

showed no change (infrared) after 5 hr., extensive rearrangement to 2-chloroethyl carbamate after 45 hr., and complete rearrangement after 6 days. There was no rearrangement after 6 days at 0°. IX appears as clear cylindrical rods under a binocular scope and becomes studded with flat prisms as rearrangement proceeds.

2-Imino-5,5-dimethyl-1,3-dioxane Hydrochloride (III).—The reaction was run at 0° as for IX using 50.0 g. (0.48 mole) of recrystallized neopentyl glycol and 30.8 g. (0.50 mole) of cyanogen chloride in 150 ml. of reagent grade chloroform, 0.284 M in hydrogen chloride. Solids were present within 1 hr. The product, collected the following morning, amounted to 54.9 g. (69.2%) of colorless solids after washing with chloroform and ether and vacuum drying. A sample in acetic acid was filtered, reprecipitated with benzene, and washed with ether for analyses, m.p. 135.5° (partial with capillary immersed at 132°, some non-melt at 270°); $\lambda_{\text{max}}^{\text{Nujol}}$ 2800–3300 (broad) and 1520 assigned to $=\text{NH}_2^+$, 1690 cm^{-1} ($\text{C}=\text{N}$).

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{ClNO}_2$: C, 43.5; H, 7.3; N, 8.5; Cl, 21.4. Found: C, 43.4, 43.4; H, 7.5, 7.6; N, 8.5, 8.7; Cl, 21.5, 21.6.

At a temperature of 100°, III showed little change after 15 min., an estimated 23% conversion to 2,2-dimethyl-3-chloropropylcarbamate after 36 min., and essentially complete conversion after 58 min. (as estimated by disappearance of a strong infrared band at 1110 and appearance of a new band at 1080 cm^{-1}). II, run simultaneously, was completely rearranged to 2-chloroethyl thiolcarbamate after 15 min. at 100°, the first point checked.

A sample of the rearranged product of III, recrystallized from hexane (colorless plates), vacuum sublimed at 70° (0.1 mm.), and melted at 79.0–80.4°; $\lambda_{\text{max}}^{\text{Nujol}}$ 3400, 1680, 1605 cm^{-1} (all CONH_2).

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{ClNO}_2$ (2,2-dimethyl-3-chloropropyl carbamate): C, 43.5; H, 7.3; Cl, 21.4. Found: C, 43.4, 43.8; H, 6.7, 7.2; Cl, 21.0.

Dimethyldithioimidocarbonate Hydrochloride (VII).—Addition of hydrogen chloride to about equal amounts of methyl mercaptan and methyl isothiocyanate in chloroform at 0° afforded an 87% yield of the colorless crystalline hydrochloride, m.p. 158–159° dec. A vacuum-sublimed sample, m.p. 160.5–161.5°, was analyzed. The free base and the hydroiodide have been reported.²⁵

Anal. Calcd. for $\text{C}_3\text{H}_8\text{ClNS}_2$: Cl, 22.5. Found: Cl, 22.2 (ionic).

Acknowledgment.—The author wishes to acknowledge the helpful unpublished work on some reactions of cyanogen chloride by Dr. B. Abramovitch. Thanks are extended to Dr. S. D. Levy and Mr. R. W. Baer for material aid, to Dr. R. J. Magee for helpful suggestions and support, and to Mr. R. S. Wayne and Mr. N. B. Colthup for assistance in the interpretation and assignment of infrared spectra.

(25) M. Delépine, *Bull. soc. chim. France*, [3]29, 58 (1902).

The Reaction of Primary and Secondary Alkylaryl and Alkyl Sulfonates with Potassium *t*-Butoxide in Dimethyl Sulfoxide¹

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Received September 3, 1963

Sulfonate esters of primary and secondary alcohols react rapidly with potassium *t*-butoxide in dimethyl sulfoxide to give alkenes and alkyl *t*-butyl ethers. The reaction is complete within 30 min. at 20–25° for 0.5 M solutions of the ester. Esters of cyclic and secondary acyclic alcohols give about 80% yields of alkenes and no appreciable quantities of ethers. Esters of normal primary alcohols and of cyclohexylcarbinol give 20–25% alkenes and 60–70% ethers. Esters of primary alcohols containing α -alkyl substituents give 20–30% alkenes and 30–40% ethers. *n*-Octyl benzenesulfonate, *p*-tosylate, and *p*-brosylate give essentially identical yields. Although the *p*-nitrobenzenesulfonate gives exceptionally low yields of alkene and ether, the ether/alkene ratio for the series is nearly constant.

