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°, $n^{25}\mathrm{D}$ 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°, $n^{25}\mathrm{D}$ 1.3849, lit.[11] b.p. 63.5°, $n^{25}\mathrm{D}$ 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°, $n^{20}\mathrm{D}$ 1.4080.[12] The infrared spectrum essentially was identical with that reported[3] for 1-octyl *t*-butyl ether.

Anal. Calcd. for $C_{10}H_{22}O$: 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.

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(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 $n^{20}\mathrm{D}$ 1.4170. A subsequent preparation and extensive purification gave a material with $n^{20}\mathrm{D}$ 1.4184. S. O. Lawesson and N. C. Yang [*J. Am. Chem. Soc.*, **81**, 4230 (1959)] report $n^{20}\mathrm{D}$ 1.4190.

Dehydration of N-(*p*-Chlorophenyl)phthalamic Acid by Acetic and Trifluoroacetic Anhydrides[1]

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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, dehydration 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 acid[14] 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

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[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).

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[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.

TABLE I

VARIATION IN PRODUCT DURING DEHYDRATION OF N-(p-CHLOROPHENYL)PHTHALAMIC ACID IN DIOXANE

Expt. no.	Amic acid, M	$(CH_3CO)_2O$, M	CH_3COONa, M	$(CF_3CO)_2O$, M	Temp., °C.	Time, sec.	% yield of product	% isoimide in product	$t_{0.5}$, sec.
1	0.25	0.53			35	1000	10	8	5400
						2600	26	12	
						4000	38	15	
						7500	49	20	
2	0.25	0.53	0.001		35	1000	18	11	3700
						2600	34	18	
						4000	54	26	
3	0.17	3.5			35	1000	41	13	1300
						2600	71	19	
						4200	75	22	
4	0.17	3.5	0.006		35	1000	92	39	<300
						2600	88	36	
						4200	86	41	
5	0.50	1.1			65	300	14	13	2000
						1000	33	28	
						2100	53	42	
						4000	63	47	
6	0.50	1.1	0.001		65	300	40	25	500
						1000	70	49	
						2100	79	51	
						4000	78	52	
7	0.25			0.53	35	10	39	79	15
						20	58	86	
						100	81	80	
						300	82	87	

temperatures using acetic anhydride the per cent of isoimide was greater rather than less (expt. 5 *vs.* 1 and 6 *vs.* 2), and the effect of added acetate was to increase rather than decrease the per cent of isoimide (expt. 2 *vs.* 1, 4 *vs.* 3, 6 *vs.* 5). The only support for the hypothesis in question is the demonstration that acetic anhydride does form appreciable amounts of isoimide. If imide arises only by isomerization of isoimide, the per cent of isoimide in the product should decrease or pass through a maximum as the reaction proceeds, whereas, if imide and isoimide arise *via* separate pathways, the per cent of isoimide should be constant, assuming that both reactions are of the same kinetic order. With acetic anhydride the ratio of isoimide to imide does indeed vary as the reaction proceeds, but it *increases* rather than decreases. No variation was observed with trifluoroacetic anhydride.

In fact, the data suggest the initial formation of imide and subsequent partial isomerization to isoimide; however, treatment of imide under these conditions caused no detectable isomerization. The isoimide similarly was unaffected by acetic anhydride in dioxane with or without acetate *in the concentrations employed in the dehydrations;* larger amounts of acetate did cause isomerization. When acetic acid, which is formed during the dehydration, was present, a slow isomerization occurred, but it was insufficient to account for the formation of imide: in 2000 sec. at 65° only 5% isomerization of pure isoimide occurred, whereas, in the dehydration of amic acid, 50% imide was formed. Thus, although isomerization of isoimide to imide does occur, the formation of imide for the most part must not proceed through an intermediate isoimide.

The failure to obtain greater amounts of imide at the higher temperature and in the presence of sodium acetate raised the question of how imides are obtained in dehydrations by acetic anhydride when no other solvent is present. Accordingly, experiments using acetic anhydride as reagent and solvent also were performed (Table II). The per cent of isoimide formed in the absence of acetate was still appreciable, but with added acetate ion—the condition normally used for the synthesis of imides—the product was almost exclusively imide. Furthermore, when the isoimide was treated under these same conditions, there was isomerization to imide, the rate of isomerization being greater in the presence of acetate. However, the data clearly demonstrate that the rate of dehydration of amic acid to imide greatly exceeds the rate of isomerization of isoimide. Thus, in the presence of acetate at 65° dehydration of amic acid is essentially complete in 200 sec. and the product is 90% imide; yet the half-time for isomerization of isoimide is approximately 2300 sec. Thus, as in dioxane, there must be at least two pathways for formation of imide: one not involving the isoimide as an intermediate and accounting for the formation of most of the imide, and a minor one involving isomerization of isoimide. In the absence of added acetate the per cent of isoimide in the dehydration product passes through a maximum, consistent with part of the imide being formed by isomerization of isoimide.

