diluted with 60 cc. of water and distilled until the temperature of the mixture reached about 98°. The residue was refluxed for two hours. It was then cooled to 10° and acidified with concd. hydrochloric acid, using Congo Red paper as an indicator. The malonic acid was separated and the aqueous liquors were extracted with ether. The separated malonic acid was also dissolved in the ether, the ether solutions mixed and dried with calcium chloride and then the ether evaporated. The residue was heated in a round-bottomed flask with an air-cooled reflux condenser for two hours at 160–165°. The residue was distilled under diminished pressure and the yields of the five monobasic acids from *n*-amyl to *n*-nonyl were, respectively, 70, 51, 55, 61 and 72% of the calculated amount.

TABLE III

Δ^2-CYCLOPENTENYL ALKYL ACETIC ACIDS

Acids	B. p., °C.	n^{20}_D	d^{20}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$C_5H_7CH(n\text{-}C_5H_{11})CO_2H$	142–145 (5 mm.)	1.4659	0.9629	73.39	73.41	10.27	10.59
$C_5H_7CH(n\text{-}C_6H_{13})CO_2H$	150–155 (5 mm.)	1.4671	.9573	74.21	73.88	10.56	10.73
$C_5H_7CH(n\text{-}C_7H_{15})CO_2H$	162–165 (4 mm.)	1.4683	.9499	74.93	75.18	10.78	11.05
$C_5H_7CH(n\text{-}C_8H_{17})CO_2H$	170–173 (4 mm.)	1.4687	.9452	75.58	76.19	10.99	11.43
$C_5H_7CH(n\text{-}C_9H_{19})CO_2H$	173–176 (3 mm.)	1.4690	.9436	75.80	76.10	11.13	11.12

Summary

1. Δ^2-Cyclopentenyl alkyl acetic acids where the alkyl varies from *n*-amyl to *n*-nonyl have been prepared.

2. The bactericidal action toward *B. Leprae* has been shown to increase rapidly with increase in molecular weight of the alkyl group.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF SASKATCHEWAN]

STUDIES IN URETHANS. IV. ACYL DI-URETHANS AND THEIR REACTIONS WITH AMMONIA AND AMINES[1]

BY S. BASTERFIELD, ESLI L. WOODS AND MYRON S. WHELEN

RECEIVED SEPTEMBER 13, 1927 PUBLISHED NOVEMBER 5, 1927

In a study of guanidine derivatives, Nencki[2] observed that dicarbethoxyguanidine was decomposed by alcoholic ammonia at 100° into monocarbethoxyguanidine and urethan. Malonyldi-urethan was found by Conrad and Schulze[3] to be decomposed by the same reagent into malonamide, ammonium barbiturate and urethan. In neither of these reactions was a urethan grouping converted into a urea as might have been expected. The products obtained by Conrad and Schulze show that from some molecules of diurethan both urethan groups were removed, while from others only one was removed, and the carbethoxymalonamide so formed then condensed to barbituric acid.

The action of ammonia and amines on carbonyldi-urethan has been

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[1] A preliminary version of this paper was received July 19, 1926.

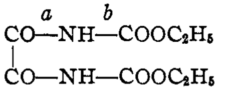
[2] Nencki, *Ber.*, **7**, 1588 (1874).

[3] Conrad and Schulze, *Ber.*, **42**, 729 (1909).

studied by Dains and his associates.[4] They report that with aqueous ammonia both amide formation and loss of carbethoxy groups by hydrolysis take place, the main products being carbethoxy-biuret and allophanic ester. Some cyanuric acid and traces of biuret were also found, but apparently no urethan. With aqueous ethylamine, allophanic ester was obtained in 80% yield, and the reaction is interpreted as hydrolysis of a carbethoxy group. With aniline at temperatures from 110 to 170°, a great variety of compounds was obtained, indicating several possible modes of fission of the di-urethan molecule, as well as secondary reactions.

