329. *The Acid-catalysed Heterolysis of Amides with Alkyl–Nitrogen Fission* (A_{AL}).

By R. N. Lacey.

Ureas, thioureas, amides, and sulphonamides with *N*-t-alkyl substituents undergo alkyl–nitrogen heterolysis in the presence of strong mineral acids. *N*-t-Butyl derivatives gave t-butyl alcohol, and *N*-(1,1,3,3-tetramethylbutyl)amides gave " di-isobutene " with boiling 30% sulphuric acid, which converted carboxylic amides into the corresponding acids; the urea derivatives and sulphonamides, however, gave products in which the *N*-t-alkyl group was replaced by hydrogen. The heterolysis of *N*-t-alkylamides in 98% sulphuric acid at room temperature was very rapid and gave amides in high yield.

The acid-catalysed alkyl–oxygen (A_{AL}) heterolysis of esters of carboxylic acids has often been observed.[1,2] The methods available for distinction between the A_{AL}-type of heterolysis and the more commonly encountered acyl–oxygen (A_{AC}) cleavage are either (i) such as restrict the alcohol component of the esters studied to those which, if liberated as R^+ as in a unimolecular mechanism, may rearrange (if mesomeric or capable of undergoing a Wagner–Meerwein rearrangement) or racemise (if optically active) and thus be recognised,

[1] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 779.
[2] Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 203.

or (ii) require the use of solvent water enriched in ^{18}O, whereby formation of the alcohol with the labelled oxygen affords unequivocal proof of alkyl–oxygen fission or appearance of ^{18}O in the acid function indicates the A_{AC} mechanism. The possibility that amides do not in all cases undergo the A_{AL}-type of hydrolysis in the presence of acids does not seem to have been previously studied. This omission is the more surprising since the recognition of the type of cleavage that may occur in the hydrolysis of amides is far simpler than for hydrolysis of esters. The well-known A_{AC} hydrolysis of amides (R'·CO·NHR) gives the parent acid and amine, whereas the A_{AL} cleavage would be expected to give the simple amide of the component acid (R'·CO·NH_2, or the acid itself should R'·CO·NH_2 be hydrolysed by A_{AC} hydrolysis) and the alcohol corresponding to the *N*-substituent, or other products that might arise from the cation R^+ in the environment in which the hydrolysis is carried out.

$$R'\cdot CO\!\!\mid\!\!NHR \longrightarrow R'\cdot CO_2H + NH_2R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad A_{AC}$$

$$R'\cdot CO\cdot NH\!\!\mid\!\!R \longrightarrow R'\cdot CO\cdot NH_2 + HOR \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad A_{AL}$$

Examples of the A_{AL} type of hydrolysis have been noted incidentally by the author [3] in the hydrolysis of *N*-t-butyl-*N'*-cyclohexylurea and *N*-cyclohexyl-*N'*-(1,1,3,3,-tetramethylbutyl)urea, both of which in boiling 15% hydrochloric acid gave *N*-cyclohexylurea. The fate of the tertiary alkyl substituents was not determined, although it was expected that formation of the corresponding alcohol or chloride and polymerisation would ensue. The ready hydrolysis of *N*-t-alkylureas (R·NH·CO·NHR') has now been shown to be general and R' may be methyl, phenyl, or cyclohexyl where R may be t-butyl, 1,1-dimethylpropyl, or 1,1,3,3-tetramethylbutyl; similarly substituted thioureas undergo acid-hydrolysis in the same fashion, although yields of the expected *N*-substituted thioureas were in some cases low and formation of hydrogen sulphide indicated the incidence of side-reactions.

Sulphuric acid (20—30%) may be used to replace hydrochloric acid, and this reagent was preferred for use in experiments designed to identify the product arising from the tertiary alkyl group. t-Butyl alcohol was obtained in 61% yield on hydrolysis of *N*-t-butylurea with 30% sulphuric acid. *N*-t-Butylurethane was hydrolysed similarly and although, in the time selected for the experiment, conversion was incomplete, t-butyl alcohol and ethanol were obtained in roughly equivalent amounts. *N*-(1,1-Dimethylpropyl)urea was hydrolysed rapidly in boiling 20% sulphuric acid, to give a 91% yield of a mixture consisting chiefly of 2-methylbut-2-ene with some 2-methylbut-1-ene and 2-methylbutan-2-ol.

