The Dipole Moment and Structure of the Imide Group. IV. Aromatic Imides: Phthalimide and Naphthalimide, Comparison of Dipole Moments of Imides and Anhydrides

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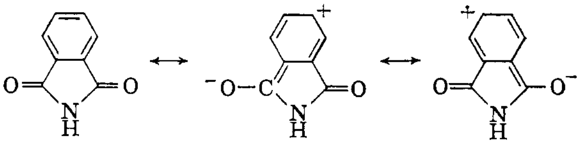
The dipole moments of the aromatic imides phthalimide I and naphthalimide II were measured in dioxane at 30°. I has a moment of 2.91 D and II a moment of 4.73 D; both moments are higher than the nonaromatic imides succinimide III, 1.47 D, and glutarimide IV, 2.58 D. The higher moment of the aromatic compared with the nonaromatic cyclic imide is due to the increased opportunity for resonance in the aromatic compound. Ultraviolet spectra confirm this. The greater increase, 2.15 D, in the moment of II over IV than the moment of I over II, 1.44 D, is due to an extra resonance form possible in II, position of the plus-minus dipoles in II and easier fusion of the imide group to naphthalene than to benzene. Comparison of the dipole moments of aromatic and nonaromatic cyclic imides and cyclic anhydrides shows the five-membered ring compounds have lower moments than six-membered compounds, aromatic compounds have higher moments than nonaromatic compounds, and anhydrides have higher moments than imides. Explanations for the above data are presented. Infrared spectra and dipole calculations show there is less resonance in anhydrides than in imides.

In the preceding papers in this series, we have discussed the dipole moments of five- and six-membered cyclic imides,[1] semicyclic imides (*N*-acetyl and *N*-benzoyl lactams),[2] and straight chain imides.[3]

The dipole moment of phthalimide I, a cyclic imide fused to a benzene ring, was measured in dioxane at 20° in 1936.[4,5] The value reported, 2.10 D, is higher than that for succinimide which has a moment of 1.47 D in dioxane at 30° (Cowley and Partington reported a value of 1.54 D, 1.74 D revised, for succinimide in dioxane at 20°).[4] The higher moment of the aromatic imide is expected to result from the additional resonance (a↔b↔c) possible with the benzene ring:



The dipole moment of cyclohexane 1,2-imide in dioxane at 30° is 2.24 D.[1] The higher moment is probably due to the additional inductive effect of the cyclohexane ring and to skewing of the angles of the imide group by being attached to the chair form of cyclohexane. It would seem that the moment for phthalimide obtained in 1936 is too low. Partington made theoretical calculations of the moment and obtained a value of 4.2 D[5]; he suggested that resonance might explain the anomaly. It seemed worthwhile, therefore, to remeasure and recalculate the moment of phthalimide.

The dipole moment of naphthalimide II, a six-membered imide attached to the naphthalene ring, was determined for the first time. Comparison of the dipole moments of the aromatic and nonaromatic imides, and infrared and ultraviolet spectra, indicates that there is considerable resonance in aromatic imides.

Results and Discussion

The dipole moments of phthalimide and naphthalimide are given in Table I; the moments of succinimide and glutarimide previously determined[1] are also given.

The dipole moment of phthalimide 2.91 D is about 0.8 D higher than that reported in 1936.[4] Our α or $d\epsilon_{12}/d\omega_2$ where ϵ_{12} is the dielectric constant of the solution of weight fraction ω_2 is 7.12 (Table IV) while the α calculated from Partington's data[4] (least squares) is 7.23. The published P_{20} value is 133.7 cc., while our value is 207.5 cc. It seemed peculiar that the two α's would be so similar, and the P_{20}'s so different. We recalculated the P_{20} from Partington's data and got a value of 198.21 cc. Partington used a value of 40.4 cc. for the P_E, while we calculated from bond refractions[6] a value of 37.3. (Popov and Holm[7] recently obtained from refractive indices a P_E of 40.0 cc. for a cyclic imide bemegride (3-ethyl-3-methylglutarimide), while calculations from bond refractions[6] gave a value of 40.3). The recalculated moment from Partington's data is 2.89 D which is close to our value of 2.91 D.

The moment of the imide group fused to the benzene ring is 1.44 D higher than the cyclic imide suc-

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[1] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4586 (1961).