Experiments with acetic anhydride as reagent and solvent at 35° were not carried out owing to the low solubility of the amic acid. The reaction of the amic acid with the same ratio of acetic anhydride to amic acid as was present when acetic anhydride was the solvent was carried out at 35° in dioxane (Table I, expt. 3 and 4); the results were similar to those obtained in dioxane with only 2 equiv. of acetic anhydride. Experiments with trifluoroacetic anhydride at 65° were not carried out because of the rapid rate of dehydration by this reagent and because of its low boiling point. It is interesting, though the significance is not clear, that injection of trifluoroacetic anhydride into a solution of

TABLE II

VARIATION IN PRODUCT DURING DEHYDRATION OF N-(*p*-CHLOROPHENYL)PHTHALAMIC ACID AND ISOMERIZATION OF N-(*p*-CHLOROPHENYL)PHTHALISOIMIDE IN ACETIC ANHYDRIDE,[a] 65°

Expt. no.	Amic acid, *M*	Isoimide, *M*	CH_3COONa, *M*	Time, sec.	% yield of product	% isoimide in product	$t_{0.5}$, sec.
1	0.14			200	50	28	200
				600	64	21	
				1200	66	37	
				3000	71	50	
				6000	69	40	
				72,000	75	27	
2	0.17		0.018	200	86	10	<200
				600	94	7	
				1200	91	5	
				3000	87	4	
				72,000	86	0	
3		0.17		200	79	94	>100,000
				600	79	95	
				1200	75	96	
				5000	75	97	
				10,000	77	93	
				72,000	82	74	
4		0.17	0.018	200	79	87	2300
				600	79	82	
				1200	88	68	
				3000	95	38	
				72,000	100	0	

[a] Containing 1% of acetic acid.

the amic acid in dioxane preheated to 65° resulted in the formation in low (20%) yield of a dehydration product that was 100% imide.

An approximation of the relative rates of dehydration under the various conditions studied can be obtained from the half-times for reactions included in Tables I and II. The values are approximate owing to the lack of precision in determining the per cent of reaction by isolation of product.

In summary, dehydration of N-(*p*-chlorophenyl)-phthalamic acid by acetic and trifluoroacetic anhydrides gives rise to both imide and isoimide in all instances, the relative amounts being greatly dependent on reaction conditions. Although there is much evidence to suggest that the dehydration of amic acids to imides proceeds through intermediate isoimides, quantitative data indicate that this path is a minor one for this amic acid.

Experimental

Procedure for the Determination of Isoimide and Imide in Product of Dehydration or Isomerization.—One mmole of N-(*p*-chlorophenyl)phthalamic acid[10] and 2 to 4 ml. of reagent grade dioxane were placed in a test tube fitted with an inner $\overline{\mathsf{T}}$ ground joint. The test tube was placed in the side neck of a 3-l. round-bottom flask in which anhydrous ether (b.p. 34.6°) or anhydrous methanol (b.p. 64.7°) was refluxed so that the tubes were heated by the vapors. The acetic and trifluoroacetic anhydrides were injected with a syringe into the heated solution of amic acid. When acetic anhydride was used as solvent as well as dehydrating agent, the amic acid was powdered to facilitate solution and added to the preheated acetic anhydride. The reaction mixture was quenched by pouring it into cold sodium bicarbonate solution, which also removed unchanged amic acid. The insoluble solid, which contained only imide and isoimide as shown by infrared spectrum, was collected, washed with water, and dried in air. The per cent yield of dehydration product was determined by the weight of the isolated product. The optical absorption of solutions of the products in dioxane was measured at 300 and at 330 mμ, and the concentrations of imide and isoimide were calculated by means of simultaneous equations[15] using the extinction coefficients of pure N-(*p*-chlorophenyl)phthalimide (ϵ_{300} 1378, ϵ_{330} 277) and N-(*p*-chlorophenyl)phthalisoimide (ϵ_{300} 7120, ϵ_{330} 10,910). Isomerization studies on imide[10] and isoimide[3] were carried out in the same manner using these compounds in place of the amic acid. When a solution of amic acid in dioxane without dehydrating agent was maintained at 65° for 7500 sec., the longest reaction time used in dioxane, no dehydration product could be isolated; the isolation procedure should have detected 5% of imide and/or isoimide.

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(15) H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," 2nd Ed., D. Van Nostrand Co., Inc., Princeton, N. J., 1951, p. 8.