80	1.045
TFE, 5 °C	H	8.66	0.079	0.023	0.18		
TFE/1000 atm, N$_2$/25 °C^e	H	7.96	0.072	0.467	3.36		
TFE/pyridine,^{f} 30 °C	H	2.12	(0.018)	g			
TFE, 30 °C	2,4,6-D	6.41	0.057	1.078	6.14		
TFA, 30 °C	H	9.05	0.083	0.778	6.46	−5.55	4.529
1 M H$_2$SO$_4$, 35 °C	H	1.89	0.016	1.67	2.67		
85% H$_3$PO$_4$, 30 °C	H	9.45	0.087	0.524	4.56		
TFE, 64 °C	4-OCH$_3$	8.28	0.075	0.026	0.19		
TFE, 40 °C	4-CH$_3$	8.94	0.082	0.647	5.31		

^{a} Percent isotopic rearrangement adjusted to exactly 70% dediazoniation. ^{b} k_r/k_s = log $(1 - 2p)/2$ log (A/A_0); $p = P/100$; A = absorbance of azo dye obtained after 70% dediazoniation; A_0 = original azo dye absorbance (ref 24). The 95% confidence limits of k_r/k_s are ±8%. ^{c} Assumed equal to the rate of disappearance of diazonium salt. ^{d} Solvent nucleophilicity (N_{BS}) and ionizing power (Y); ref 12, 27, and 28; see also, D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970). ^{e} In a glass-lined autoclave. ^{f} 5 ml of pyridine/18.4 ml of TFE; see ref 30. ^{g} Not first-order kinetics.

tillate (60-100 ml) acidified (HCl). Subsequent removal of the solvent by rotary evaporation yielded the aniline hydrochloride, which was dissolved in a couple of drops of methanol and reprecipitated by addition of ether. The filtered hydrochloride was washed with three additional portions of ether. The usual yield was about 30 mg (~57%) of material (mp 195 °C). The *p*-methoxy and *p*-methyl azo dyes were reduced by the same procedure. The presence of the *p*-nitro group complicated the reduction of the respective azo dye as the nitro group was reduced too. The product could not be used for a reliable mass spectral analysis.

Mass Spectral Analysis of Aniline Hydrochloride. The aniline hydrochloride samples were analyzed directly by mass spectrometry for the nitrogen-15 content and not converted to nitrogen gas as is generally done for analysis of samples containing nitrogen-15.[20]

The fraction (p) of nitrogen-15 incorporated in a sample was calculated from the ratio of the peak heights at m/e 93 and 94 according to the following equation:

$$p = (f_x - f_0)/(1 + f_x - f_0)$$

In the equation, f_x equals the ratio of peak heights 94/93 after x% dediazoniation, f_0 equals the peak height ratio 94/93 for the reference aniline derived from the *same* labeled diazonium salt after 0% dediazoniation, and p is equal to the fraction of nitrogen-15 in the sample. Analysis of standard solutions containing as little as 2.5% nitrogen-15 aniline demonstrated the reliability of this procedure. The observed peak height ratio 94/93 for the reference compound is 0.0778 ± 0.004 which compares with the theoretical intensity ratio[20] of 0.0711. The presence of an M + 1 peak due to an ion-molecule reaction is seen to be small and constant. No correction for this effect was attempted.

The nitrogen-15 content of the azo dye, 1-phenylazo-2-naphthol, was determined in a similar manner as above. The intensity ratio of peak heights for m/e 248/249 was determined from the reference azo compound containing 99.2% $^{14}N=^{15}N$ and corrected to 100%. This ratio could then be compared with that for the azo dye derived from the *same* diazonium salt after 70% dediazoniation under high pressure of nitrogen-14. The fraction of nitrogen-15 [N(15)] incorporated in the sample can be calculated from the following equation:

$$N(15) = 1/(1 + f_x - f_0)$$

where f_x is equal to the peak height ratio 248/249 after x% dediazoniation and f_0 is the reference peak 248/249 for 0% dediazoniation of the *same* diazonium salt. Experimentally determined peak ratios for the azo reference compounds varied less than ±2%.

Mass spectral analyses of the substituted azo dyes proceeded similarly.