[2] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **84**, 565 (1962).

[3] C. M. Lee and W. D. Kumler, *ibid.*, **84**, 571 (1962).

[4] E. G. Cowley and J. R. Partington, *J. Chem. Soc.*, 47 (1936).

[5] J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. V, London, Longmans Green, 1954, pp. 530–533.

[6] A. J. Vogel, W. T. Cresswell G. J. Jeffery, and J. Leicester, *Chem. Ind.*, 358 (1950).

[7] A. I. Popov and R. D. Holm, *J. Phys. Chem.*, **65**, 774 (1961).

TABLE I

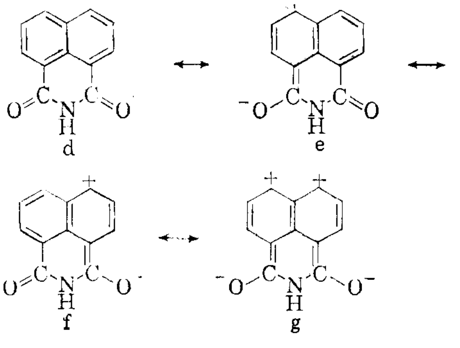
DIPOLE MOMENTS OF IMIDES AND ANHYDRIDES IN DIOXANE AT 30°

I.	Phthalimide	2.91 D	II.	Naphthalimide	4.73 D
III.	Succinimide	1.47 D	IV.	Glutarimide	2.58 D
	Difference	1.44 D			2.15 D
V.	Phthalic anhydride (Benzene 30°)	5.27 D	VI.	Naphthalic anhydride (Benzene 20°)	6.45 D
VII.	Succinic anhydride	4.22 D	VIII.	Glutaric anhydride	5.31 D
	Difference	1.05 D			1.14 D
IX.	Cyclohexane 1,3-anhydride	4.97 D			

cinimide and 0.73 D higher than cyclohexane 1,2-imide which is as anticipated.

The dipole moment of naphthalimide II, 4.73 D, is 2.15 D higher than glutarimide, 2.58 D. A comparison of the moments of the four imides in Table I reveals that five-membered cyclic imides have lower moments than six-membered cyclic imides. This has been previously explained[1] as being caused by two factors. In the five-membered ring as compared with the six-membered ring, the angle between the two carbonyl groups is greater (about 154° compared to about 120°) because of the smaller ring angles in the five-membered ring compound. Additionally, in the six-membered ring compound the two carbonyl groups and the nitrogen are on a straight line; the N^+O^- dipoles cancel; in the five-membered ring, the resultant of the N^+O^- dipoles is directed away from the carbonyl resultant because of the more acute ring angle. There is a smaller amount of resonance in five-membered ring imides as contrasted to six-membered ring imides which would tend to decrease the moment of the five-membered ring compounds. The higher carbonyl frequencies in the five-membered ring compounds as shown in the next section is evidence of the smaller amount of resonance.

The higher moments of the aromatic imides are probably due in part to the additional resonance a ↔b↔c. Naphthalimide has an additional resonance form g which would cause its moment to be higher than that of phthalimide. Stuart-Briegleb models indicate there is more ring strain in phthalimide than in succinimide and considerably more than in naphthalimide.



Infrared and Ultraviolet Spectra of Aromatic Imides.—The infrared carbonyl frequencies for imides shown in Table II are as follows:

TABLE II

INFRARED CARBONYL FREQUENCIES OF IMIDES AND ANHYDRIDES CM.$^{-1}$

Glutaric imide	1695	Glutaric anhydride	1781
	1661 sh.		1739
Succinic imide	1770	Succinic anhydride	1852
	1689		1776
Acetic imide	1734	Acetic anhydride	1822
	1700		1758
Cyclohexane 1,3-imide	1701	Cyclohexane 1,3-anhydride	1802
			1770

The results indicate that there is more single bond character (lower frequency) in the carbonyl groups of succinimide than in phthalimide and in glutarimide than in naphthalimide.

The ultraviolet spectrum of benzene[8] (Table III) shows two strong peaks at 184 mμ and 202 mμ with several low intensity bands around 250 mμ. The increased resonance possible in naphthalene is indicated by the intense band at a lower frequency (220 mμ) than benzene and the strong band at 275 mμ.