Examination of the heterolysis of simple amides bearing *N*-t-alkyl substituents has shown A_{AL} cleavage to be a general reaction in strongly acid media. Semiquantitative results on the heterolysis of a variety of *N*-t-alkylamides in both 98% sulphuric acid at room temperature and boiling 30% sulphuric acid are shown in Table 1.

The classical work of Whitmore [4] has shown that the free neopentyl cation undergoes rearrangement to the 1,1-dimethylpropyl cation. Thus, if heterolysis of a *N*-neopentylamide were to follow the $A_{AL}1$ mechanism, it should give rise to the products (2-methylbut-2-ene, 2-methylbut-1-ene, and 2-methylbutan-2-ol) that would be expected to arise from the 1,1-dimethylpropyl cation. It was found, however, that *N*-neopentylbenzamide was resistant to acid-hydrolysis; treatment with 98% sulphuric acid was virtually without effect; prolonged boiling with 30% sulphuric acid gave only partial hydrolysis and no detectable C_5 alcohol or hydrocarbon.

N-t-Butyltoluene-*p*-sulphonamide and the *N*-(1,1,3,3-tetramethylbutyl) derivative were rapidly hydrolysed with boiling 30% sulphuric acid, giving (*a*) the expected products arising from the *N*-alkyl fragments and (*b*) toluene-*p*-sulphonamide, unlike the *N*-t-alkyl carboxylic amides which gave the respective acids under these conditions. The sulphonamide evidently survives the hydrolysis conditions because of its relatively greater resistance

[3] Lacey and Ward, *J.*, 1958, 2134.
[4] Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3431; 1939, **61**, 1586.

TABLE 1. *Heterolysis of* N-*t-alkylamides* R′·CO·NHR.

		With 98% H_2SO_4 at 15—20°			With boiling 30% H_2SO_4		
R′	R	5 min.	1 hr.	20 hr.	Time (hr.)	Conversion (%)	Yield (%)
H	Bu^t	—	—	—	6	100	Nil
Me	,,	—	—	—	3	100	88 [1]
CH_2Cl	,,	54% C	80% C	—	4	— [4]	23 [1]
Ph	,,	99% Y	—	—	4	100	72 [1]
p-MeO·C_6H_4	,,	58·5% Y	41% Y	—	3	100	52 [1]
p-Cl·C_6H_4	,,	70% C	99% Y	—	6	97	44 [1]
p-NO_2·C_6H_4	,,	59% C	93% C	100% Y	6	60	49 [1]
3,5-$(NO_2)_2C_6H_3$	,,	84% C	99% Y	—	6	73	31 [1]
H	"t-octyl" [3]	—	—	—	3	100	11 [2]
Me	,,	81% C	—	—	1·5	100	89 [2]
CH_2Cl	,,	—	100% C	—	2·5	— [4]	43 [2]
Ph	,,	95% Y	—	—	2	100	96 [2]
p-MeO·C_6H_4	,,	60% Y	—	—	1·5	100	72·5 [2]
p-Cl·C_6H_4	,,	100% Y	—	—	5	100	64 [2]
p-NO_2·C_6H_4	,,	97% Y	—	—	5	100	68 [2]
3,5-$(NO_2)_2C_6H_3$	,,	100% Y	—	—	—	—	— [5]

Y = yield of R′·CO·NH_2 in experiments with 100% conversion; C = conversion of R′·CO·NHR. [1] Yield of t-butyl alcohol (on amide consumed). [2] Yield of "octenes" (on amide consumed). [3] "t-octyl" signifies 1,1,3,3-tetramethylbutyl. [4] Complete conversion prevented by steam-distillation and crystallisation of the *N*-alkylamide in the reflux condenser. [5] Material charred and decomposed.

to acid, and its formation provides a useful illustration of the A_{AL} hydrolysis. Treatment of *N*-t-alkyltoluene-*p*-sulphonamides with 98% sulphuric acid rapidly gave toluene-*p*-sulphonamide in high yield.