Experiments under High Pressure. All high-pressure experiments were carried out in a stainless steel autoclave equipped with a specially designed glass insert which allowed the reaction solution to be shaken continuously without contacting the metal surface during dediazo-

niation. Aliquots of the reaction solution were extracted and quenched in R-Salt before and after pressurization to determine the exact extent of reaction. Temperature control was difficult to maintain due to the nature of the apparatus and estimated to be ±2 °C. Thus first-order rate constants calculated contain large uncertainties. However, the ratio k_r/k_s is unaffected since it has been shown to depend very little on temperature. The time lag between initiation of dediazoniation and attainment of the final working pressure in the autoclave was about 10 min.

Dediazoniation under Carbon Monoxide. This experiment was performed exactly as above using unlabeled benzenediazonium tetrafluoroborate. The autoclave was pressurized to 320 atm with CO instead of N$_2$. GLC analysis indicated the presence of trifluoroethyl benzoate in addition to the normal reaction products (fluorobenzene and trifluoroethyl phenyl ether).[15] A 5-m column of 10% Apiezon L on Chromosorb W (80/100) at 150-200 °C with 30 ml/min He and a 4.8-m column of 10% silicon SE-30 on Aeropak 30 (70/80) at 200-220 °C with 30 ml/min He were used to separate the products. The benzoate was identified by addition of an authentic sample to the reaction mixture. For determination of yields, toluene was used as an internal standard. Standard solutions were prepared to determine the response factor for each compound. Yields were calculated by cutting out peaks and weighing. Two or three runs were made for each solution, and the reproducibility of areas was usually within ±2%.

It was noted that after the dediazoniation reaction under carbon monoxide was complete, the solution appeared red in contrast to the slight yellow color observed when reaction is carried out under nitrogen. Addition of small amounts of trifluoroethyl benzoate to a spent reaction solution (under nitrogen) generates the same red color.

Results

Isotopic Rearrangement. The results of our several experiments are collocated in Table I. The first point of interest is that our value of k_r/k_s for H$_2$O (line 1) corroborates that of Lewis[21] (0.014) and agrees exactly with the value (0.016) recently reported by Swain.[10] The consistency of the data argues strongly for the reliability of our novel direct mass spectrometric analysis procedure. All previously reported methods[10,20,21] involved tedious decomposition procedures and gas-handling techniques. Obviously under carefully controlled conditions the reproducibility of modern mass spectrometers can be very high.

Any doubts about the reality of isotopic nitrogen rearrangement,[22] if not removed by earlier work,[23,24] should now disappear, particularly since by varying the solvent, almost 10% rearrangement may be obtained at 70% dediazoniation.

We originally chose TFE as a solvent because of its low

Table II. Exchange of Para-Substituted β-N^{15} Diazonium Ions with External N_2 in TFE

Substituent	% dediazoniation	Conditions	$^{15}N={}^{14}N$ content of azo dye (%)
H	0	1 atm, air, 25 °C	99.20^a
H	70.4	1 atm, air, 25 °C	98.60 ± 0.44^b
H	73.2	20 atm, $^{14}N_2$, 25 °C	98.23 ± 0.48^b
H	69.9	300 atm, $^{14}N_2$, 25 °C	96.23 ± 0.47^b
H	70.1	300 atm, $^{14}N_2$, 25 °C	96.99 ± 0.26^b
H	72.5	300 atm, $^{14}N_2$, 25 °C	96.89 ± 0.27^b
H	62.5	1000 atm, $^{14}N_2$, 25 °C	94.71 ± 0.43^b
H	0	1 atm, air, RT	99.40^a
H	56.0	300 atm, $^{14}N_2$, 23.0 °C	97.42 ± 0.24^b
H	65.0	300 atm, $^{14}N_2$, 24.5 °C	96.32 ± 0.59^b
H	0	1 atm, air, RT	99.31 ± 0.42^b
H	80.0	315 atm, $^{14}N_2$, 40.0 °C	97.60 ± 0.15^b
NO$_2$	0	1 atm, air, RT	99.33^a
NO$_2$	62.1	325 atm, $^{14}N_2$, 40.0 °C	97.98 ± 0.30^b
NO$_2$	0	1 atm, air, RT	99.28^a
NO$_2$	65.4	315 atm, $^{14}N_2$, 64.0 °C	98.33 ± 0.23^b
OCH$_3$	0	1 atm, air, RT	98.87^a
OCH$_3$	67.3	310 atm, $^{14}N_2$, 64.0 °C	97.55 ± 0.44^b