In the present study, oxalyl-, malonyl- and phthalyldi-urethans have been found to have a strong tendency to lose urethan groups under the action of ammonia and amines, both in aqueous and non-aqueous media, and we regard the reaction as a general one of ammonolysis. Some experiments with carbonyldi-urethan and solutions of ammonia and ethylamine both in water and alcohol also indicate that the interpretation of Dains and his collaborators regarding the loss of carbethoxy groups by hydrolysis is not adequate. Doubtless there is some hydrolysis with aqueous reagents, but the presence of urethan and ethylurethan among the products of decomposition can only be explained by ammonolysis.

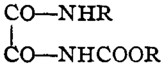
It is of interest to consider whether a urethan group is removed as a unit, fission taking place at *a* in the formula below, or whether a carbethoxy group is removed and converted into urethan by splitting of the molecule at *b*.



$$\begin{array}{l}\text{CO}\overset{a}{—}\text{NH}\overset{b}{—}\text{COOC}_2\text{H}_5\\ |\\ \text{CO—NH—COOC}_2\text{H}_5\end{array}$$

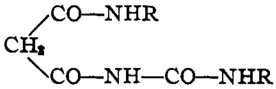
Reactions with ammonia cannot settle this point, since the results may be interpreted either way. Reactions with substituted ammonias, however, show that the first alternative represents the predominant mode of decomposition for oxalyl-, malonyl- and phthalyldi-urethans. For example, with aqueous ethylamine at room temperature, both oxalyl- and malonyldi-urethans gave the di-ethylamides in large yield and urethan. If the carbethoxy groups had been removed by ammonolysis then the products should have been the unsubstituted amides and ethylurethan.

With aniline at the boiling point there was fairly complete decomposition into the anilides and urethan, the latter being converted by excess of aniline into diphenylurea. At lower temperatures intermediate products of the types



$$\begin{array}{l}\text{CO—NHR}\\ |\\ \text{CO—NHCOOR}\end{array}$$

I



$$\text{CH}_2\begin{array}{l}\diagup\text{CO—NHR}\\ \diagdown\text{CO—NH—CO—NHR}\end{array}$$

II

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[4] Dains, Greider and Kidwell, THIS JOURNAL, **41**, 1004 (1919).

were obtained in varying quantities, depending on the time of heating and the concentrations of initial components of the reaction. These intermediate products yielded the anilides readily on further heating with aniline and their presence may be regarded as indicative of the course of the reactions.

Further evidence of the removal of urethan groups by ammonolysis was found in an experiment with malonyldibenzyldi-urethan. This compound was decomposed by alcoholic ammonia at room temperature into malonamide and benzylurethan and by alcoholic ethylamine into diethylmalonamide and benzylurethan.

In none of these experiments with di-urethans was there found evidence of the formation of di-ureas.

The decomposition of carbonyldi-urethan offers interesting points of contrast with the decomposition of the other di-urethans. Since with ethylamine this compound yields allophanic ester and ethylurethan, among other products, there must be a removal of carbethoxy groups by ammonolysis. The great variety of products obtained by Dains and his collaborators from the reactions of aniline with the di-urethan also indicates a more complex type of decomposition than is found with the di-urethans studied in this Laboratory.

In considering a possible explanation of these facts there are two points to be noted. In the first place, the non-formation of di-ureas and the ready formation of the amides of oxalic, malonic and phthalic acids are significant. With carbonyldi-urethan and aniline, Dains and his co-workers[4] observed the formation of carbonyldiphenyldi-urea, but this is the only instance of di-urea formation. In the second place, the formation of the amides by the removal of urethan groups rather than of carbethoxy groups is especially interesting.

In carbonyldi-urethan there is present only one kind of acyl radical, that of carbonic acid, while in the other three di-urethans are present, the radicals of much stronger acids in addition to that of carbonic acid. We know nothing of the free energies of formation of either the di-urethans or their products of decomposition but it seems evident that the presence of the radicals of the stronger acids has a very definite influence on the type of decomposition. There seems to be little chance of formation of carbamides except as secondary products when the radicals of stronger acids are present in competition. It may be well to note here that Dains and his collaborators found that methylenedi-urethan and similar compounds were not decomposed by amines even when heated.