Dimethyl sulfoxide has been used widely as a solvent to facilitate base-promoted reactions.² Cyclohexyl and 1-octyl benzenesulfonates have been shown to react rapidly with potassium *t*-butoxide in this solvent at room temperature to give, respectively, cyclohexene (83%, gas chromatography), and a mixture of 1-octene (24%, g.c.) and octyl *t*-butyl ether (67%, g.c.).³ Because of the potential synthetic importance of this facile reaction, the effects of structural variations in both the alkyl and sulfonate moieties upon the reaction products have been examined.

In the previous study³ it was shown that a maximum yield of cyclohexene was obtained after 30 min. stirring at 20–25° of a solution 0.5 M in cyclohexyl benzenesulfonate and 1.0 M in potassium *t*-butoxide. Although decreases in alkoxide stoichiometry produced significant decreases in the yield of cyclohexene, a reaction time of only 10 min. still yielded 74% alkene.

In the present study, therefore, a reaction time of 30 min. at 20–25° was used with solutions 0.5 M in ester and 1.0 M in alkoxide.

In Table I are presented the results of variations in the alkyl moiety of the benzenesulfonates. To examine effects of variations in the leaving group on relative and absolute yields, a number of sulfonates of 1-octanol and 1-hexanol were investigated and the results are presented in Table II. Each run was duplicated.

With the following exceptions, all alkenes were identified by boiling points, refractive indices, and g.c. comparison with authentic samples. 2-Methyl-1-butene was identified by g.c. comparison with an authentic sample; 2-ethyl-1-butene and 2-ethyl-1-hexene were identified by g.c. relative retention times.

Octyl *t*-butyl ether was identified by its boiling point, refractive index, chromatographic behavior, and infrared spectrum.³ Hexyl *t*-butyl ether was identified similarly, with an elemental analysis also (see Experimental). Cyclohexylcarbinyl *t*-butyl ether was identified by g.c. comparison with material prepared by a Williamson synthesis. All other ethers were identified by relative g.c. retention times.

(1) Presented before the Organic Division at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

(2) C. Walling and L. Bollyky, *J. Org. Chem.*, **28**, 256 (1963), is a recent example.

(3) C. H. Snyder, *Chem. Ind. (London)*, 121 (1963).

TABLE I

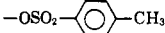
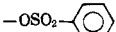
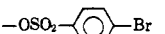
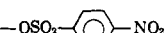
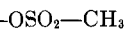
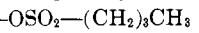
PRODUCTS OF THE REACTION OF ALKYL BENZENESULFONATES WITH POTASSIUM *t*-BUTOXIDE IN DIMETHYL SULFOXIDE AT 20–25°

Parent alcohol	Alkene obtained	% yield alkene		% yield alkyl <i>t</i> -butyl ether, g.c.
		g.c.	(distn.)	
Cyclohexanol	Cyclohexene	83	(37)	Trace
Cyclopentanol	Cyclopentene	76 ^a	(48)	None observed
<i>l</i> -Menthol ^b	Δ^2 -Menthene		(26) ^c	None observed
	Δ^3 -Menthene		(24) ^c	
2-Octanol	1-Octene	51	(50)	Trace
	2-Octenes	28		
1-Octanol	1-Octene	24	(16)	67 (46, distn.)
1-Hexanol	1-Hexene	20	(11)	69 (27, distn.)
2-Methyl-1-butanol	2-Methyl-1-butene	22		39
2-Ethyl-1-butanol	2-Ethyl-1-butene	27, 28 ^d		40, 39 ^d
		27 ^e		40 ^e
2-Ethyl-1-hexanol	2-Ethyl-1-hexene	22, 24 ^d		36, 43 ^d
Cyclohexylcarbinol	Methylene cyclohexane	26, 26 ^d		60, 60 ^d

^a G.c. analysis on a Dow 710 silicone column. ^b Run as solution 0.33 *M* in ester and 0.67 *M* in alkoxide because of ester insolubility. ^c 50% on distillation. Isomeric ratio determined by product racemization [H. R. Nace, *J. Am. Chem. Soc.*, **81**, 5428 (1959)]. ^d Duplicate experiments. ^e 1-hr. reaction time.