DISCUSSION

Although the bimolecular mechanism for the acid-catalysed hydrolysis of esters involving alkyl–oxygen fission ($A_{AL}2$) is conceivable, it has not been observed and all instances of such hydrolysis have been assigned a unimolecular mechanism.[1,2] The heterolysis of *N*-t-alkylamides described virtually certainly follows a unimolecular mechanism in 98% sulphuric acid, *i.e.*, the cleavage of the *N*-t-alkylamide is supposed to arise from the unimolecular fission of the molecule in a protonated form without the intervention of other molecular species until the fragments are well separated, and it is probable that A_{AL} hydrolysis is also unimolecular in the weaker acid medium. The two steps involved in the $A_{AL}1$ hydrolysis of an ester (R′·CO_2R) involve (*a*) addition of proton to give a conjugate acid and (*b*) unimolecular cleavage of the conjugate acid to R′·CO_2H and R^+, the latter rapidly reacting with water or polymerising. The reaction rate is held to be controlled by the second step, the first being fast, and to be influenced by polar substituents in R′, being accelerated by electron-attracting substituents. The analogous mechanism for $A_{AL}1$ hydrolysis of amides may be written:

$$R'\cdot CO\cdot NHR + H^+ \rightleftharpoons R'\cdot CO\cdot NH_2R^+ \quad . . . . . (a)$$

$$R'\cdot CO\cdot NH_2R^+ \longrightarrow R'\cdot CO\cdot NH_2 + R^+ \quad . . . . . (b)$$

Table 1 shows that in 98% sulphuric acid the effects of substituents in *N*-t-butylbenzamide are in the order *p*-MeO > H > 3,5-$(NO_2)_2$ > *p*-Cl > *p*-NO_2 (in order of decreasing reaction rate). Less clear indications are available from other series. Conversion of all the aromatic *N*-(1,1,3,3-tetramethylbutyl)amides was very rapid in 98% sulphuric acid and the effects of substituents could not be discerned; the faster reactions of amides with the higher *N*-t-alkyl substituent were also found with 30% sulphuric acid. With the more dilute acid the same order of effects of substituents was apparent, although the situation was obscured by the low yields of t-butyl alcohol or di-isobutene obtained

[5] Lang, B.P. 796,796.

with amides bearing electronegative substituents (and, unexpectedly, from *p*-methoxybenzamide derivatives, hydrolysis of which was very rapid), possibly owing to the incidence of A_{AC} hydrolysis, and, since dissolution of the amides was not obtained, by solubility factors. The effect of electronegative chlorine in R′ is powerfully to inhibit the reaction, *i.e.*, $CH_3 > CH_2Cl$. *N*-t-Alkylformamides, however, are hydrolysed in 30% sulphuric acid predominantly by an A_{AC} mechanism, and the hydrolysis of such amides has been described in recent patent specifications as a technical method for the preparation of t-alkylamines, *e.g.*, *N*-(1,1,3,3-tetramethylbutyl)formamide is claimed by Lang [5] to give a 97% yield of 1,1,3,3-tetramethylbutylamine by two hours' refluxing with 30% aqueous sulphuric acid. In this case the normal A_{AC} mechanism is probably particularly favoured, and Krieble and Holst [6] observed that formamide was hydrolysed by 30% sulphuric acid about 57 times faster than acetamide.

