ing nitric oxide into a mixture of 5.6 g. of bromine in 200 cc. of dry ether in an ice–salt bath. The solution was then slowly added to 7.0 g. of ζ-truxinic-a-amino acid just covered with dry ether. The temperature was kept below −5°. After addition was completed, the reaction mixture stood until the evolution of nitrogen ceased. It was then shaken with a sodium bisulfite solution until the ether was colorless, followed by a similar shaking with a potassium carbonate solution. Acidification of this latter solution yielded only a small amount of an oil from which no crystals could be obtained.

The ether solution was dried over anhydrous potassium carbonate, then concentrated to give a total of 3.5 g. of white needles, m. p. 130–133°. Upon decolorizing with charcoal from a benzene solution, crystals were formed by the addition of petroleum ether (b. p. 60–70°), m. p. 133°. The known m. p. of lactone II was 133°.[8]

The lactone was boiled with 10% alcoholic potassium hydroxide for one minute, diluted with water, and hydrochloric acid added. The resulting precipitate was filtered, dried and recrystallized from benzene to give crystals of m. p. 148–149° (d.). The m. p. of 1^c-carboxyl-2^c-benzoxyl-3^c-phenylcyclopropane was reported[8] as 145–146°. Treatment of the above acid in methyl alcohol with diazomethane in ether yielded lactone II, m. p. and mixed m. p. 132–133°. This dehydrating action of diazomethane had been observed previously with the optically active acid.[5]

Reaction of ζ-Truxinic-b-amino Acid with Nitrosyl Bromide.—The nitrosyl bromide solution was added to 7.0 g. of the b-amino acid as described in the previous experiment. The reaction seemed slower. There was a small amount of ether insoluble material, m. p. 230–233°, possibly α,γ-diphenylbutadiene tetrabromide.[8] The ether was shaken with sodium bisulfite solution, then a potassium carbonate solution as above. Acidification of the latter solution yielded an oil which gradually solidified to yield 3.5 g. of crystals, m. p. 125–137°. Recrystallization from aqueous alcohol gave needles of m. p. 137–139°. Elementary analysis showed bromine to be present. This product will be thoroughly studied at a later date.

The ether solution was dried over potassium carbonate, and the ether evaporated off leaving an oil from which no crystals could be obtained. Treatment of the oil with boiling 10% alcoholic potassium hydroxide for one minute, dilution with water, and acidification also yielded an oil. From this oil, by means of decolorization with charcoal and two recrystallizations was obtained a small quantity of crystals, m. p. 168–169°.

Reaction of ζ-Truxinic-a-amino Acid with Nitrous Acid.—A solution of 1.5 g. of ζ-truxinic-a-amino acid in 150 cc. of dilute hydrochloric acid was warmed to 40°, and 1.5 g. of sodium nitrite in 10 cc. of water was slowly added. A solid gradually formed, and a gas was evolved containing oxides of nitrogen. One hour after addition had been completed, the flask was cooled, and the contents filtered. There was obtained 0.5 g. of crystals, which when decolorized and recrystallized from a benzene–petroleum ether solution had a m. p. of 131–133°. The mixed m. p. with the lactone II prepared above was 131–132°, demonstrating their identity.

Reaction of ζ-Truxinic-b-amino Acid with Nitrous Acid.—The reaction with nitrous acid was performed as above. The initial product was an oil, which was extracted from the solution using ether. The ether extract was washed with potassium carbonate solution. Only an oil resulted from acidification of the latter. Evaporation of the ether resulted in an oil, from which by recrystallization from a benzene–petroleum ether solution was obtained a few mg. of solid of m. p. 188–189°.

We wish to thank Dean Frank C. Whitmore of the Pennsylvania State College for his many helpful suggestions.

Summary

Deamination of ζ-truxinic-a-amino acid (1^c-carboxyl-2^c-amino-3^c,4^t-diphenylcyclobutane) with both nitrosyl bromide and nitrous acid gave the lactone of 1^c-carboxyl-2^c-benzoxyl-3^c-phenylcyclopropane. This change cannot be explained by any existing theory of molecular rearrangements without the assumption of an inversion of a carbon atom not directly involved in the reaction. Only a bromo-acid of unknown structure could be isolated from the reaction of nitrosyl bromide and ζ-truxinic-b-amino acid.