Succinimide, glutarimide, and their *N*-methyl derivatives all show moderate bands between 190 and 210 mμ.[1]

In 1907, Hartley and Hedley[9] published some early work on the absorption spectra of phthalimide. Our study gives the following ultraviolet spectrum in ethanol:

Phthalimide		Naphthalimide	
λ_{max}	ϵ	λ_{max}	ϵ
217	40,500	214	20,500
230	16,600	232	48,100
238	10,700		
292	1,900	333	12,800
298	1,870	342	12,400

The peak due to imide resonance which was found at 190–210 mμ in succinimide, and other imides, has been moved to lower frequencies and higher extinction. There are also new bands for phthalimide and naphthalimide around 295 mμ and 340 mμ, respectively. Naphthalimide has a bright yellow color, while phthalimide is tan; both suc-

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[8] M. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* (London), **A152**, 299 (1935); **A158**, 634 (1937).

[9] W. N. Hartley and E. P. Hedley, *J. Chem. Soc.*, **91**, 314 (1907).

TABLE III

ULTRAVIOLET SPECTRA OF AROMATIC RINGS AND IMIDES

	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
Benzene[8]	184	48,000	202	6,800	255	230		
Naphthalene[8]			220	112,000	275	5600	312	250
Succinimide[1]			194?	12,000				
N-Methylsuccinimide[1]			204	13,000	42	110		
Glutarimide[1]			204	14,700				
N-Methylglutarimide[1]			210	15,600				

cinimide and glutarimide are white. These results indicate that there is increased conjugation in both phthalimide and still more in naphthalimide.

Comparison of the Dipole Moments of Imides and Anhydrides.—It is of interest to compare the dipole moments of cyclic and aromatic imides with their respective anhydrides (Table I). Rau and Anantanarayanan[10] measured the dipole moments of phthalic and succinic anhydride and Coomber and Partington[5] measured the moments of phthalic and naphthalic anhydride and discussed the theoretical calculation of moments of the two compounds. We have measured the moment of glutaric anhydride VIII in dioxane at 30°.

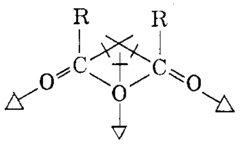
The anhydrides behave like the imides in that the five-membered ring compounds have lower moments than the six-membered ring compounds and the aromatic anhydrides have higher moments than the alicyclic anhydrides. The explanations given for the imides would apply also to the anhydrides.

In all four sets of data the anhydrides have the higher moment. The difference between the nonaromatic imides and anhydrides (VII and III, VIII and IV) is about 2.7 D in each case. There is less difference between aromatic imides and aromatic anhydrides, 2.4 D in the case of phthalimide and phthalic anhydride and 1.7 D in the case of naphthalimide and naphthalic anhydride.

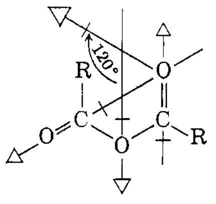
The dipole moment of the straight chain, acetic anhydride, has been reported[11] to be 2.7–2.8 D from 47°–267° and Piekara and Piekara[12] reported a value of 2.87 D at 25° in carbon disulfide. More recently, Ekelund[13] gave the moment of acetic anhydride in the following solvents at 20°: benzene, 3.15 D; pentane, 3.15 D; hexane, 3.12 D.

Oesper and Smyth[14] have pointed out that cyclic acid anhydrides have higher moments than similar alicyclic anhydrides because "their major dipoles are forced by the rings to point more nearly in the same direction."

