7.46×10^{-4} min.$^{-1}$	Total rate of 2,5-dichlorovaleric acid
-0.92×10^{-4} min.$^{-1}$	Rate due to displacement of 2-chloro group (rate of 2-chlorovaleric acid)
6.54×10^{-4} min.$^{-1}$	Sum of displacement of 5-chloro group by ammonia and by α-chlorocarboxylate anion
-6.0×10^{-4} min.$^{-1}$	Rate due to displacement of 5-chloro group by ammonia (rate of 9-chlorononanoic acid)
5.4×10^{-5} min.$^{-1}$	Rate due to displacement of 5-chloro group by α-chlorocarboxylate anion

From this and the rate of chloride appearance from 5-chlorovaleric acid, one may conclude that the nucleophilicity of carboxylate anion is roughly forty times greater $\left(\frac{2.07 \times 10^{-3}}{5.4 \times 10^{-5}}\right)$ than that of α-chlorocarboxylate anion in attacking the 5-position intramolecularly.[13] The lowered yield of product (2 - tetrahydrofuramide) from 2,5 - dichlorovaleric acid compared to that (5-hydroxyvaleramide) from 5-chlorovaleric acid due to carboxylate attack may be rationalized on this basis. Further, the ratio of displacement by ammonia on the 5- and 2- positions is about six to one $\left(\frac{6.0 \times 10^{-4}}{9.2 \times 10^{-5}}\right)$ and hence, six times as much proline is formed by initial ammonia attack on the terminal as on the alpha carbon atom.

Acknowledgment. We are indebted to Dr. W. Potts for infrared spectral data and interpretation and to Dr. S. Shrader and associates for microanalyses.

MIDLAND, MICH.

(13) This conclusion is tenuous since it is based on the subtraction of two large numbers. The order of magnitude is probably correct, however, because nucleophilicity parallels basicity in most cases. The electrolytic dissociation constants for valeric acid[14] and 2-chlorobutyric acid[15] at 25° are 1.50×10^{-5} and 1.39×10^{-3}, respectively, a factor of about 90 in basicity.

(14) E. Franke, *Z. Phys. Chem.*, **16A**, 483 (1895).

(15) D. Lichty, *Ann.* **319**, 380 (1901).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF STEVENS INSTITUTE OF TECHNOLOGY]

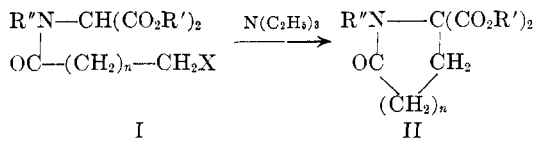
Studies on Lactams. III.[1] Mechanism of Cyclization

AJAY K. BOSE AND M. S. MANHAS[2]

Received November 10, 1961

The cyclization of diethyl *N*-(α,β-dibromo)propionylanilinomaolonate with triethylamine led exclusively to a γ-lactam In an analogous experiment a β-lactam was formed exclusively in preference to a δ-lactam. It was found that the amides from the *N*-acylation of diethyl anilinomalonate with (substituted) acrylic acids do not cyclize in presence of a base. On the basis of this and other observations, it was possible to conclude that a β-haloacylaminomalonate cyclizes by intramolecular alkylation rather than through an internal Michael addition.

In a previous publication[1] it was shown that the cyclization of ω-haloacylaminomalonic esters (I) in presence of a base proceeds in high yield when $n = 0$ or 1, but when $n = 2$ or 3, no cyclization takes place. Since, in general, six-membered and five-membered rings are formed more easily than



I II

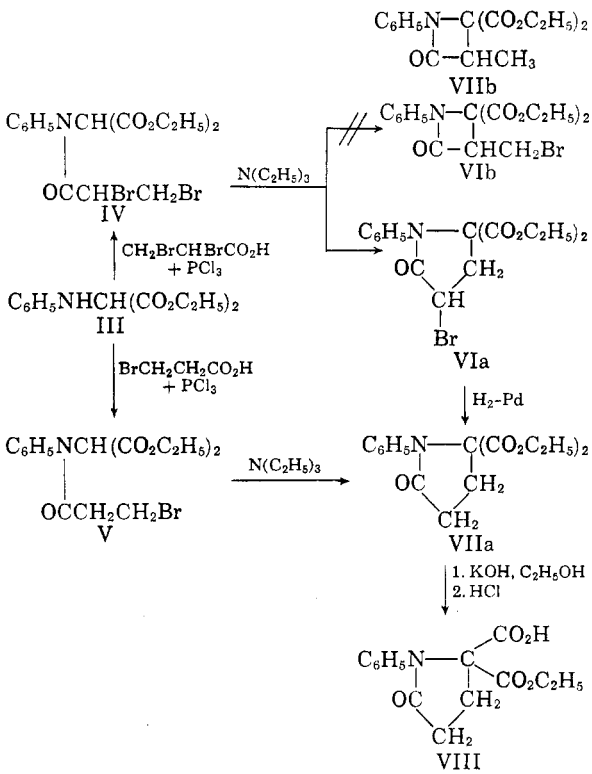
four-membered rings, it seemed to be of interest to further investigate this type of cyclization.