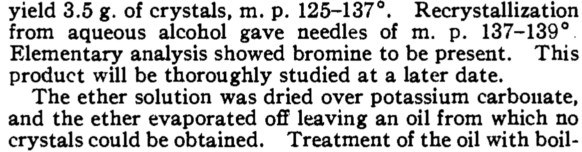
CHICAGO, ILLINOIS RECEIVED JULY 19, 1943

[CONTRIBUTION FROM THE LABORATORY OF HIGH MOLECULAR CHEMISTRY, THE HEBREW UNIVERSITY]

Reaction of Diazomethane with Ammonium Salts of Organic Acids

BY MAX FRANKEL AND EPHRAIM KATCHALSKI

In a previous paper[1] dealing with derivatives of N-carboxy α-amino acid esters, it has been shown that diazomethane reacts with the salt formed between N-carboxyglycine ester and glycine ester (I), yielding N-carbomethoxyglycine ester and glycine ester in about equimolecular amounts. The reaction proceeds according the scheme



$$\underset{\text{COOR}}{\text{CH}_2}\text{NHCOOH}_3\text{N}\underset{\text{COOR}}{\text{CH}_2} + CH_2N_2 = \underset{\text{COOR}}{\text{CH}_2}\text{NHCOOCH}_3 + H_2NCH_2COOR$$

I

R = CH_3 or C_2H_5

(I) is a substituted ammonium salt of an organic acid; thus the above scheme represents a reaction between diazomethane and an ammonium salt of an organic acid. As far as we are aware the literature does not contain any references to reactions between diazomethane and ammonium or N-substituted ammonium salts of organic or inorganic acids (*cf.* ref. 2); we therefore included in the paper mentioned[1] experimental results concerning the action of diazomethane on ammonium propionate and on ammonium benzoate. In both cases the methyl esters of the corresponding acids, and ammonia, were obtained.

The object of the present paper is to extend the investigation of this reaction to ammonium salts of dibasic acids and to N-substituted ammonium salts.

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(1) Frankel and Katchalski, THIS JOURNAL, **65**, 1670 (1943).

(2) Sidgwick, "Organic Chemistry of Nitrogen," 351–361 (1937); Smith, *Chem. Rev.*, **23**, 193 (1938).

TABLE I

N-SUBSTITUTED DIAMMONIUM PHTHALATES

Phthalate prepared	Formula	Amine used, g.	Yield	Analyses, % N Calcd.	Analyses, % N Found
Di-(methylammonium)	$C_{10}H_{16}N_2O_4$	1.1	Quant.[a]	12.28	12.40
Di-(ethylammonium)	$C_{12}H_{20}N_2O_4$	1.6	Quant.[a]	10.93	10.96
Di-(dimethylammonium)	$C_{12}H_{20}N_2O_4$	1.7	Quant.[b]	10.93	11.02
Di-(triethylammonium)	$C_{20}H_{36}N_2O_4$	3.6	90%[c]	7.67	7.69

[a] White crystals. [b] Separated as a viscous liquid which crystallized overnight in ice box. [c] Separated as oily drops which formed a viscous liquid but did not crystallize. Sixty ml. of ether required for the precipitation.

TABLE II

REACTION OF DIAZOMETHANE WITH AMMONIUM AND N-SUBSTITUTED AMMONIUM SALTS

Salt used	Dimethyl ester formed	Yield, %	B. p., °C., 690 mm.	Analyses for OCH_3, % Calcd.	Analyses for OCH_3, % Found
Diammonium malonate	Malonate	85	178	46.97	46.58
Diammonium succinate	Succinate	85	189	42.96	42.20
Diammonium phthalate[a]	Phthalate	88	278	31.96	32.21
Di-(methylammonium) phthalate	Phthalate	[b]	278	31.96	31.55
Di-(ethylammonium) phthalate	Phthalate	90	279	31.96	31.79
Di-(dimethylammonium) phthalate[a,c]	Phthalate	82	279	31.96	31.60
Di-(triethylammonium) phthalate[a,d]	Phthalate	72	278	31.96	32.10

[a] Solution of 0.8 g. of diazomethane in 70 ml. of ether used. [b] Reaction very slow. Ten ml. of alcohol added to accelerate. After standing for 48 hours, residue of 0.3 g. of ammonium salt was filtered off. Filtrate yielded 0.15 g. of product. [c] Residue of 0.05 g. remained after overnight treatment. [d] Fractionally distilled to remove triethylamine and redistilled twice for analysis.