TABLE II

EFFECT OF LEAVING GROUP ON REACTIONS OF 1-HEXYL AND 1-OCTYL SULFONATES^a

Leaving group	% 1-alkene, g.c.	% alkyl <i>t</i> -butyl ether
	20, ^b 16.3 ^{c,d}	67, ^b 49 ^{c,d}
	20, ^b 24 ^c	69, ^b 67 ^c
	20, ^c 17.7 ^c	76, ^c 66 ^c
	8.2, ^c 1.97 ^c	29, ^c 7.7 ^c
	12.5, ^b 12.8 ^b	33, ^b 34 ^b
	20, ^b 20 ^b	46, ^b 46 ^b

^a All runs are duplicate. ^b 1-Hexene and hexyl *t*-butyl ether from 1-hexyl sulfonates. ^c 1-Octene and octyl *t*-butyl ether from 1-octyl sulfonates. ^d 1-Octyl tosylate decomposed partially during purification, *n*_D²⁰ 1.5020; N. Kornblum, *et al.*, *J. Am. Chem. Soc.*, **78**, 1497 (1956), give a value of 1.4946.

Pyrolytic and solvolytic generation of alkenes were ruled out. All esters were demonstrated to be either insoluble in the extraction solvents used in isolation procedures or, if soluble, to undergo no pyrolysis to alkenes when injected as 1 *M* solutions under conditions of the g.c. analysis (injector block temperatures were maintained at 85–90°). Attempted solvolysis of cyclohexyl benzenesulfonate under the conditions used in this study, but in the absence of alkoxide, produced 0.75% cyclohexene. Further, no alkenes were obtained on similar attempted solvolyses of 1-hexyl benzenesulfonate and 1-octyl *p*-bromo- and *p*-nitrobenzenesulfonates. While no attempt was made to recover unchanged hexyl benzenesulfonate, over 90% of the *p*-bromo and *p*-nitro esters was recovered from attempted solvolyses. Finally, accuracy of the isolation and analytical procedures was indicated by a 93% recovery of cyclohexene and 90% recoveries of 1-octene and octyl *t*-butyl ether from synthetic reaction mixtures. No reported yields were corrected for these small losses.

The results presented in Table I indicate that benzenesulfonates of secondary alcohols can be converted to corresponding alkenes in yields of about 80% by treatment of the ester with potassium *t*-butoxide in dimethyl sulfoxide for 30 min. at room temperature. Alkene yields from esters of primary alcohols are

lower (20–30%), presumably because of competing ether formation. α -Alkyl substitution does not affect alkene yields significantly although ether yields are lowered appreciably, except in the case of the cyclohexylcarbinyl ester. This decrease may be due to a steric retardation of covalent bond formation between the carbinyl carbon and the alkoxide oxygen. Incorporation of the substituent in a ring, as in the case of the cyclohexylcarbinyl ester, may decrease its effective bulk in the bimolecular transition state. Finally it is noted that over-all yields range from 58% (2-ethyl-1-hexyl benzenesulfonate) to 83% (cyclohexyl benzenesulfonate). The fate of the remainder of the ester is not known now.

In Table II is presented a summary of the effects of the leaving group on the reaction products. A survey of the results obtained with arylsulfonates suggests an approximately constant ether/alkene ratio, even in the cases of impure starting material (*p*-methyl) and extraordinarily low yields (*p*-nitro). Since it was demonstrated that both 1-octene and octyl *t*-butyl ether survive reaction, isolation, and analysis conditions to give 90% recovery of each with no evidence of interconversion, the observed ether/alkene ratios must be due to the kinetic product control.

To estimate quantitatively the sensitivity of the product ratio to the electrical nature of the leaving group, the product ratios for the arylsulfonates in Table II were subjected to a treatment analogous to the Hammett treatment for rate constant ratios. In the relationship

$$\log \left(\frac{\% \text{ substitution}}{\% \text{ elimination}} \right) = k\sigma$$

k represents the sensitivity of the product ratio to the *para* substituent in the leaving group. In terms of the Hammett equation *k* would represent (ρ substitution – ρ elimination) if rate constants, rather than yield ratios, were used. A least squares treatment of the data in Table III gives *k* = +0.083 with a probable error of ± 0.029 . The small, positive value of *k* would indicate a small increase in the substitution/elimination ratio with increasing electron withdrawal by the departing group. This is in contrast to the slight decrease observed in the second-order reaction of 2-

TABLE III
 SUBSTITUTION/ELIMINATION RATIO AS A FUNCTION OF σ

<i>para</i> substituent	σ^a	% ether/ % alkene	log % ether/ % alkene
-CH ₃	-0.170	3.35	0.525
		3.01	0.479
-H	0.000	3.45	0.538
		2.79	0.446
-Br	+0.232	3.80	0.580
		3.73	0.572
-NO ₂	+0.778	3.55	0.550
		3.90	0.591

^a H. H. Jaffe, *Chem. Rev.*, **53**, 222 (1953).

pentyl arenesulfonates with sodium ethoxide in ethanol.⁴ The mechanism of the reaction is being investigated.