The first point to be studied was the relative ease of formation of four- and five-membered lactams under competitive conditions. Diethyl *N*-(α,β-dibromo)propionylanilinomalonate (IV) was prepared by the acylation of diethyl anilinomalonate (III) with α,β-dibromopropionic acid in the presence of phosphorus trichloride. When a benzene solution of IV was treated with triethylamine at room temperature, there was a ready separation of triethylamine hydrobromide. The product VI (83% yield) from this reaction appeared to be essentially homogeneous. A comparison of the NMR spectra of the recrystallized material and the mother liquor confirmed the absence of any other product.

The product from the cyclization of IV could be either the β-lactam VIb or the γ-lactam VIa. Both infrared and NMR spectra were compatible with the latter structure. For further confirmation VI was hydrogenated in presence of a palladium catalyst to a halogen-free liquid VII. An unequivocal decision between the alternative structures VIIa and VIIb was possible on the basis of the NMR spectrum. The absence of a split methyl

(1) (a) Presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., September 1961. (b) Part I, A. K. Bose, B. N. Ghosh-Mazumdar, and B. G. Chatterjee, *J. Am. Chem. Soc.*, **82**, 2382 (1960). (c) Part II, A. K. Bose, M. S. Manhas, and B. N. Ghosh-Mazumdar, *J. Org. Chem.*, **27**, 1458 (1962).

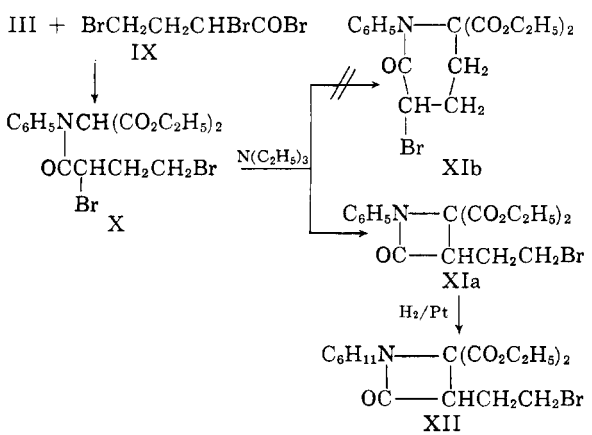
(2) On leave of absence from the University of Saugar, India.



peak (other than those given by the ester groups) characteristic of VIIb established that the product was the γ-lactam VIIa. Finally, this structure was fully confirmed by the comparison of the physical properties and infrared spectrum of VIIa with a sample obtained by the cyclization of diethyl *N*-(β-bromo)propionylanilinomalonate V. On selective hydrolysis VIIa could be converted to a crystalline acid VIII in 33% yield.

Both the β-lactam II (n = 0) and the γ-lactam II (n = 1) have been observed to be formed easily from the corresponding ω-haloacylmalonate. It is therefore noteworthy that the cyclization of the dibromo compound IV leads exclusively to the γ-lactam VIa.

The cyclization of diethyl *N*-(α,γ-dibromo)-butyroylanilinomalonate (X) was also studied. This amide X was obtained as a crystalline solid in

