

CCCCXXXVI.—*The Decomposition of Substituted Carbamyl Chlorides by Hydroxy-compounds. Part III. The Influence of Substituent Groups.*

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THE reaction between phenylmethylcarbamyl chloride and ethyl alcohol at various temperatures has already been studied (J., 1924, 125, 115). An account is now given of the reaction between ethyl alcohol and other substituted carbamyl chlorides at 100°.

Materials.—All the substituted carbamyl chlorides used, with the exception of the diphenyl compound, which was obtained from Kahlbaum, were prepared by passing carbonyl chloride through a benzene solution of the requisite secondary amine. After removal of any unchanged amine and of hydrogen chloride and benzene, the product was purified by several distillations under reduced pressure, if a liquid, or by repeated crystallisation from light petroleum, if a solid.

Phenyl-n-propylcarbamyl chloride was prepared by passing carbonyl chloride into a solution of *n*-propylaniline (30 g.) in benzene (150 c.c.), cooled by ice-cold water, until the solution was saturated. The solution, which now contained *n*-propylaniline hydrochloride in

suspension, was washed with water, dried, and evaporated, leaving 13 g. of crude *phenyl-n-propylcarbamyl chloride*. This crystallised from light petroleum in colourless, short prisms (6 g.), m. p. 45.5—46°. The compound has a penetrating but not unpleasant odour and is easily soluble in alcohol, ether, chloroform, benzene, ethyl acetate, or acetone, but insoluble in water (Found: Cl, 17.8. $C_{10}H_{12}ONCl$ requires Cl, 18.0%).

Phenylisopropylcarbamyl chloride, similarly prepared from *iso*-propylaniline, crystallised from light petroleum in colourless prisms, m. p. 90—90.5°. It is very soluble in alcohol, ether, chloroform, benzene, or acetone, but insoluble in water, and has a penetrating odour similar to that of the *n*-propyl compound (Found: Cl, 17.9%).

Phenyl-n-butylcarbamyl chloride, obtained from *n*-butylaniline, is a pungent, colourless liquid, b. p. 165—166°/20 mm., miscible in all proportions with alcohol, ether, benzene, and other organic solvents, but insoluble in water (Found: Cl, 16.7. $C_{11}H_{14}ONCl$ requires Cl, 16.8%).

Phenylisobutylcarbamyl chloride, b. p. 149—151°/19 mm., resembles the *n*-butyl compound in its physical properties (Found: Cl, 16.6%).

Phenylisoamylcarbamyl chloride, obtained from *iso*amylaniline, is a colourless liquid, b. p. 153—153.5°/10 mm., with a strong, sweet odour; it is miscible in all proportions with alcohol, ether, benzene, or acetone, but insoluble in water (Found: Cl, 15.7. $C_{12}H_{16}ONCl$ requires Cl, 15.7%).

o-Tolylethylcarbamyl chloride was prepared from ethyl-*o*-toluidine and repeatedly crystallised from light petroleum. The colourless, short prisms, m. p. 36.5—37°, obtained were easily soluble in alcohol, ether, benzene, or chloroform, but insoluble in water, and had a sweet odour (Found: Cl, 17.9. $C_{10}H_{12}ONCl$ requires Cl, 18.0%).

The Reactions between Ethyl Alcohol and the Substituted Carbamyl Chlorides.

The ethyl alcohol was commercial absolute alcohol which had been treated twice at the boiling point with fresh calcium turnings (1.0 and 0.5% by weight) and fractionated. It distilled sharply at 78.6°.

The method of working was that described in Part I, section C (*loc. cit.*, p. 118), and the velocity coefficient of the reaction was calculated in each case from a knowledge of the amount of unchanged carbamyl chloride left in the system at any given time by means of the expression $k = 1/(t_2 - t_1) \cdot \log_e \{(a - x_1)/(a - x_2)\}$, where t_1 is 5 minutes after insertion of the tube into the bath kept at 100°.

In each experiment, a weight of carbamyl chloride equivalent to 25 c.c. of *N*/10-solution was dissolved in 5 c.c. of absolute alcohol.

Results.—In Table I, where the results for phenylethyl- and phenyl-*n*-propyl-carbamyl chloride are given in detail, the first column gives the duration of heating in minutes (*t*), the second the amount of hydrogen chloride present, expressed as c.c. of *N*/10-solution (*b*), and the third the amount of hydrogen chloride plus carbamyl chloride present, expressed as c.c. of *N*/10-solution (*c*). The fourth column gives the amount of carbamyl chloride present, also expressed as c.c. of *N*/10-solution (*d*) and obtained by subtracting the figures in column 2 from those in column 3. The fifth column gives the velocity coefficient for the reaction, calculated from the figures in column 4.