We have previously calculated[1] and shown[2] that the dipole moments of imides in the *cis-cis* conformation would be greater than the dipole moment of imides in the *cis-trans* conformation. The situation is different with anhydrides where we are concerned with only two resultants: the carbonyl resultant and the C—O—C resultant. If we take all angles to be 120°, then the resultant of the two carbonyl groups will be equal to one carbonyl bond moment and parallel to the resultant of the ether (C—O—C) resultant. In the *cis-cis* conformation, both resultants add up and the moment would be expected to be high.



cis-cis



cis-trans

In the *cis-trans* conformation, the ether resultant and the carbonyl resultant are 120° from each other so the moment of the *cis-trans* conformation would be predicted to be less than the *cis-cis* conformation. The moment μ may be calculated from the following equation:

$$\mu^2 = (C - E\cdot\cos 60^0)^2 + C\cdot\sin 60^0)^2$$

where C is the carbonyl resultant and E is the ether resultant. Use of bond moments is risky as resonance, inductive, and ring effects are operative, but if one assumes the following bond moments (and all angles 120°): C—C, 0 D; C=O, 2.8 D (moment of acetone and cyclohexanone); C—O—C 1.2 D. (ethyl and *n*-propyl ether); one calculates the following:

Conformation	Compound	Actual moment	Predicted moment
cis-cis	Glutaric anhydride	5.3 D	4.0 D
cis-trans	Acetic anhydride	3.1 D	3.0 D

The moment of acetic anhydride in the *cis-trans* conformation is about that predicted and is lower than the moment of the anhydride in the *cis-cis* conformation as predicted. The moment of the six-membered cyclic anhydride, however, is higher than forecast. Ekelund[13] has suggested from dipole data and experimental relaxation times that the acetic anhydride molecule is not rigid but that there is rotation of the acetyl groups around the central oxygen atom. This would indicate that there is less resonance in anhydrides than in imides:

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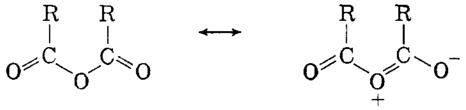
[10] G. Rau and N. Anantanarayanan, *Proc. Indian Acad. Sci.*, **5A**, 185–192 (1937).

[11] C. T. Zahn, *Physik Z.*, **34**, 461 (1933).

[12] A. Piekara and H. Piekara, *Compt. rend.*, **198**, 1018 (1934).

[13] B. Ekelund, *Acta Acad. Aboensis, Math et Phy.*, **19**, 1–93 (1954).

[14] P. F. Oesper and C. P. Smyth, *J. Am. Chem. Soc.*, **64**, 769 (1942).

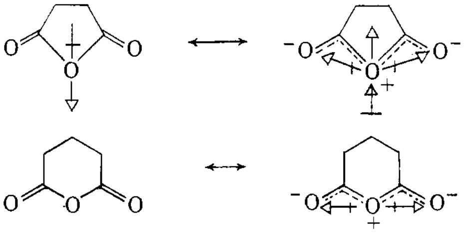


The nitrogen atom would be more likely to assume a positive charge than the oxygen atom, so one might predict less resonance in anhydrides. There is a greater amount of resonance in γ-pyridone than in γ-pyrone.[4]

Infrared carbonyl frequencies of anhydrides and imides (Table II) show that there is more double bond character (hence less resonance) in anhydrides than in corresponding imides.

As in acetic anhydride, the loss of resonance permits the carbonyl groups to rotate around the ether oxygen permitting the molecule to be in more flexible and stable conformations. This allows a more acute angle between the carbonyl groups as the two groups are not in one plane and would increase the carbonyl resultant over that in the coplanar imide molecule.

Rau and Anantanarayanan[10] suggested that the high dipole moments of phthalic and succinic anhydrides compared to phthalimide and succinimide were due to resonance which "reverses the normal direction of moment to be expected from vectoral addition." They postulated an excited moment of 5.9 D for succinic anhydride. This explanation is very improbable. It implies more resonance in anhydrides than in imides while the carbonyl frequencies indicate just the opposite. If the moment direction is reversed, the reversal will be less in glutaric anhydride where the dipoles from the separation of charge are nearly opposed and so the resultant moment would be expected to be less, but the opposite is the case, as glutaric anhydride has a higher moment than does succinic anhydride. There is no evidence for a large amount of resonance in cyclic anhydrides and the normal vector addition of the moments is adequate to account for their values.



Another factor in cyclic anhydrides comes into operation, namely, the particular bond moment to use. The dipole moment of both ethyl and *n*-propyl ether is 1.2 D[15] and the dipole moment of the six-membered ether tetrahydropyran is 1.9 D. Smyth[15] relates the higher dipole moment of the six-membered cyclic ether to a change in bond angle which alters the charge distribution and the individual bond moments. If one takes 1.9 D for the bond moment of the C—O—C ether resultant, the predicted moment of the *cis-cis* conformation in six-membered rings would be 2.8 D + 1.9 D = 4.7 D, which is close to the experimental value of 5.3 D, considering we have not taken into account the smaller angle between the carbonyl groups.