^{a} Reference standard. ^{b} 95% confidence limits.

nucleophilicity[12-14,25,26] and ability to dissolve ionic solutes. We were pleasantly surprised to find that TFE also produced better than a fourfold increase in k_r/k_s. This result is not simply attributable to decreased solvent nucleophilicity since the dediazoniation reaction (k_s) is actually 1.5 times faster in the less nucleophilic TFE than in water. However, the rearrangement rate (k_r) increases almost eightfold on passing from water to TFE. When the data for trifluoroacetic acid is included along with that for H$_2$O, TFE, and their several binary mixtures, no correlation with solvent nucleophilicity (N_{BS})[12,27,28] or ionizing power (Y) is apparent. In pure TFE there is no significant change in k_r/k_s on changing the temperature by 25 °C or upon increasing the pressure from 1 to 1000 atm of N$_2$. The rearrangement measurements with substituted benzenediazonium ions had to be made at higher temperatures due to their lower rate of dediazoniation. The ratios k_r/k_s with the p-methoxy and the p-methyl derivative are not significantly different from those found with the unsubstituted diazonium ion.

The relative independence of k_r/k_s in pure TFE on temperature and pressure changes and on substituents in the aromatic nucleus is consistent with a common rate-limiting intermediate or transition state for both dediazoniation and rearrangement. The significant decrease in both k_r and k_s on increasing pressure suggests an intermediate or transition state in which the phenyl–nitrogen bond is considerably stretched if not completely broken.[29]

An apparent discrepancy exists in the results on the influence of substituents in the N$_\alpha$,N$_\beta$-rearrangement *in water* as measured by Lewis and Holliday.[23] They found the following values for k_r/k_s: no substituent, 0.014; m-CH$_3$, 0.018; p-Cl, 0.023; p-CH$_3$, 0.031; p-OCH$_3$, 0.038. Lewis and Holliday also demonstrated, however, that there is a linear relationship between log k_r and log k_s (see their Figure 1). The only difference between the rearrangement in water and in TFE seems to be that in water the correlation between log k_r and log k_s has a slope which is slightly lower than 1 (0.93), whereas the respective slope of the measurements in TFE does not seem to be significantly different from 1.[30]

When the dediazoniation is conducted in a mixture of TFE and pyridine, conditions which have been shown to produce radical derived products,[31] the percent rearrangement decreases markedly, and first-order kinetics are no longer observed.

The marked retardation of dediazoniation and rearrangement on substituting deuterium in the 2, 4, and 6 positions of benzenediazonium tetrafluoroborate is consistent with a highly electron-deficient intermediate or transition state for the two processes.[9]

The weakly nucleophilic TFA and the highly viscous 85% H$_3$PO$_4$[32] solvents produced the greatest ratios of k_r/k_s. That this is not due to their great acidity is indicated by the low k_r/k_s value found in 1 M H$_2$SO$_4$.

Reaction with External Nitrogen. If dediazoniation in TFE proceeds via a free or weakly complexed phenyl cation, such an intermediate would be expected to be highly reactive. Perhaps the ultimate test would be reaction with molecular nitrogen—a nonpolar molecule of unusually high bond strength often used in organic chemistry as an "inert" atmosphere. Our results along these lines are listed in Table II.

Using benzenediazonium tetrafluoroborate labeled with ^{15}N in the β nitrogen, dediazoniation was allowed to proceed to 70% completion in a glass-lined autoclave under various pressures of nitrogen of normal isotopic abundance ($\sim$0.4% ^{15}N). As the pressure is increased, increasing amounts of ^{15}N are lost from the "unreacted" diazonium salt. This finding is completely consistent with the intermediacy of a free phenyl cation which reacts almost indiscriminately.