Whether the influence of the acid radicals parallels the strength of the corresponding acids cannot be stated as yet. Rough observations on the rates of decomposition of the three di-urethans show that for a given base at a given temperature phthalyldi-urethan is decomposed most rapidly, oxalyldi-urethan next, and malonyldi-urethan least rapidly.

The ionization constants for the four acids involved in the di-urethans considered here are as follows.

TABLE I

IONIZATION CONSTANTS[a]

	K (first hydrogen)	K (second hydrogen)
Carbonic acid	3.0×10^{-7}	3.0×10^{-11}
Oxalic acid	3.8×10^{-2}	4.9×10^{-5}
Malonic acid	1.6×10^{-3}	2.1×10^{-6}
Phthalic acid	1.2×10^{-3}	3.1×10^{-6}

[a] Landolt-Börnstein Tabellen.

Experimental Part

Oxalyldi-urethan, $(CONHCOOC_2H_5)_2$, was prepared by Hantzsch[5] from oxalic ester and urethan in the presence of sodium ethoxide. It was obtained by Bornwater[6] in small quantity in cold ether from oxalyl chloride and urethan. In boiling benzene, Bornwater found that carbonyldi-urethan was formed. In the present study the di-urethan was obtained in quantitative yield by mixing oxalyl chloride and urethan in the required proportions without a solvent. The mixture liquefied and hydrogen chloride was rapidly evolved. In the course of a few minutes the liquid became viscid and finally solidified. The solid crystallized from 95% alcohol in pearly plates; m. p. 172°.

Malonyldi-urethan, $CH_2(CO.NHCOOC_2H_5)_2$.—This was prepared by Conrad and Schulze[3] by heating malonic acid and urethan in acetic anhydride. It was obtained by Backes, West and Whiteley[7] by warming together malonic acid, urethan and phosphoryl chloride at 80°; yield, 71%. In the present study it was readily obtained in 85% yield by refluxing malonyl chloride and urethan in required proportions in benzene until hydrogen chloride was no longer evolved; white, sandy crystals from alcohol; m. p. 124°.

Phthalyldi-urethan, $C_6H_4(CONHCOOC_2H_5)_2$.—Phthalyl chloride and urethan in required proportions were heated together at 130° until evolution of hydrogen chloride had ceased. The mixture solidified on cooling and the solid was recrystallized from alcohol; yield, 60%; fine, crystalline powder of slight aromatic odor. The substance softens at 80° and gradually decomposes as the temperature is raised.

Refluxing the acid chloride and urethan in boiling benzene for many hours gave poor results.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: N, 9.09. Found: 9.28, 9.36.

Oxalyldi-urethan

1. ACTION OF AMMONIA.—Oxalyldi-urethan was treated with cold, concentrated, aqueous ammonia. An insoluble, white powder was rapidly formed which was identified as oxamide. The filtrate on evaporation yielded urethan and a little urea.

When dry ammonia gas was passed over the di-urethan heated to 90–100° in a water-jacketed tube, a sublimate of urethan was formed in the cooler part of the tube in the course of half an hour.

2. ACTION OF ETHYLAMINE.—The di-urethan was mixed with 33% aqueous ethylamine in the proportion of one to six molecular equivalents and the mixture allowed to stand in a corked flask for twenty-four hours. A precipitate of fine needles was then filtered off and the substance identified as di-ethyloxamide, m. p. 176°. The

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[5] Hantzsch, *Ber.*, **27**, 1250 (1894).

[6] Bornwater, *Rec. trav. chim.*, **31**, 105 (1912).

[7] Backes, West and Whiteley, *J. Chem. Soc.*, **119**, 371 (1921).

amount was 70% of the theoretical. From the filtrate, after evaporation at 50–60°, was obtained urethan with a few drops of oil which was not identified.

3. ACTION OF ANILINE.—(*a*) At 190 and 150°. Mixtures of six molecular equivalents of aniline to one of di-urethan were heated for one and a half hours at the stated temperatures. The solid mass obtained after the reaction mixtures were allowed to cool was extracted with hot alcohol. The insoluble residue was oxanilide (m. p. 244–245°) in almost quantitative yield. The alcohol extract gave several crops of diphenylurea (m. p. 236°).