The rate of hydrolysis is clearly inhibited by electronegative substituents and the effect of these substituents on step (*a*) must be dominating. If it is assumed that step (*a*) must be fast, the observed effects may be ascribed to the greater influence of electronegative substituents on the position of the equilibrium (*a*) than on the rate of step (*b*), the overall effect being one of retardation. The order of effects of substituents in *N*-t-alkylbenzamides is broadly the reverse of that exhibited by the dissociation constants of the respective benzoic acids, as would be expected from the polar influences involved:

Substituent in benzoic acid	*p*-MeO	H	*p*-Cl	*p*-NO_2	3,5-$(NO_2)_2$
Dissociation constant ($\times 10^5$)	3·4	6·3	10·5	37	160

The anomalous position of 3,5-$(NO_2)_2$ may be attributable to a large increase in the rate of step (*b*) which may offset the equilibrium shift in (*a*).

It may readily be shown (cf. ref. 1, p. 772) that the rate of the $A_{AL}1$ process, whether controlled by step (*a*) or by step (*b*), will be proportional to h_0, where $h_0 = -$antilog H_0 (H_0 being the Hammett acidity function in the concentration of acid used). The apparent first-order velocity constant for the heterolysis of *N*-t-butylbenzamide in 98% sulphuric acid at 25° is of the order 10^2 hr.$^{-1}$ (*i.e.*, at least 99% complete within 5 min.). On the other hand, the apparent first-order velocity constant for hydrolysis of this amide in 30% sulphuric acid must be less than that of benzamide under these conditions ($2{\cdot}0 \times 10^{-3}$ hr.$^{-1}$ at 25° [7]), since this intermediate may not be isolated. Thus, the ratio of the velocity constants in these two concentrations of sulphuric acid, for which the ratio of the respective values of h_0 is of the order 10^7, must be greater than 10^5. The probable order of the ratio of the velocity constants is therefore consistent with the $A_{AL}1$ mechanism (rate $\propto h_0$), and not with the $A_{AL}2$ mechanism (rate $\propto [H_3O^+]$).

The rapid heterolysis of *N*-t-butylamides contrasts with the failure of *N*-neopentylbenzamide to undergo hydrolysis. The main driving force behind the reaction must therefore lie in the inductive and electromeric effects of the t-alkyl group and the stability of the t-alkyl cation. The unimolecular step in the reaction may be regarded as an example of a system undergoing combined $E1$ and S_N1 reaction of which the unimolecular reaction of t-alkyldimethylsulphonium ions is typical: [8]

$$R{\cdot}CH_2{\cdot}CMe_2{\cdot}SMe_2^+ \xrightarrow{\text{Slow}} R{\cdot}CH_2{\cdot}CMe_2^+ + Me_2S$$

$$R{\cdot}CH_2{\cdot}CMe_2^+ \xrightarrow{\text{Fast}} R{\cdot}CH{:}CMe_2 + H^+ \quad \ldots\ldots\ldots\ E1$$

$$R{\cdot}CH_2{\cdot}CMe_2^+ + OH^- \xrightarrow{\text{Fast}} R{\cdot}CH_2{\cdot}CMe_2{\cdot}OH \quad \ldots\ldots\ldots\ S_N1$$

In this class of reaction, elimination is of the Saytzeff type, *i.e.*, if R = Me the 1,1-dimethylpropyl cation gives predominantly 2-methylbut-2-ene rather than the isomeric

[6] Krieble and Holst, *J. Amer. Chem. Soc.*, 1938, **60**, 2976.
[7] Edward and Meacock, *J.*, 1957, 2000.
[8] Ingold, *op. cit.*, p. 445.

α-olefin, and reaction rate is increased by substitution β to the eliminated group, *i.e.*, $CMe_2Et > CMe_3$. The hydrolysis of *N*-t-alkylamides shows many points of similarity, *N*-t-butylamides giving the S_N1 type of reaction (from the reaction of the cation with H_2O rather than with OH^-), and the *N*-1,1-dimethylpropyl and *N*-1,1,3,3,-tetramethylbutylamides giving *E*1 reaction. The reaction rates are enhanced by β-substitution, *i.e.*, $Bu^t{\cdot}CH_2{\cdot}CMe_2 > CMe_3$. The olefin eliminated from *N*-(1,1-dimethylpropyl)urea on hydrolysis with 20% sulphuric acid is, indeed, predominantly 2-methylbut-2-ene, but this evidence should be discounted since prototropic changes in the acid medium would certainly influence the composition of the olefin.