On the basis of the experiments reported here it seems that there is no appreciable temperature effect on the amount of exchange with external nitrogen.

As in the investigation of the N$_\alpha$,N$_\beta$-rearrangement of the diazonium group, substitution of the aromatic nucleus has little influence on the amount of exchange, indicating again that a common intermediate is able to react by the same mechanism with a nitrogen molecule or a TFE molecule.

The average of 15 separate mass spectrometric determinations from three independent experiments at 25 °C and 300 atm of nitrogen give an average value of 2.46 $\pm$ 0.40% "external" nitrogen incorporation at 70% dediazoniation.

Reaction with Carbon Monoxide. Another compelling demonstration of the intermediacy of a phenyl cation or similar species[33] is found in our experiment under 320 atm of carbon monoxide. Along with the normal products (fluorobenzene and 2,2,2-trifluoroethyl phenyl ether), a 5.2% yield of 2,2,2-trifluoroethyl benzoate was found. This result is in contrast to experiments in water[34] where, at lower pressures of CO (700 psi, 47.6 atm), no benzoic acid was found.

Discussion

Our experiments demonstrate that two new reactions take place during dediazoniation of arenediazonium tetrafluoroborates in TFE in addition to the expected substitution of the diazonium group by the solvent (trifluoroethoxydediazoniation in Bunnett's[35] systematic nomenclature of reactions) and by fluoride ions (fluorodediazoniation). These new reactions are the displacement of the diazonium group by external nitrogen molecules and by carbon monoxide.

In addition, the rearrangement of the two nitrogen atoms of the diazonium group, found first by Lewis et al. in 1963 for dediazoniations in water,[21,23,24,36] becomes more significant by a factor of 3 to 4 in solvents like TFE, TFA, and 85% H_3PO_4.

As indicated already in the Results section, all data are explainable by postulating a common intermediate or transition state for all five reactions (solvolysis, fluorination, nitrogen exchange, N_α,N_β rearrangement, and carbonylation). It is highly electron deficient and has an almost or completely broken C–N bond.

Intermediates like the spirodiazirine cation II or a bimolecular displacement are not consistent with our data.
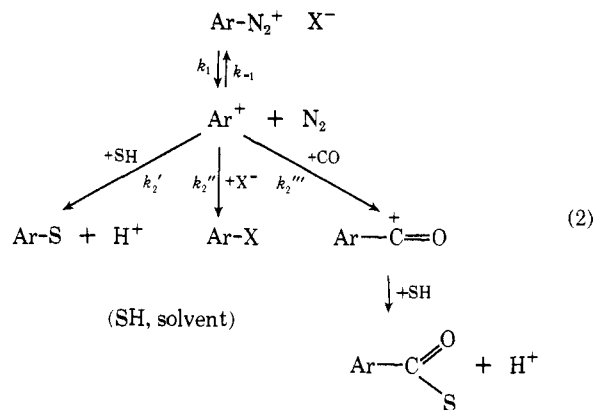
$$N\!\!=\!\!N$$

II

The very large negative volume of activation for hydrolysis of arenediazonium ions ($\Delta V_s^\ddagger = -10.0$ cm^3/mol at 29.3 °C in water)[29] and the considerable nitrogen isotope effect recently observed in water[10] both argue strongly against a spiro intermediate. Since $\Delta V_s^\ddagger$ for solvolysis is of similar magnitude in TFE (-11.4 cm^3/mol at 25 °C),[37] and since k_r/k_s is unchanged or increasing the external nitrogen pressure from 1 to 1000 atm (indicating that $\Delta V_s^\ddagger \approx \Delta V_r^\ddagger$), it is likely that such an intermediate as II is not involved in the N_α,N_β rearrangement process as well.