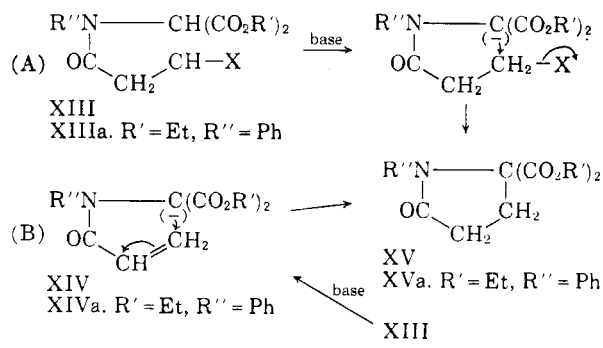


80% yield by the acylation of diethyl anilinomalonate (III) with crude α,γ-dibromobutyroyl bromide (IX) prepared by the reaction of phosphorus and bromine with butyrolactone.[3] The structure of X was fully confirmed by infrared and NMR spectra. On treating a benzene solution of X with triethylamine at room temperature the cyclization product XI could be isolated as a liquid in 90% yield. Six-membered lactams are characterized[4] by a band at about 5.95 μ (1680 cm.$^{-1}$) due to the amide carbonyl. Further, Sheehan and Bose[5] have found that the β-lactam carbonyl in structure II (n = 0) shows an intense band at 5.60–5.65 μ (1786–1770 cm.$^{-1}$). The absence of an infrared band near 6 μ (1667 cm.$^{-1}$) and the presence of a 5.62 μ (1779 cm.$^{-1}$) band in the spectrum of XI indicated the β-lactam structure XIa rather than the δ-lactam structure XIb.

Attempts to remove the bromine from XI by hydrogenation in presence of palladium or platinum catalysts were unsuccessful. Hydrogenation in glacial acetic acid in presence of Adam's catalyst at 50–60° under low pressure resulted in the selective reduction of the phenyl ring to afford the compound XII.

The cyclization of I when n = 0 to the β-lactam II is obviously a case of intramolecular displacement. The same mechanism (Chart 1,A) may also be involved in the cyclization of XIII to a γ-lactam XV. On the other hand the γ-lactam formation may proceed *via* the unsaturated intermediate XIV which then undergoes intramolecular Michael addition (Chart 1, B). The failure of cyclization of I (n = 2 or 3) to six- and seven-membered lactams could then be ascribed to the nonavailability of a suitable unsaturated intermediate for intramolecular Michael addition. The mechanism of cyclization of the γ-lactam XV is, therefore, of considerable interest.

Chart 1



When triethylamine was added to a benzene solution of diethyl *N*-(β-bromo)propionylanilinomalonate (XIIIa), separation of triethylamine hydrobromide started almost immediately indicat-

(3) H. Plieninger, *Chem. Ber.*, **83**, 265 (1950).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, New York, 1958, p. 205.

(5) J. C. Sheehan and A. K. Bose, *J. Am. Chem. Soc.*, **72**, 5158 (1950); **73**, 1761 (1951).

ing a fast reaction. The reaction was stopped after different periods of time and the product was examined spectroscopically. The main product in each case was the γ-lactam XVa in high yield. After one hour only a small fraction of the starting material XIIIa remained. After six hours there were only traces of XIIIa present. No XIIIa could be detected after twenty-four hours. In none of these samples could the unsaturated amide XIVa be detected in a study of the infrared and NMR spectra.

When a benzene solution of *N*-benzyl-β-bromopropionamide (XVI) was treated with triethylamine, the separation of triethylamine hydrobromide proceeded at a much slower rate than in the cyclization of XIII. Furthermore, the yield of *N*-benzylacryloylamide (XVII) was only about 15%. On the basis of these results it would seem unlikely that the cyclization of XIII proceeds *via* an unsaturated amide XIVa.

$$\underset{\text{XVI}}{C_6H_5CH_2NHCOCH_2CH_2Br} \xrightarrow{N(C_2H_5)_3} \underset{\text{XVII}}{C_6H_5CH_2NHCOCH{=}CH_2}$$

To throw further light on the mechanism of cyclization, diethyl *N*-acryloylanilinomalonate (XVIII) was prepared by the interaction of III with acryloyl chloride. The structure of this liquid intermediate was confirmed by a study of its infrared and NMR spectra. Furthermore, on the addition of one mole of bromine to a carbon tetrachloride solution of XVIII a solid product was obtained, the NMR spectrum of which indicated it to be the dibromo compound IV slightly contaminated with some impurity (probably a tribromo compound).