Experimental

M. p.s are corrected. Gas–liquid chromatography was carried out in 8 ft. × 6 mm. columns with nitrogen as carrier gas and a hydrogen-flame detector, acetone being added to aqueous t-butyl alcohol samples as an " internal standard."

Hydrolysis of N-*t-Alkylurea Derivatives.*—The following general procedure was used. The urea (1 g.) was refluxed for 2 hr. with a mixture of concentrated hydrochloric acid (2 ml.) and water (2 ml.). The product was concentrated to about half its original volume and made just alkaline with 10% aqueous sodium hydroxide. After cooling, the solid product was collected and washed with a little cold water.

Table 2. *Hydrolysis of* N-*t-alkylurea derivatives.*

	R·NH·CX·NHR′		Yield of R′·NH·CX·NH_2
R′	R	X	(%)
Cyclohexyl	Bu^t	O	85
Ph	Bu^t	O [1]	83
Cyclohexyl	$Bu^t{\cdot}CH_2{\cdot}CMe_2$	O	96
Ph	$Bu^t{\cdot}CH_2{\cdot}CMe_2$	O [2]	28
Cyclohexyl	Bu^t	S	90
Ph	Bu^t	S	39
Me	Bu^t	S	79 [3]

[1] N-*t-Butyl*-N′-*phenylurea*, prepared in ether from t-butylamine and phenyl isocyanate, gave needles, m. p. 166°, from aqueous ethanol (Found: N, 14·2. $C_{11}H_{16}ON_2$ requires N, 14·55%). [2] N-*Phenyl*-N′-(1,1,3,3-*tetramethylbutyl*)*urea*, prepared in ether from 1,1,3,3,-tetramethylbutylamine and phenyl isocyanate, gave needles, m. p. 136°, from aqueous methanol (Found: N, 11·75. $C_{15}H_{24}ON_2$ requires N, 11·3%). [3] The hydrolysis product was neutralised and evaporated to dryness; *N*-methylthiourea was isolated by extraction of the residue with hot ethanol.

N-*t-Butylurea*. The urea (10 g.) was boiled with 30% sulphuric acid (100 g.) for 4 hr. and distillate of b. p. 80—95° was removed at the head of a short fractionating column. Analysis of the distillate by gas-liquid chromatography (stationary phase, glycerol; support, kieselguhr; column temperature, 56°) showed that a 61% yield of t-butyl alcohol had been obtained.

N-(1,1-*Dimethylpropyl*)*urea*. The urea (50 g.) was treated as in the previous experiment with 20% sulphuric acid (100 g.). An oily layer (25 g.) was decanted and collected at the column head, evolution of oil being substantially complete in 1 hr. Analysis of the distillate as above indicated 2-methylbut-2-ene (80%), 2-methylbut-1-ene (14%) (separated by ethylene glycol saturated with silver nitrate on kieselguhr; 20°), and 2-methylbutan-2-ol (6%) (separated by tritolyl phosphate on kieselguhr; 100°), equivalent together to a 91% yield of C_5 hydrolysis products.

N-*t-Butylurethane*. The urethane (10 g.) was boiled with 30% sulphuric acid (100 g.) for 4 hr. and distillate of b. p. 80—95° removed from the head of a short fractionating column during the course of the experiment. The presence of a substantial remaining oily layer showed that conversion was incomplete. Analysis of the product by chromatography on a glycerol–kieselguhr column at 56° indicated a 30% yield of t-butyl alcohol together with a 32% yield of ethanol.

Hydrolysis of N-*t-Alkylamides*.—New amides were prepared as follows: The acid chloride (0·1 mole, dissolved in benzene if a solid) was added during 20—30 min. to a stirred, cooled mixture of 10% aqueous sodium hydroxide (50 ml.) and the t-alkylamine (0·1 mole). After a further 20 minutes' stirring the product was isolated. Yields in general were 80—90%. In the case of *N*-t-butyl-*p*-chlorobenzamide it was found necessary to use a 50% excess of amine to

give a product capable of being satisfactorily purified. *N*-Acetylamides were prepared in ether with acetic anhydride.