The strongly decreased percentage of N_α,N_β rearrangement in TFE/pyridine mixtures argues strongly against a homolytic rearrangement, as radical reactions were found to be predominant in that system.[31]

In part VI of this series[13] we demonstrated that a mechanism in which TFE and water enter the rate-determining part of the reaction *as nucleophiles* is not consistent with the experimental data for dediazoniation in TFE/H$_2$O mixtures. Swain et al.[8-11] also provided strong evidence against a bimolecular displacement. Additional evidence for the N_α,N_β rearrangement comes from Table I. The extent of isotopic rearrangement is almost unchanged on passing from pure TFE to 85 wt% TFE (1:1 mole ratio of TFE:H$_2$O). It seems therefore to be reasonable to explain our finding with a rate-limiting formation of the free phenyl cation and competitive additions of this highly electrophilic reagent to the solvent, to the gegenion,[11] to the β atom of the nitrogen molecule split off in the dediazoniation, and in particular to external nitrogen molecules or to carbon monoxide if present.

Most significant in our results is the evidence for the reversibility of the rate-determining part of the dediazoniation of arenediazonium ions. This is, to our knowledge, the first example of the reaction of nitrogen molecules with a purely organic reagent in solution.[38]

Although an S$_N$1 mechanism with competing (parallel) additions of the free phenyl cation to the various nucleophiles (eq 2) after the rate-limiting step coincides with all qualitative results of our investigation, it does not explain all data on the basis of the phenyl cation being the only steady-state intermediate. The arguments for (2) being a much too simplified

$$
\begin{array}{c}
\text{Ar–N}_2{}^+ \quad \text{X}^- \\
k_1 \big\downarrow\big\uparrow k_{-1} \\
\text{Ar}^+ \ + \ \text{N}_2 \\
\end{array}
$$

(SH, solvent)

$$
\text{Ar–S} + \text{H}^+ \qquad \text{Ar–X} \qquad \text{Ar–}\overset{+}{\text{C}}\!\!=\!\!\text{O}
$$

(2)

$$
\text{Ar–C}\overset{\displaystyle O}{\underset{\displaystyle S}{\diagdown}} + \text{H}^+
$$

mechanism are the following. (1) If the reverse first step (rate constant k_{-1}) is the same for the N_α,N_β rearrangement and the exchange with external nitrogen, one expects a decreased ratio k_r/k_s for the reaction under high pressure of external nitrogen $^{14}N_2$. This is, however, not the case (Table I, experiment at 1000 atm N$_2$). (2) On the basis of the rate equation

$$
\text{rate} = [\text{ArN}_2{}^+]
$$

$$
\times \frac{k_1(k_2'[\text{SH}] + k_2''[\text{X}^-] + k_2'''[\text{CO}])}{k_{-1}[\text{N}_2] + k_2'[\text{SH}] + k_2''[\text{X}^-] + k_2'''[\text{CO}]}
\quad (3)
$$

for mechanism 2, an initial linear increase of exchange with external nitrogen as the pressure of nitrogen is increased would be expected. At very high nitrogen pressures a more than linear increase of exchange is expected.[39] Inspection of the exchange results demonstrates, however, that the ^{15}N–^{14}N content of the azo dye formed decreases about 2.5% from 1 atm (air) to 300 atm of N$_2$, but only another 1.7% by increasing the pressure from 300 to 1000 atm of N$_2$. On the basis of eq 3, one expects a decrease of about 5% or more for that second range of pressure increase provided that Henry's law is obeyed.

There is, however, no doubt that external nitrogen has not only a purely physical effect (pressure), but also a chemical influence. Dediazoniations under 300 atm of argon are *faster* than those under 300 atm of nitrogen (but not as fast as under atmospheric conditions).[37] This demonstrates again the reversibility of the first step.

All these detailed problems are still under investigation. At the present time, we suspect, as indicated in our preliminary communication,[7] that the rate-determining part of heterolytic dediazoniations does not go directly to the phenyl cation but through a molecule–ion pair of a phenyl cation and molecular nitrogen in which the nitrogen has lost its axial dissymmetry and may be "entropically activated".