The exceptionally low yields obtained with the *p*-nitro ester require comment. The low yields are evidently not due to incomplete reaction: in one run 5% of the ester was recovered from the reaction mixture and another 5%, undissolved, from the addition funnel. The fate of the majority of the ester is not known now. Although excessive foaming of the reaction mixture during isolation suggests alkyl sulfonate formation by a nucleophilic aromatic displacement of the sulfonate moiety, *g.c.* examination of both ligroin and benzene extracts of the aqueous phase (see Experimental) for 1 hr. at 200° failed to reveal any significant peak attributable to *p*-nitrophenyl *t*-butyl ether.

Finally, a comparison of this reaction with other preparative eliminations is in order. Reported procedures include the classic method of solvolysis by prolonged reflux of aryl sulfonates, generally in alcohols,⁵ reaction with alkoxide in diglyme at 120–140° for several hours,⁶ solvolysis in dimethyl sulfoxide at 90–95° for several hours,⁷ and solvolysis of the parent alcohol in dimethyl sulfoxide for 9–16 hr. at 160–185°.⁸ Nace has reported that solvolysis of aryl sulfonates of primary alcohols gives no alkenes, while Traynelis reported solvolyses of secondary and tertiary benzylic, and tertiary aliphatic alcohols only.

In our investigations we compared the alkoxide-sulfoxide technique to base-alcohol and alcoholysis techniques. It is notable that results reported in Table IV involve conditions more rigorous in alkali stoichiometry, reaction time, and/or temperature than those used in the alkoxide-sulfoxide technique.

TABLE IV

YIELD OF CYCLOHEXENE FROM REACTION OF 0.5 *M* CYCLOHEXYL BENZENESULFONATE WITH 1.5 *M* BASE FOR 1 HR.

Solvent	Base	Temp., °C.	% cyclohexene, <i>g.c.</i>
Ethanol	NaOEt	20–25	3
Ethanol	NaOH	20–25	3
Ethanol	None	Reflux	22
Methanol	NaOMe	20–25	1
Methanol	NaOH	20–25	1
Methanol	None	Reflux	12

(4) A. K. Colter and R. D. Johnson, *J. Am. Chem. Soc.*, **84**, 3289 (1962).

(5) W. Hueckel, *Ann.*, **477**, 99 (1930), and subsequent papers.

(6) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961), and a personal communication.

(7) H. R. Nace, *ibid.*, **81**, 5428 (1959); H. R. Nace and J. J. Monagle, *J. Org. Chem.*, **24**, 1792 (1959).

(8) V. J. Traynelis, *et al.*, *ibid.*, **27**, 2377 (1962).

The reaction described here may find use in conversions of temperature sensitive, but alkoxide insensitive (at 20–25°), sulfonate esters of secondary alcohols to alkenes. It may find more limited use with primary alcohols because of low yields and competing ether formation. Finally, the reaction should be useful for the preparation of *t*-butyl ethers of primary alcohols. A study of the reaction is continuing.

Experimental

Materials.—Potassium *t*-butoxide was obtained from M.S.A. Corp.; dimethyl sulfoxide was J. T. Baker reagent grade. Both materials were used as received. Because potassium *t*-butoxide is rapidly hydrolyzed to the alcohol and potassium hydroxide, which is essentially insoluble in dimethyl sulfoxide at 20–25°, preparation of a 2 *M* solution of the alkoxide in dimethyl sulfoxide was considered a sufficient criterion of reagent purities for this work.

Esters were prepared by the usual pyridine technique.⁹ Esters not previously reported or insufficiently described were characterized by elemental analysis or saponification equivalent, as shown in Table V.