TABLE 3. N-*t-Alkylamides* R'·CO·NHR.

R'	R	M. p.		Found (%) C	Found (%) H	Found (%) N	Calc. (%) C	Calc. (%) H	Calc. (%) N
CH_2Cl	Bu^t	84° [1]	$C_6H_{12}ONCl$	48·05	8·2	9·6	48·15	8·1	9·35
p-MeO·C_6H_4	Bu^t	116 [2]	$C_{12}H_{17}O_2N$	70·75	7·95	6·55	69·55	8·25	6·75
p-Cl·C_6H_4	Bu^t	138 [2]	$C_{11}H_{14}ONCl$	62·7	6·65	6·65	62·4	6·65	6·6
p-NO_2·C_6H_4	Bu^t	161 [2]	$C_{11}H_{14}O_3N_2$	59·6	6·5	12·85	59·45	6·35	12·6
3,5-$(NO_2)_2C_6H_3$	Bu^t	184 [2]	$C_{11}H_{13}O_5N_3$	49·8	5·05	15·4	49·45	4·9	15·7
Me	" t-octyl " [5]	100·5 [1]	$C_{10}H_{21}ON$	70·45	12·35	8·2	70·15	12·3	8·2
CH_2Cl	,,	63 [2]	$C_{10}H_{20}ONCl$	58·0	10·0	7·1	58·4	9·8	6·8
Ph	,,	68·5 [3]	$C_{15}H_{23}ON$	77·65	10·0	5·8	77·2	9·95	6·0
p-MeO·C_6H_4	,,	103 [2]	$C_{16}H_{25}O_2N$	73·3	9·1	5·4	72·95	9·55	5·35
p-Cl·C_6H_4	,,	107 [2]	$C_{15}H_{22}ONCl$	66·85	8·2	5·4	67·25	8·3	5·25
p-NO_2·C_6H_4	,,	115·5 [4]	$C_{15}H_{22}O_3N_2$	64·45	7·7	9·95	64·75	7·95	10·05
3,5-$(NO_2)_2C_6H_3$	,,	126·5 [2]	$C_{15}H_{21}O_5N_3$	56·05	6·5	12·75	55·7	6·55	13·0

[1] Needles from light petroleum (b. p. 60—80°). [2] Needles from aqueous ethanol. [3] Needles from light petroleum (b. p. 40—60°). [4] Needles from benzene–light petroleum (b. p. 60—80°). [5] " t-octyl " signifies 1,1,3,3,-tetramethylbutyl.

(a) *Hydrolysis with* 30% *sulphuric acid.* The amide (10—12 g.) was boiled with 30% sulphuric acid (100 g.), and distillate (b. p. 80—99°) was removed from a total-reflux still head, at which a brisk reflux was maintained, fitted to the head of a short fractionating column. For *N*-t-butylamides, 5—7 g. of distillate were normally collected, which was analysed for t-butyl alcohol by gas–liquid chromatography (glycerol–kieselguhr at 56°). With *N*-(1,1,3,3-tetramethylbutyl)amides, the distillate was continuously decanted, the water phase being continuously returned to the head of the column, and the oil phase collected; infrared examination and gas–liquid chromatography (liquid paraffin–kieselguhr at 78°) confirmed that the product was essentially " di-isobutene," *i.e.*, 90% of 2,4,4-trimethylpent-1-ene, 5% of 2,4,4-trimethylpent-2-ene, and minor quantities of impurities. In all experiments the apparatus was vented to a cold trap cooled with acetone and solid carbon dioxide, but no material was ever found in the trap.

The solid contents of the hydrolysis vessel were isolated and separated by extraction with sodium hydrogen carbonate solution and subsequent acidification of the filtered solution into acid components, the identities of which as the expected carboxylic acids were established by comparison with authentic specimens, and non-acid residual products, which were shown in all cases to be substantially pure starting materials.