The fact that the nitrogen exchange and the carbonylation reactions have been detected, up to now, only in TFE and that the N_α,N_β-rearrangement is more dominant in TFE than in water can be explained by the observation[41] that TFE is a generally poor solvating species for cations. In water, the diazonium ion is well solvated, and the reaction is slow. Once the process of splitting the C–N bond begins, the aryl cation benefits much more from solvation than does the molcule–ion pair; isotopic rearrangement is therefore low. In TFE, the diazonium salt is poorly solvated and thus reacts faster. The phenyl cation is not appreciably stabilized and so the molecule–ion pair has a relatively longer lifetime allowing significantly more rearrangement. The slightly different relationship between N_α,N_β-rearrangement and solvolysis in water and in TFE as a function of substituent effects may indicate that the rate-limiting transition state of the rearrangement in water is somewhat earlier (less dependent on phenyl cation substituent effects) than that of the hydrolysis. The practically nonexistent

influence of substituents on k_r/k_s in TFE indicates identical transition states for both reactions in that solvent.

References and Notes
(1) Paper VI: P. Burri, G. H. Wahl, Jr., and H. Zollinger, *Helv. Chim. Acta*, **57**, 2099 (1974).
(2) On leave from the Department of Chemistry, North Carolina State University, Raleigh, N.C. 27607.
(3) An excellent review: L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, **52**, 80 (1975).
(4) Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, **97**, 836 (1975).
(5) H. Zollinger, *Acc. Chem. Res.*, **6**, 335 (1973).
(6) C. G. Swain, J. E. Sheats, D. G. Gorenstein, K. G. Harbison, and R. J. Rogers, *Tetrahedron Lett.*, 2973 (1974).
(7) R. G. Bergstrom, G. H. Wahl, Jr., and H. Zollinger, *Tetrahedron Lett.*, 2975 (1974).
(8) C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Am. Chem. Soc.*, **97**, 783 (1975).
(9) C. G. Swain, J. E. Sheats, D. G. Gorenstein, and K. G. Harbison, *J. Am. Chem. Soc.*, **97**, 791 (1975).
(10) C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Am. Chem. Soc.*, **97**, 796 (1975).
(11) C. G. Swain and R. J. Rogers, *J. Am. Chem. Soc.*, **97**, 799 (1975).
(12) D. J. Raber, M. D. Dukes, and J. Gregory, *Tetrahedron Lett.*, 667 (1974).
(13) P. Burri, G. H. Wahl, Jr., and H. Zollinger, *Helv. Chim. Acta*, **57**, 2099 (1974).
(14) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Am. Chem. Soc.*, **91**, 4838 (1969).
(15) P. Burri and H. Zollinger, *Helv. Chim. Acta*, **56**, 2204 (1973).
(16) E. J. Bourne, M. Stacey, J. C. Tatlow, and R. Worrall, *J. Chem. Soc.*, 3268 (1958).
(17) E. B. Starkey, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 225.
(18) A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 28 (1938).
(19) G. A. Swan and P. Kelley, *J. Chem. Soc.*, 416 (1954).
(20) R. M. Caprioli in "Biochemical Applications of Mass Spectrometry", G. R. Waller, Ed., Wiley-Interscience, New York, N.Y., 1972, p 735, Chapter 27.
(21) E. S. Lewis and J. M. Insole, *J. Am. Chem. Soc.*, **88**, 5043 (1966).
(22) A. K. Bose and I. Kugajevsky, *J. Am. Chem. Soc.*, **88**, 2325 (1966).
(23) E. S. Lewis and R. E. Holliday, *J. Am. Chem. Soc.*, **91**, 426 (1969).
(24) E. S. Lewis and P. G. Kotcher, *Tetrahedron*, **25**, 4873 (1969).
(25) W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968).
(26) M. D. Bentley and J. A. Lacadie, *Tetrahedron Lett.*, 741 (1971).
(27) P. E. Peterson and F. J. Waller, *J. Am. Chem. Soc.*, **94**, 991 (1972).
(28) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 992 (1972).
(29) K. R. Brower, *J. Am. Chem. Soc.*, **82**, 4535 (1960).
(30) This conclusion is justified by the fact that the measurements with benzenediazonium ions at 5 and 30 °C do not show a significant influence of temperature. These k_r/k_s values are therefore comparable with those of the *p*-methyl and the *p*-methoxy compound which were measured at 40 and 64 °C, respectively.
(31) P. Burri, H. Loewenschuss, H. Zollinger, and G. K. Zwolinski, *Helv. Chim. Acta*, **57**, 395 (1974).
(32) We thank Professor E. S. Lewis for suggesting that we try this solvent.
(33) H. Hogeveen, *Adv. Phys. Org. Chem.*, **10**, 29 (1973).
(34) E. S. Lewis and J. M. Insole, *J. Am. Chem. Soc.*, **86**, 32 (1964).
(35) J. F. Bunnett, *J. Chem. Soc.*, 4717 (1954).
(36) J. M. Insole and E. S. Lewis, *J. Am. Chem. Soc.*, **85**, 122 (1963); **86**, 32, 24 (1964).
(37) R. G. M. Landells and H. Zollinger, to be submitted for publication.
(38) C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, **41**, 3504 (1964), demonstrated that the photolysis of CH_2N_2 in *solid* N_2 produces CH_2 which subsequently reacts with the N_2 matrix.
(39) This statement is based on the assumption that Henry's law is obeyed. Data on the solubility of N_2 in TFE at various pressures are not yet available. In ethanol, the concentration of N_2 is proportional to pressure.[40] However, even at pressures of 100–200 atm there is a general tendency for the solubility to increase less rapidly than called for by a straight-line relationship.
(40) P. K. Frohlich, E. J. Tauch, J. J. Hogan, and A. A. Peer, *Ind. Eng. Chem.*, **23**, 548 (1931).
(41) D. F. Evans, J. A. Nadas, and M. A. Matesich, *J. Phys. Chem.*, **75**, 1708 (1971).