Diazomethane was allowed to react with di-ammonium succinate, di-ammonium malonate, di-ammonium phthalate and with di-(methylammonium) phthalate, di-(ethylammonium) phthalate di-(dimethylammonium) phthalate and di-(triethylammonium) phthalate. The action of diazomethane on ammonium chloride, as representative of an inorganic ammonium salt, was also investigated.

In all cases a reaction analogous to that previously described[1] was observed, *i. e.*, the dimethyl esters of the corresponding dibasic organic acids were obtained, while ammonium chloride yielded methyl chloride. During these esterifications ammonia, methylamine, ethylamine, dimethylamine and triethylamine were evolved from the corresponding ammonium and substituted ammonium salts. In our experiments no appreciable methylation of the ammonia or amines liberated was observed.

Experimental

(a) **Preparation of the Ammonium Salts.**—The ammonium salts of malonic, succinic and phthalic acids were prepared by passing a stream of dried ammonia through an ethereal or alcoholic solution of the corresponding organic acid.[3] In the former case the ammonium salt was precipitated at once, while in the latter it was precipitated by the addition of ether.

The methylammonium, ethylammonium and dimethylammonium salts of phthalic acid were prepared by passing a stream of the appropriate dried gas through a suspension of 2 g. of *o*-phthalic acid in 10 ml. of alcohol. Di-(triethylammonium) phthalate was obtained by adding liquid triethylamine to a similar alcoholic solution of phthalic acid. After the addition was complete and the solution had cooled, separation of the salt was induced or completed by the addition of ether (generally 20 ml.). The products were filtered, washed with ether and dried.

All but the first of these salts seem to be described for the first time. Di-(methylammonium) phthalate has been obtained previously by a different method.[4] A tabulation of their yields and analyses is given in Table I.

(b) **Reaction of Ammonium and N-Substituted Ammonium Salts with Diazomethane.**—In all cases except those specified an ethereal solution of 1 g. of diazomethane in 70 ml. of ether prepared according to Adamson and Kenner[5] was used. This amount was greatly in excess of the theoretical quantity required in every instance. The ethereal solution of diazomethane was poured onto 0.5 g. of the solid ammonium salt. In general the evolution of nitrogen started immediately, but in some cases where the reaction was too slow it was accelerated by adding alcohol. The reaction mixtures were allowed to stand overnight at room temperature to complete the process. Moisture was excluded by means of a calcium chloride tube. The evolution of the ammonia or amines liberated in the reaction was indicated by their odor or their effect on litmus paper.

During the reaction the solid salt disappeared; the ethereal solution was filtered and the ether, excess of diazomethane and excess of ammonia were removed by distillation at normal pressure. The remaining viscous residue was dissolved in ether and dried over sodium sulfate. After filtration the ether was removed and the residue distilled to give the product. The esters thus obtained were redistilled before analysis. In addition to methoxyl determination a quantitative hydrolysis by alcoholic potassium hydroxide was carried out and the liberated carboxyl groups determined by back titration. In all cases this confirmed the formation of the methyl ester from the corresponding ammonium salt.

Data on the specific compounds are shown in Table II.

Action of Diazomethane on Ammonium Chloride.—One gram of diazomethane in 50 ml. of ether was added to 535 mg. of ammonium chloride. On adding 50 ml. of alcohol gas evolution started. The gases evolved were passed through a second vessel containing alcohol to absorb ammonia and methyl chloride which were only partly retained in the reaction vessel.

After twenty-four hours the residual solid ammonium chloride was filtered off (104 mg.). The alcohol–ether mixture of the reaction vessel contained a small amount of unchanged ammonium chloride in solution; this was de-

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(3) McMaster. *Am. Chem. J.*, **49**, 294 (1913).

(4) Gibbs, THIS JOURNAL, **28**, 1411 (1906).

(5) Adamson and Kenner, *J. Chem. Soc.*, 1551 (1937).

termined by a Volhard titration (43 mg.). The amount of ammonium chloride which underwent reaction was therefore 388 mg.