(*b*) At 100°. The solid product from a reaction at this temperature contained oxanilide in 60% yield. The alcohol extract gave a product which after many recrystallizations finally yielded a small fraction melting at 136–137°. A much larger amount of this substance was obtained by heating the reaction mixture for only half an hour. At the end of this time there was considerable unchanged di-urethan, but it was quite easy to separate the new product from it. The substance is apparently α-carbethoxy-β-phenyloxamide, $C_6H_5NHCOCONHCOOC_2H_5$. It is rapidly decomposed by aqueous ammonia at room temperature yielding phenyloxamide (m. p. 224°).

Anal. Calcd. for $C_{11}H_{12}N_2O_4$: N, 11.86. Found: 11.84, 11.86, 12.02.

There was no diphenylurea found in the reaction mixture at this temperature but monophenylurea and urethan were isolated. The last named was obtained by extracting the solid reaction product with water. The aqueous extract was evaporated and the brownish, crystalline residue recrystallized from ligroin. The purified substance melted at 48° and was identified as urethan.

Malonyldi-urethan

1. ACTION OF AMMONIA.—Malonyldi-urethan left in contact with concentrated aqueous ammonia at room temperature yielded malonamide, ammonium barbiturate and urethan. This result was similar to that of Conrad and Schulze[3] who decomposed the di-urethan with hot alcoholic ammonia.

The di-urethan was not decomposed by dry ammonia at 100°, as was oxalyldi-urethan.

2. ACTION OF ETHYLAMINE.—The reaction was carried out as with oxalyldi-urethan except that the mixture was allowed to stand for one week. Evaporation of the mixture to small volume at 60° gave large, waxy crystals of di-ethylmalonamide in 92% of the theoretical yield. The substance was identified by a mixed-melting-point determination with a known sample of the amide.

3. ACTION OF ANILINE.—(*a*) At 190°. The reaction was carried out as with oxalyldi-urethan. The solid product was dissolved in hot alcohol. Several fractions of crystals melting at 201–202° were obtained. This material was finally separated by fractional crystallization into malonanilide, m. p. 223°, and diphenylurea, m. p. 236°. No other compound was present.

(*b*) At 150°. The solid product obtained after two hours' heating was extracted with hot alcohol and the mixture filtered. The filtrate contained malonanilide and diphenylurea. The relatively insoluble residue was finally dissolved in a large volume of boiling alcohol from which it separated on cooling in masses of silky needles, m. p. 234–235°. The substance was not decomposed in the cold by ammonia, but was transformed on being warmed with aniline for half an hour into malonanilide and diphenylurea. It was apparently α-phenyl-β-phenylcarbamylmalonamide (phenylureidomalonylaniline), $C_6H_5NHCOCH_2CONHCONHC_6H_5$.

Anal. Calcd. for $C_{16}H_{15}N_3O_3$: N, 14.14. Found: 13.92, 14.09.

(*c*) At 120°. At this temperature a larger proportion of the above compound was obtained, with malonanilide and monophenylurea. There was no diphenylurea.

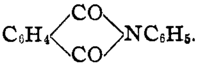
(*d*) At 100°. Very little change after several hours' heating. Malonyldi-urethan is evidently less sensitive to decomposition by aniline than is oxalyldi-urethan.

Phthalyldi-urethan

1. Action of Ammonia.—The diurethan was treated with cold, concentrated, aqueous ammonia. A white, insoluble powder was rapidly precipitated. It was identified as phthalamide, $C_6H_4(CONH_2)_2$, m. p. 220°. Urethan was recovered from the filtrate. The decomposition was quantitative.

Anal. Calcd. for $C_8H_8O_2N_2$: N, 17.07. Found: 17.07.

2. Action of Aniline.—(*a*) At 190°. One molecular proportion of di-urethan and four of aniline were heated together for one hour. The solid mass obtained after cooling was extracted with cold alcohol. The extract yielded diphenylurea, m. p. 237°. The more insoluble residue melted at 203° and was identified as phthalanil,



$C_6H_4\langle{}^{CO}_{CO}\rangle NC_6H_5$.