Synthesis of β-Acylacrylic Esters and α,β-Butenolides via β-Keto Sulfoxide Alkylation

Paul A. Bartlett

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received September 3, 1975

Abstract: Alkylation of the anions derived from (methylsulfinyl)methyl ketones (**1**) with methyl bromoacetate proceeds readily to afford the 3-(methylsulfinyl)-4-oxobutanoates (**2**). These intermediates are converted to the corresponding unsaturated keto esters (**3**) in excellent overall yield (Table I) by thermal elimination of methylsulfenic acid. Alternatively, the γ-substituted-α,β-butenolides (**5**) are obtained on sodium borohydride reduction of the alkylated intermediates (**2**), followed by lactonization and loss of CH_3SOH. These sequences have been applied to aliphatic and aromatic β-keto sulfoxides and used to prepare the isocardenolide 3β-acetoxy-20-hydroxy-21-nor-5,22-choladien-24-oic acid γ-lactone in excellent yield. The relative configurations of the diastereomeric intermediates **2** have been deduced from their thermal stabilities, and the absolute configurations of the diastereomeric steroidal sulfoxides **1c** have been determined from their circular dichroism spectra.

We have embarked on a program directed toward the synthesis of medium- and large-ring natural products. Several of these compounds incorporate a γ-oxidized α,β-unsaturated lactone moiety,[1] and we sought an efficient method for the construction of this functional array. While a variety of methods are available for the synthesis of β-acylacrylic esters,[2] none appeared to meet our needs of simplicity and efficiency. Many routes involve condensation steps which are capricious or low-yield reactions, or which require relatively inaccessible starting materials. The most generally efficient synthesis of β-acylacrylates is that of Bestmann,[2d] using an alkylation-elimination sequence involving stabilized phosphoranes. This method, however, requires relatively vigorous conditions and a twofold excess of the ylide component.

The sulfinyl group has received attention in organic synthesis by virtue of its ability to stabilize carbanions[3] and to function as an alkene precursor.[3f-i,4] The anions derived from α-sulfinyl ketones and esters may be alkylated under favorable conditions,[3] and, on heating, sulfoxides with hydrogens in the β position which can adopt a syn conformation readily eliminate a sulfenic acid with introduction of a double bond.[3f-i,4] Trost has recently taken advantage of these properties for the synthesis of α,β-unsaturated esters[3i,k] and other conjugated alkenes.[3j] α-Sulfinyl carbonyl compounds are accessible by a variety of methods, including oxidation of the corresponding sulfides,[3f,4] enolate sulfinylation,[5a,b] and sulfinyl anion acylation.[3b,5c-e] In view of the ready availability of β-keto sulfoxides from the corresponding carboxylic esters,[3b,5c-e] the pos-