Tetrahydrofuran has a moment of 1.7 D[15] and a similar calculation gives a value of 2.8 D + 1.7 D = 4.5 D for the five-membered cyclic anhydride which is 0.3 D over the experimental value. This is not too bad as we have not taken into account the greater angle between the carbonyl groups in the five-membered ring due to the more acute ring angles.

It would thus appear that theoretical considerations would predict the higher dipole moments of anhydrides over imides.

TABLE IV

DIPOLE MOMENTS OF AROMATIC IMIDES IN DIOXANE AT 30°

I. Phthalimide

	ω_2	ϵ_{12}	ν_{12}
	0.00	2.20935	0.97384
	.0021316	2.22502	.97363
	.0030146	2.23221	.97341
	.0044857	2.24240	.97319
μ 2.91 ± 0.03 D	.0055946	2.24967	.97308
	.0063686	2.25455	.97286

ϵ_1 2.20991 ν_1 0.97388 P_{20} 207.45 Mol. wt. 147.13
α 7.12091 β −0.15239 P_E 37.30 calcd

II. Naphthalimide

	ω_2	ϵ_{12}	ν_{12}
	0.00	2.20867	...
	.0005851	2.21843	0.97319
	.0018475	2.23461	.97297
	.0034989	2.25643	.97264
μ 4.73 ± 0.03 D	.0039814	2.26456	.97253
	.0057019	2.28879	.97221

ϵ_1 2.20917 ν_1 0.97332 P_{20} 493.66 Mol. wt. 197.2
α 13.83047 β .19376 P_E 44.34 calcd.

DIPOLE MOMENTS OF ANHYDRIDES IN DIOXANE AT 30°

VIII. Glutaric anhydride

	ω_2	ϵ_{12}	ν_{12}
	0.0012111	2.23133	0.97805
	.0016340	2.24161	.97796
	.0019097	2.24885	.97788
	.0024534	2.26375	.97768
μ 5.31 ± 0.02 D	.0030763	2.27961	.97760
	.0033590	2.28667	.97756

ϵ_1 2.19951 ν_1 0.97833 P_{20} 591.82 Mol. wt. 130.12
α 26.0015 β −0.23847 P_E 24.76 calcd.

IX. Cyclohexane 1,3-anhydride

	ω_2	ϵ_{12}	ν_{12}
	0.00	2.19960	...
	.0010497	2.22122	0.97835
	.0015400	2.23115	.97821
	.0019471	2.23774	.97810
	.0024682	2.24815	.97804
μ 4.97 ± 0.04 D	.0029227	2.25861	.97797
	.0033994	2.26767	.97780

ϵ_1 2.19980 ν_1 0.97855 P_{20} 530.79 Mol. wt. 150.17
α 19.9249 β −0.21404 P_E 34.86 calcd.

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(15) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, 1955, pp. 297-300.

Experimental

Dipole moments of I, II, VIII, and IX were measured in dioxane at 30° and calculations made using the equation and method of Halverstadt and Kumler.[16]

We wish to thank Dr. H. K. Hall, Jr., of DuPont for providing glutaric anhydride and cyclohexane 1,3 anhydride.[17]

Phthalimide was from Eastman and naphthalimide was through the courtesy of C. W. French, Jr., of Pfister Chemical Works, Ridgefield, N. J. The latter compounds were recrystallized from dioxane. All spectrographic measurements were made by Mr. M. K. Hrenoff of the Spectrographic Laboratory of the School of Pharmacy. Infrared spectra were run on Perkin-Elmer Model 21 and ultraviolet spectra on Cary Model 11.

Acknowledgment.—This paper has been aided by U. S. Public Health Service Grant CY-3211 (C4).

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[16] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[17] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **80**, 6412 (1958).