Prolonged treatment of a benzene solution of XVIII with triethylamine failed to produce any change. Analogous experiments showed that diethyl *N*-(α-methyl)acryloylanilinomalonate (XIX) also failed to undergo cyclization to a γ-lactam. Yet another unsaturated amide that did not suffer intramolecular Michael addition was diethyl *N*-(β-phenyl)acryloylanilinomalonate (XX).

$$\text{III} + CH_2{=}CRCOCl \longrightarrow \underset{\text{XVIII. R = H}}{\underset{\text{XIX. R = CH}_3}{C_6H_5NCH(CO_2C_2H_5)_2}} \\ | \\ OCCR{=}CH_2$$

$$\underset{\text{XX}}{C_6H_5NCH(CO_2C_2H_5)_2 \\ | \\ OCCH{=}CHC_6H_5}$$

The overwhelming evidence, therefore, is against the involvement of an intramolecular Michael addition in the cyclization of XIII to the corresponding γ-lactam. Intramolecular displacement seems to be indicated for the formation of β-lactams as well as γ-lactams of structure II. A satisfactory explanation is yet to be found for the failure of this type of intramolecular alkylation to afford six- and seven-membered lactams.

EXPERIMENTAL[6]

A typical acylation procedure is described for the preparation of IV. Unless otherwise mentioned similar conditions were used for the other acylations reported.

Diethyl N-(α,β-dibromo)propionylanilinomalonate (IV). A solution of 2 g. of diethyl anilinomalonate[7] in 25 ml. of benzene was heated under reflux with 1 g. of α,β-dibromopropionic acid and 1 ml. of phosphorus trichloride for 3 hr.[8] The reaction mixture after cooling was washed successively with sodium bicarbonate solution, dilute hydrochloric acid, and water. The benzene layer was dried over anhydrous sodium sulfate and the solvent removed from it under reduced pressure when 3.6 g. (97%) of a slightly colored solid, m.p. 110–111°, was obtained. Recrystallization from a mixture of benzene and ligroin afforded colorless needles, m.p. 116° (83% recovery); λ_{max}^{Nujol} 5.68 μ (1761 cm.$^{-1}$, β-lactam carbonyl), 5.75 μ (1739 cm.$^{-1}$, ester), 5.95 μ (1681 cm.$^{-1}$, amide carbonyl).

Anal. Calcd. for $C_{16}H_{19}Br_2NO_5$: C, 41.31; H, 4.12; N, 3.01. Found: C, 42.16; H, 4.11; N, 3.36.

Diethyl β-bromo-N-propionylanilinomalonate (V). A solution of 2.5 g. of diethyl anilinomalonate, 1.5 g. of β-bromopropionic acid, and 1 ml. of phosphorus trichloride in 25 ml. of benzene was heated under reflux for 4 hr. The reaction mixture was worked up as in the preparation of IV. The product was 3.65 g. (94%) of a viscous, pale yellow liquid [λ_{max} 5.95 μ (1681 cm.$^{-1}$, amide)] which showed satisfactory infrared and NMR spectra. This crude product was used directly for the next step.

1-Phenyl-3-bromo-5,5-dicarbethoxypyrrolidine-2-one (VIa). On the addition of 1 g. of triethylamine to a solution of 3.7 g. of diethyl α,β-dibromo-*N*-propionylanilinomalonate (IV) in 25 ml. of benzene a crystalline precipitate of triethylamine hydrobromide started to separate immediately with slight evolution of heat. The reaction mixture was allowed to stand for 2 days. Triethylamine hydrobromide was then removed by filtration, and the filtrate was washed with dilute hydrochloric acid and water. After drying over anhydrous sodium sulfate, the solvent was removed from the benzene solution leaving 2.5 g. (83.3%) of a colored solid. Crystallization from ligroin gave 1.3 g. of colorless needles (54.4% recovery), m.p. 64–65°; λ_{max}^{Nujol} 5.78 μ (1730 cm.$^{-1}$, ester) and 5.81 μ (1721 cm.$^{-1}$, γ-lactam).

Anal. Calcd. for $C_{16}H_{18}BrNO_5$: C, 50.00; H, 4.72; N, 3.64. Found: C, 50.10; H, 4.29; N, 3.63.

1-Phenyl-5,5-dicarbethoxypyrrolidine-2-one (VIIa). A. To a solution of 3.65 g. crude diethyl β-bromo-*N*-propionamideanilinomalonate (V) in 20 ml. of benzene there was added 1 g. of triethylamine. The mixture warmed spontaneously and triethylamine hydrobromide separated out. The contents were refluxed for 3 hr., then washed with dilute hydrochloric acid and water and dried over anhydrous sodium sulfate. Removal of the solvent gave 2.7 g. (88%) of a pale yellow oil which was purified by two successive evaporative distillations (120–130°/1 mm.). The final distillate, $n^{25}D$ 1.5180, gave satisfactory infrared, λ_{max} 5.8 μ (1724 cm.$^{-1}$, γ-lactam carbonyl), and NMR spectra.