 TABLE V
 ESTER CHARACTERIZATION

Ester	M.p., °C.	Elemental analyses, %			
		Calcd.		Found	
		C	H	C	H
1-Octyl <i>p</i> -nitrobenzenesulfonate	70.5–71.9	53.31	6.71	53.13	6.63
				52.99	6.74
1-Octyl <i>p</i> -bromobenzenesulfonate	32.7–34.0	48.14	6.06	47.83	5.81
Cyclohexylmethyl benzenesulfonate	52.0–54.0	61.39	7.13	61.33	6.81
				61.36	6.87
		Sapon. equiv.			
		Calcd.		Found	
2-Methyl-1-butyl benzenesulfonate		228		227	
2-Ethyl-1-butyl benzenesulfonate		242		240	
2-Ethyl-1-hexyl benzenesulfonate		270		279	

Analyses.—Analyses were performed on a 10-ft. 20% Carbowax 20M on 60/80-mesh Chromasorb column in an Aerograph A-90-P gas chromatograph. Yields were determined by comparison of reaction extracts with standard solutions of alkene and ether, either prepared independently, obtained commercially, or isolated from the reaction mixture. For the 2-methyl-1-butyl, 2-ethyl-1-butyl, and 2-ethyl-1-hexyl benzenesulfonates, 2-methyl-1-butene was used as an external standard; thermal conductivity ratios for product alkenes and ethers were assumed equal to molecular weight ratios. This approach was shown to be valid by the data in Table VI for related alkenes and ethers.

TABLE VI

COMPARISON OF MOLECULAR WEIGHT AND THERMAL CONDUCTIVITY RATIOS FOR RELATED ETHERS AND ALKENES

Ether/alkene	Mol. wt. ratio	Thermal cond. ratio
<i>n</i> -Octyl <i>t</i> -butyl ether/ 1-octene	1.66	1.62
<i>n</i> -Hexyl <i>t</i> -butyl ether/ 1-hexene	1.88	1.95

Illustrative Reaction.—A solution of 12.16 g. (0.0500 mole) of freshly distilled 1-hexyl benzenesulfonate, n_D^{25} 1.4944, lit.¹⁰ n_D^{25} 1.4952, in 50 ml. of dimethyl sulfoxide was added with stirring to a solution of 11.2 g. (0.100 mole) of potassium *t*-butoxide in 50 ml. of dimethyl sulfoxide. The reaction vessel was a 300-ml. three-necked flask equipped with an addition funnel, a thermometer, a condenser, and a magnetic stirring bar. The reaction was protected only against atmospheric moisture by a calcium

(9) C. D. Nenitzescu, *et al.*, *Ber.*, **90**, 589 (1957).

(10) F. L. M. Pattison and J. E. Mallington, *Can. J. Chem.*, **34**, 757 (1956); B. L. Emling, *J. Am. Chem. Soc.*, **74**, 4702 (1952).

chloride drying tube fitted to the condenser. A mildly exothermic reaction was observed throughout the 10-min. addition (but not after completion of addition) and an ice bath was used to maintain a reaction temperature of 20–25°. The mixture was stirred for 30 min. at this temperature after completion of addition.

n-Heptane (15 ml.) was added to the reaction mixture which was stirred an additional minute, and then was poured into 150–200 ml. of ice-water in a separatory funnel. The hydrocarbon phase was separated and the aqueous phase was extracted with several 5–10-ml. portions of *n*-heptane until the combined organic extracts totaled nearly 25 ml. These were washed with 10-ml. portions of brine and dried over calcium chloride. The volume of the dried extracts was brought to 25 ml. in a volumetric flask by addition of *n*-heptane.

Analysis of the combined extracts by g.c. as described above revealed 20% 1-hexene and an additional, larger peak of longer retention time. Solvent removal and distillation at 768 mm. gave 0.250 g. of 1-hexene, b.p. 64.5–66.5°, n_D^{25} 1.3838; and a second fraction which was redistilled to give 0.217 g. of 1-hexene (total yield 11%), b.p. 65.0–67.0°, n_D^{25} 1.3849, lit.¹¹ b.p. 63.5°, n_D^{25} 1.3850. Continued distillation gave 2.13 g. (27%) of hexyl *t*-butyl ether, b.p. 167.0–168.0°. Redistillation gave a series of

homogeneous fractions, b.p. 167.5–168.0°, n_D^{20} 1.4080.¹² The infrared spectrum essentially was identical with that reported⁹ for 1-octyl *t*-butyl ether.

Anal. Calcd. for C₁₀H₂₂O: C, 75.88; H, 14.01. Found: C, 76.23; H, 14.02.

This ether was shown to be chromatographically identical with the large peak in the extracts' chromatogram. Comparison of a standard solution of the ether with one of 1-hexene indicated a 69% yield of the ether.

Acknowledgment.—This research was supported by a University of Miami National Science Foundation Institutional Grant. We wish to thank M.S.A. Corporation for a generous supply of potassium *t*-butoxide.