Anal. Calcd. for $C_{14}H_9NO_2$: N, 6.27. Found: 6.08.

(*b*) At 100°. At this temperature, after the mixture had been heated for thirty minutes, phthalanil was obtained in large amounts and a small quantity of a substance consisting of fine, white needles, m. p. 225°. In order to obtain a larger quantity of this compound a mixture of di-urethan and aniline was heated for only eight minutes. As was expected a considerably greater quantity of the new substance was obtained and much less phthalanil. It was apparently α-phenyl-β-carbethoxyphthalamide, $C_6H_5NHCOC_6H_4CONHCOOC_2H_5$.

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: N, 8.98. Found: 8.83, 8.98.

The nitrogen content of diphenylphthalamide $C_6H_4(CONHC_6H_5)_2$ is 8.87%, but its melting point is 245°. To eliminate any doubt as to the identity of the new substance, diphenylphthalamide was prepared by the method of Rogow.[8] The prepared sample melted at 245° and a mixture of it with the substance melting at 225° melted at 200°. It seems safe to conclude that the new substance is the product resulting from the removal of one urethan group by the action of aniline.

Carbonyldi-urethan

In view of the results obtained by the action of ammonia and ethylamine on oxalyl- and malonyldi-urethans, and also because Dains and his associates make no mention of finding urethan in their study of the decomposition of carbonyldi-urethan, we made a few experiments with the latter substance to determine if urethan was a product of its decomposition by ammonia and ethylamine. (Cf. Decomposition of Dicarbethoxyguanidine.)[2,9]

1. Action of Ammonia.—Two and four-tenths grams of the di-urethan was mixed with concentrated aqueous ammonia and allowed to stand at room temperature for three days. One gram of allophanic ester (m. p. 192°) was separated by filtration and the filtrate evaporated on the steam-bath. From the solid residue 0.2 g. of pure urethan was isolated. The remainder was allophanic ester and urea and a small quantity of a substance which did not melt below 300°, and which was probably cyanuric acid. Traces of biuret were also found.

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[8] Rogow, *Ber.*, **30**, 1442 (1897).

[9] Basterfield and Paynter, This Journal, **48**, 2176 (1926).

Somewhat similar results were obtained by heating the di-urethan with alcoholic ammonia under pressure at 100°.

The quantity of urethan isolated was only 20% of the theoretical, but it probably indicates the main trend of the reaction, since urea, biuret and cyanuric acid may be formed through the medium of urethan.[10]

2. ACTION OF ETHYLAMINE.—The di-urethan in 33% aqueous ethylamine after standing for four hours at room temperature gave, contrary to expectations, allophanic ester in 75% yield. On longer standing the yield was diminished. In twenty-four hours only 30% of allophanic ester was obtained, and in seventy-two hours the ester had completely disappeared. The clear solution was evaporated in a vacuum, and a residue of oil and crystals was left. The oil was taken up in chloroform and, on being fractionated, yielded a portion boiling at 174–175° which was identified as ethylurethan, $C_2H_5NH-COOC_2H_5$. The crystalline material contained urea and a substance melting at 155° which was not identified.

Some experiments were made on the action of diethylamine on oxalyl- and malonyl-di-urethans in alcoholic solution at 100°. After removal of the alcohol by evaporation oils were obtained which, on being fractionated, invariably gave urethan as one of the products. The other products have not yet been identified.

Summary

1. The decompositions of oxalyl-, malonyl and phthalyldi-urethans by ammonia, ethylamine and aniline have been studied, and the strong tendency for urethan groups to be detached by ammonolysis noted.

2. A comparison with the decomposition of carbonyldi-urethan by the same reagents is made and the different results are indicated.

3. It is suggested that the mode of decomposition of acyldi-urethans is strongly influenced by the nature of the acyl radical. The tendency for urethan groups to be detached may be correlated with a tendency toward the formation of amides of the stronger acids in preference to formation of amides of carbonic acid.

SASKATOON, SASKATCHEWAN, CANADA

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[10] Werner, "The Chemistry of Urea," Longmans and Co., New York, 1923, Chaps. 3, 4 and 7.