The whole of the results are summarised in Table II.

TABLE I.

Phenylethylcarbamyl chloride.					Phenyl- <i>n</i> -propylcarbamyl chloride.				
<i>t</i> .	<i>b</i> .	<i>c</i> .	<i>d</i> .	<i>k</i> .	<i>t</i> .	<i>b</i> .	<i>c</i> .	<i>d</i> .	<i>k</i> .
5	5.11	24.77	19.66	—	5	4.03	24.84	20.81	—
10	10.30	24.48	14.18	0.0655	8	6.92	24.79	17.87	0.0508
15	13.61	24.05	10.44	0.0633	10	8.59	24.48	15.89	0.0540
20	15.74	23.33	7.59	0.0634	13	10.62	24.23	13.61	0.0531
25	16.76	22.49	5.73	0.0617	15	11.83	24.10	12.27	0.0528
30	17.25	21.47	4.22	0.0617	20	13.98	23.53	9.55	0.0519
35	17.45	20.45	3.00	0.0627	25	15.40	22.56	7.16	0.0534
			Mean	0.0631				Mean	0.0527

TABLE II.

Carbamyl chloride.	Limits of <i>k</i> .	Mean <i>k</i> .
Phenyl-methyl	0.0437 —0.0417	0.0427
„ ethyl	0.0655 —0.0617	0.0631
„ <i>n</i> -propyl	0.0540 —0.0508	0.0527
„ isopropyl	0.223 —0.210	0.215
„ <i>n</i> -butyl	0.0550 —0.0540	0.0545
„ isobutyl	0.0297 —0.0280	0.0290
„ isoamyl	0.0422 —0.0403	0.0414
„ benzyl	0.0217 —0.0209	0.0214
Diphenyl	0.00128—0.00115	0.00123
<i>o</i> -Tolyethyl	0.0396 —0.0362	0.0376

The experiments with phenylmethyl-, phenylethyl-, phenyl-*n*-propyl-, and phenyl-*n*-butyl-carbamyl chloride were repeated with the following results for the respective mean velocity coefficients: 0.0430, 0.0635, 0.0529, 0.0550.

The results in Table II show that so far as the compounds containing a straight-chain alkyl radical are concerned, the reactivity of the carbamyl chloride with ethyl alcohol, as measured by the ease with which the chlorine atom is removed, does not vary regularly with the weight of the alkyl radical. The order of reactivity (denoting the compound by the alkyl radical which is attached to

the nitrogen atom) is ethyl>*n*-butyl>*n*-propyl>methyl, a pronounced alternation in the value of the velocity coefficient being observed. This behaviour is not exceptional, having been found with other homologous series. Thus Crocker (J., 1907, **91**, 593), in the hydrolysis of aliphatic amides by hydrochloric acid, found an alternation in the bimolecular velocity coefficient in passing from formamide to butyramide. Crocker and Lowe, however (*ibid.*, p. 952), found no corresponding alternation when the same amides were hydrolysed by alkalis, the velocity coefficient decreasing as the weight of the alkyl radical increased. Clarke (J., 1910, **97**, 416) found an alternation in the reactivity of bromoacetic esters with pyridine in alcoholic solution, the bimolecular velocity coefficients being in the order ethyl>methyl>*n*-butyl>*n*-propyl ester.

For the branched-chain compounds a similar alternation is found, the reactivity being in the order *isopropyl*>*isoamyl*>*isobutyl*. The value of the velocity coefficient for the phenyl-*isopropyl* compound is exceptionally high and is probably connected with the fact that this is the only compound examined in this series in which nitrogen is attached to a >CH- group.

The replacement of the methyl group in phenylmethylcarbonyl chloride by a phenyl group decreases the reactivity considerably, causing the diphenyl compound to be the least reactive of all those examined. The introduction of a phenyl group into the alkyl chain also lowers the reactivity, as shown by the figures for the velocity coefficients of phenylmethyl- and phenylbenzyl-carbonyl chlorides. The replacement of the phenyl group by the *o*-tolyl group decreases the reactivity, as shown by a comparison between the figures for the phenylethyl and *o*-tolylethyl compounds.

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