(11) F. D. Rossini *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p. 55.

(12) The refractive index reported for octyl *t*-butyl ether in ref. 3 is n_D^{20} 1.4170. A subsequent preparation and extensive purification gave a material with n_D^{20} 1.4184. S. O. Lawesson and N. C. Yang [*J. Am. Chem. Soc.*, **81**, 4230 (1959)] report n_D^{20} 1.4190.

Dehydration of N-(*p*-Chlorophenyl)phthalamic Acid by Acetic and Trifluoroacetic Anhydrides¹

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Received July 22, 1963

In the dehydration of N-(*p*-chlorophenyl)phthalamic acid by acetic anhydride, the major path for formation of imide does not involve the isoimide as an intermediate.

Dehydration of N-substituted phthalamic and maleamic acids by acetic anhydride yields imides, whereas dehydration by trifluoroacetic anhydride yields isoimides.^{3,4} One hypothesis, first suggested by Cotter, *et al.*,⁴ to account for this marked difference in the action of two similar reagents is that the isoimide is the initial product of dehydration with both reagents. The isoimide is stable and hence is isolated under the conditions used with trifluoroacetic anhydride (equivalent amount in dioxane at room temperature) but is isomerized to imide under the more vigorous conditions used with acetic anhydride (large excess, serving as solvent as well as dehydrating agent, in the presence of acetate ion at 70–80°). There is considerable evidence that isoimides can be isomerized to imides, although there are discrepancies in the conditions reported as necessary for isomerization.^{4–13} Furthermore, de-

hydration of certain maleamic acids by acetic anhydride recently has been reported to yield isoimides.^{5,6} The report of Kretov, *et al.*,⁶ that dehydration of N-substituted maleamic acids with acetic anhydride and sodium acetate gave isoimides when the reaction time was 2 min. but imides when the reaction time was 30 min., is most indicative of isomerization of initially formed isoimides, although these workers did not suggest this explanation.

It was, therefore, desirable to compare the products from the action of acetic and trifluoroacetic anhydrides under comparable conditions and to show that isoimides could be isomerized under the conditions in which imides are the major products. These studies were performed by treating N-(*p*-chlorophenyl)phthalamic acid¹⁴ with 2 equiv. of the dehydrating agent in dioxane at 35 and 65° for various lengths of time. The per cent yield of dehydration product was obtained from the weight of the product after removal of unchanged amic acid, and the composition of the product was determined spectrophotometrically, the data being reproducible to ±5%. It should be emphasized that the data were obtained with only one amic acid and that as a consequence the conclusions of this study may not apply to all amic acids.

The results of dehydration in dioxane, summarized in Table I, show that under comparable conditions acetic and trifluoroacetic anhydrides do not give the same product ratios (compare expt. 1 and 7). At the higher

(1) Partial support of this work by a Frederick Gardner Cottrell grant from the Research Corporation is gratefully acknowledged. Presented in part at the Southeast-Southwest Regional Meeting of the American Chemical Society, New Orleans, La., 1961.

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(3) W. R. Roderick and P. L. Bhatia, *J. Org. Chem.*, **28**, 2018 (1963).

(4) R. J. Cotter, C. K. Sauers, and J. M. Whelan, *ibid.*, **26**, 10 (1961).

(5) T. L. Fletcher and H. L. Pan, *ibid.*, **26**, 2037 (1961).

(6) A. E. Kretov, N. E. Kul'chitskaya, and A. F. Mal'nev, *J. Gen. Chem. USSR*, **31**, 2415 (1961).

(7) S. Hoogewerff and W. A. van Dorp, *Rec. trav. chim.*, **13**, 12 (1893); **13**, 93 (1894).

(8) P. H. van der Meulen, *ibid.*, **15**, 282 (1896).

(9) R. Pummerer and G. Dorfmueller, *Ber.*, **45**, 292 (1912).

(10) M. L. Sherill, F. L. Schaeffer, and E. P. Shoyer, *J. Am. Chem. Soc.*, **50**, 474 (1928).

(11) C. K. Sauers and R. J. Cotter, U. S. Patent 2,980,694 (1961); *Chem. Abstr.*, **55**, 19,868 (1961).

(12) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 98 (1957).

(13) The colors often observed on dehydration of N-aryl amic acids by heating either alone or with acetic anhydride also suggest the intermediacy of isoimides.

(14) This amic acid was selected because it could be purified, because it undergoes negligible thermal dehydration at 65°, and because the corresponding isoimide is relatively stable toward hydrolysis.