Acid Hydrolysis of N-Butyryl-γ-butyrolactam

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The hydrolysis of N-butyryl-γ-butyrolactam in aqueous solution is a pseudo-first-order reaction catalyzed by general acids. The hydronium ion–catalyzed reaction produces butyric acid and γ-butyrolactam. At very low acid concentrations the rate appears to be nonlinear in acid. The reaction exhibits a deuterium solvent isotope effect; $k_H/k_D = 0.83 \pm 0.03$ and it was found that $\Delta H^{\ddagger} = 18.2 \pm 0.9$ kcal./mole and $\Delta S^{\ddagger} = -16 \pm 2.5$ e.u. The mechanism of the reaction is discussed and an explanation is offered for the unusual dependence of the rate on acid concentration.

The hydrolysis of carboxylic acid derivatives has long been a favorite field for quantitative investigation and the theory underlying organic chemistry has benefited from these studies. The mechanisms for many of these reactions have been systematized to a certain extent.[1,2] Although the hydrolysis of imides and N-acyllactams with basic reagents has been studied,[3,4] the hydrolysis of these materials under acidic conditions has not been investigated in detail.[5–8]

The work herein reported was undertaken in an effort to obtain quantitative information relating to the acid-catalyzed hydrolysis of N-butyryl-γ-butyrolactam (I). The rate of hydrolysis was studied in relatively dilute aqueous solution by following the rate of formation of carboxylic acid.

Experimental

N-Butyryl-γ-butyrolactam was prepared by the method of Reppe from γ-butyrolactam and butyric anhydride.[9] The product had b.p. 136°/19 mm. and n^{25}_D 1.4760.

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.9; H, 8.44; N, 9.03. Found: C, 61.3; H, 8.5; N, 8.99.

The infrared spectrum of the pure liquid showed no NH or OH absorption and no acidic material was detected by titration.

The hydrolysis of I was carried out in sealed glass ampoules immersed in a silicon oil thermostat of conventional design. The temperature was controlled to ±0.1°. The reaction was followed by periodically removing an ampoule from the oil bath, quenching in cold water, and titrating a pipetted portion (usually 2.0 ml.) of the ampoule's contents conductometrically with standard sodium hydroxide after dilution to an appropriate volume. The total acid concentration in the sample was determined graphically using standard methods.[10] The amount of carboxylic acid produced was then assessed by subtracting the catalyzing acid's concentration where applicable. The results obtained in this way agreed well with carboxylic acid concentrations obtained directly from the conductance curves.

Reaction mixtures used to fill the ampoules were prepared in volumetric flasks from pipetted amounts of stock solutions of the various reagents. It was found that aqueous stock solutions of the substrate underwent slow decomposition at room temperature. Consequently, fresh stock solutions were prepared frequently. This was always done for runs in which the "spontaneous" reaction and acetic acid catalysis were studied. A stock solution of the substrate in deuterium oxide was used for runs in which the solvent isotope effect was investigated.

All of the water employed in preparing the stock solutions, reaction mixtures, and that used in the conductometric titrations was distilled and deionized and had a specific resistance greater than 2×10^6 ohm-cm. The salts employed were Mallinckrodt Analytical Reagent grade. The hydrochloric and acetic acids were DuPont reagents. The deuterium oxide was a product of the Stuart Oxygen Co. containing greater than 99 atom per cent deuterium. Commercial dioxane was purified using the method outlined by Wyness.[11]

The course of the reaction was determined by hydrolyzing 0.233 mole of N-butyryl-γ-butyrolactam with 0.002 mole of p-toluenesulfonic acid (0.008 M) in aqueous solution by refluxing for several days. The reaction mixture was then exhaustively steam distilled until aliquots of the fresh distillate were free of acid. Titration indicated that 0.228 mole of carboxylic acid was present in the distillate and 0.004 mole of carboxylic acid in addition to the expected p-toluenesul-

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. XIV.

[2] M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

[3] H. K. Hall, Jr. *et al.*, *J. Am. Chem. Soc.*, **80**, 6420 (1958).

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[6] W. Hückel and F. Stefp, *Ann.*, **453**, 163 (1927).

[7] E. Bamberger and S. Williamson, *Ber.*, **27**, 1458 (1894).

[8] W. Hentschel, *ibid.*, **23**, 2394 (1890).

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[10] F. Daniels *et al.*, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 169.

[11] K. G. Wyness, *J. Chem. Soc.*, 2934 (1958).