(b) *Heterolysis with* 98% *sulphuric acid.* The powdered amide (2 g.) was added to 98% " AnalaR " sulphuric acid (10 ml.) and rapidly stirred; in general it quickly dissolved. After being kept at room temperature, the product was poured in a thin stream into water (50 ml.) with shaking and cooling, and isolated conventionally. The product was freed from oily isobutene polymers by washing it with a little light petroleum (b. p. 40—60°). Products from the heterolysis of *N*-t-butyl- and *N*-(1,1,3,3-tetramethylbutyl)-benzamide were worked up by pouring them into a suspension of excess of sodium carbonate in a little water, followed by ether-extraction in a Soxhlet apparatus. Experiments in which complete conversion was achieved could be reproduced, giving yields within 2—3%; the conversions in experiments involving incomplete conversion were calculated from the weight loss observed, quantitative recoveries and absence of side-reactions being assumed.

N-*Neopentylbenzamide.*—The *amide* was prepared from neopentylamine and benzoyl chloride by the general procedure; crystallisation from aqueous ethanol gave needles, m. p. 114° (Found: C, 75·3; H, 8·55; N, 7·3. $C_{12}H_{17}ON$ requires C, 75·35; H, 8·95; N, 7·3%). Boiling the amide (10 g.) for 6 hr. with 30% sulphuric acid (100 g.) gave no detectable C_5 hydrocarbon or alcohol; the amide was recovered with 80% efficiency; benzoic acid was the only recognised product. Treatment of the amide (2 g.) with 98% sulphuric acid (10 ml.) for 1 hr. followed by pouring of the product into water gave only pure starting material with 98% recovery.

N-*t-Butyltoluene*-p-*sulphonamide.*—Toluene-*p*-sulphonyl chloride (19 g.) in benzene (55 ml.) was added during 20 min. to a stirred mixture of t-butylamine (8·7 g.) and 10% aqueous sodium hydroxide (50 ml.). After a further 20 minutes' stirring, the benzene layer was separated, washed with dilute sulphuric acid, and evaporated, to give the *amide* (10 g., 41%), which

crystallised from aqueous ethanol as needles, m. p. 113·5° (Found: C, 58·1; H, 7·9; N, 6·15. $C_{11}H_{17}O_2NS$ requires C, 58·0; H, 7·55; N, 6·15%).

The amide (2·00 g.) was left for 5 min. in solution in 98% sulphuric acid (10 ml.). The solution was poured into water to give toluene-*p*-sulphonamide (1·452 g., 96%), m. p. and mixed m. p. 136·5—138°. The amide (10 g.) was boiled with 30% aqueous sulphuric acid (100 g.) for 3 hr. and distillate (4·6 g. containing 23·5% of t-butyl alcohol; 41% yield) was removed at the head of a fractionating column. The less volatile residue deposited a solid (6·7 g.) which, on being washed with aqueous sodium hydrogen carbonate, gave a residue of toluene-*p*-sulphonamide (6·07 g., 81%), m. p. and mixed m. p. 138°.

N-(1,1,3,3-*Tetramethylbutyl*)*toluene*-p-*sulphonamide*.—Prepared from toluene-*p*-sulphonyl chloride and 1,1,3,3-tetramethylbutylamine by the procedure described in the previous section, the *amide* (57% yield) crystallised from aqueous ethanol as prisms, m. p. 133—134° (Found: C, 63·8; H, 9·05; N, 4·9. $C_{15}H_{25}O_2NS$ requires C, 63·55; H, 8·9; N, 4·95%). Hydrolysis of the amide with boiling 30% sulphuric acid was complete within 2·5 hr. to give a 47% yield of " octenes " and a 74% yield of toluene-*p*-sulphonamide. Heterolysis in 98% sulphuric acid at room temperature for 5 min. gave toluene-*p*-sulphonamide in 83% yield.

CHEMICAL DIVISION, THE DISTILLERS COMPANY LIMITED,
HEDON, HULL.

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