The methyl chloride was determined in both solutions as methyl iodide.[6] A total amount of 195 mg. of methyl chloride was found. Ammonia was determined by direct titration, 85 mg. was found. The yield of methyl chloride calculated on the basis of ammonium chloride which underwent reaction was 53%; that of ammonia 69%.

The authors acknowledge the assistance of Miss H. Berliner.

Summary

Diazomethane was allowed to react with diammonium malonate, di-ammonium succinate, di-ammonium phthalate, di-(methylammonium) phthalate, di-(ethylammonium) phthalate, di-(dimethylammonium) phthalate, and di-(triethylammonium) phthalate.

In all cases the dimethyl esters of the corresponding dibasic acids were obtained.

Reaction of diazomethane with ammonium chloride yielded methyl chloride.

During these esterifications ammonia, methylamine, ethylamine, dimethylamine and triethylamine were evolved from the corresponding ammonium and N-substituted ammonium salts.

JERUSALEM, PALESTINE RECEIVED JANUARY 24, 1944

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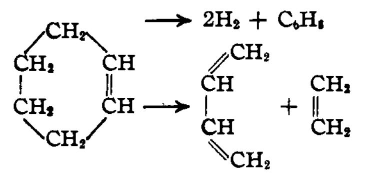
(6) Roka and Fuchs, *Z. anal. Chem.*, **71**, 381 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Substituted Cyclohexenes[1]

BY F. O. RICE[2a] AND MARY THOMAS MURPHY[2b]

1. **Introduction.**—If cyclohexene is heated above its decomposition point, at low pressures and for a time sufficiently short that only a small fraction is decomposed, it undergoes a simple dissociation into smaller molecules. The particular conditions mentioned have been selected in order to avoid as far as possible bimolecular reactions of the products with each other or with the substrate. Several thermodynamically possible decompositions may occur such as



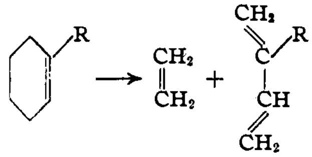
(1)

(2)

Reactions of these types have been discussed in a recent paper[3] in the light of a principle called the principle of least motion. In the case of several reactions such as those listed above which are all thermodynamically possible, the principle states that that reaction is favored which involves as little motion of the atoms as possible in passing from the old to the new configuration. The second half of the principle states that a reaction will be favored which involves least change of the electronic configuration of the reacting system. From both these standpoints, it is plausible to assume that the reaction will be favored which involves breaking or making as few bonds as possible.

On the basis of this principle we would predict with some confidence that reaction (2) would be greatly favored over reaction (1) and this has actually been found experimentally[4]; no benzene is found in the products but butadiene and ethylene are formed in almost theoretical yield. An investigation, therefore, of the decomposition of substituted cyclohexenes would provide not only a further test of the principle of least motion but also a method of preparing substituted butadienes.

2. **1-Methylcyclohexene.**—We found that this compound decomposes to the extent of about 80% according to the equation ($R = CH_3$)



(3)

As might be expected, secondary reactions occur to a larger extent than in the decomposition of cyclohexene. For every 100 molecules of methylcyclohexene decomposed, about 40 molecules of hydrogen and 30 molecules of methane are formed in subsidiary reactions. Since separate experiments showed that isoprene itself is decomposed to the extent of only a few per cent. under the experimental conditions, doubtless the secondary reactions are due in greater part to attack of free radicals on the substrate.

Zelinski and co-workers[5] pyrolyzed a number of substituted cyclohexenes both alone and diluted with water vapor. They obtained a yield of 75% ethylene and 35.3% isoprene by heating 1-methylcyclohexene at 690°.

3. **1-Ethylcyclohexene.**—There seems to be extensive decomposition which produces much methane and hydrogen; presumably there must be highly unsaturated C_8 or C_6 hydrocarbons formed although we could not identify anything in the higher fractions in spite of a careful search for ethylbutadiene which would be expected ac-

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(1) Original manuscript received June 28, 1943.

(2) (a) Present address, Catholic University, Washington, D. C. (b) Present address, College of Chestnut Hill, Philadelphia, Pa.

(3) Rice and Teller, *J. Chem. Phys.*, **6**, 489 (1938).

(4) Rice, Ruoff and Rodowskas, THIS JOURNAL, **60**, 955 (1938).

(5) Zelinski, Mikhailov and Arbuzov, *J. Gen. Chem.* USSR, **4**, 856 (1934).