Anal. Calcd. for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 63.23; H, 6.32; N 4.56.

(6) All melting points are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y., and Alfred Bernhardt, Mikroanalytisches Laboratorium in Max-Planck-Institut, Mülheim (Ruhr), West Germany.

(7) R. Blank, *Ber.*, **31**, 1815 (1898).

(8) A. K. Bose, *J. Indian Chem. Soc.*, **31**, 108 (1954).

Cyclization was also carried out at room temperature. The reaction mixture was worked up in the usual way after a reaction period of 1 hr., 6 hr., and 24 hr. The composition of the crude product was estimated from the carbonyl bands in the infrared spectrum.

B. 1-Phenyl-3-bromo-5,5-dicarbethoxypyrrolidine-2-one (VIa) (0.26 g.) was reduced with hydrogen using palladium-on-charcoal (5%) as a catalyst in 20 ml. of ethyl alcohol containing a suspension of magnesium oxide. Filtration and removal of the solvent gave 0.2 g. (theoretical) of diethyl 1 - phenyl - 5,5 - dicarbethoxy - pyrrolidine - 2 - one. Evaporative distillation of 0.15 g. of the crude material afforded 0.1 g. (66% recovery) of VIIa, $n^{25}D$ 1.5186; λ_{max} 5.82 μ (1718 cm.$^{-1}$ γ-lactam).

1-Phenyl-5-carboxy-5-carbethoxypyrrolidine-2-one. (VIII). To a solution of 1.85 g. of 1-phenyl-5,5-dicarbethoxypyrrolidine-2-one (VIIa) in 5 ml. of ethyl alcohol was added an alcoholic solution of 0.26 g. of potassium hydroxide. A crystalline precipitate of the monopotassium salt began to appear on scratching. After allowing the reaction mixture to stand overnight at room temperature excess ether was added. The white gum that separated was extracted with the minimum quantity of water, and the aqueous solution was washed with ether and then acidified with concd. hydrochloric acid. The reaction mixture was next extracted with ether, and the ether solution was dried over anhydrous sodium sulfate. Removal of the solvent and crystallization of the residue from an alcohol and petroleum ether mixture gave 0.6 g. (33%) of a colorless solid, m.p. 142–144°; $\lambda_{max}^{CHCl_3}$ 5.82 μ (1718 cm.$^{-1}$, γ-lactam carbonyl).

Anal. Calcd. for $C_{14}H_{15}NO_6$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.43; H, 5.75; N, 5.27.

Diethyl N-(α,γ-dibromo)butyroylanilinomalonate (X). A solution of 2.5 g. of diethyl anilinomalonate in 25 ml. of benzene and an excess of α,γ-dibromobutyrylbromide[8] was heated under reflux for 4 hr. On working up the reaction mixture as in the preparation of IV there was obtained 4.8 g. (theoretical yield) of a solid. Crystallization of 1 g. of this solid from benzene–ligroin mixture gave 0.8 g. of colorless needles, m.p. 87°. The infrared spectrum of this compound was satisfactory for structure X.

Anal. Calcd. for $C_{17}H_{21}Br_2NO_5$: C, 42.61; H, 4.42; N, 2.92. Found: C, 42.79; H, 4.28; N, 3.10.

1-Phenyl-3-(2'-bromoethyl)-4,4-dicarbethoxyazetidine-2-one (XIa). To a solution of 2.4 g. of X in 25 ml. of benzene was added 0.5 g. of triethylamine. Triethylamine hydrobromide began to separate gradually after about 5 min. The contents were kept at room temperature for 2 days. The precipitate of triethylamine hydrobromide was filtered off and the filtrate worked up as in the preparation of IV to give 1.8 g. (90%) of a viscous oil; λ_{max} 5.6 μ (1786 cm.$^{-1}$, β-lactam carbonyl), $n^{25}D$ 1.5340.

Anal. Calcd. for $C_{17}H_{20}BrNO_5$: C, 51.26; H, 5.06; N, 3.51. Found: C, 51.13; H, 5.16; N, 3.52.

Attempts to reduce this compound catalytically in the presence of palladium on charcoal catalyst were unsuccessful.

1-Cyclohexyl-3-(2'-bromoethyl)4,4-dicarbethoxyazetidine-2-one (XII). To a solution of 0.7 g. of XIa in 25 ml. of glacial acetic acid 2 drops of concd. hydrochloric acid were added. The mixture was warmed to 60° and 0.65 g. of Adam's catalyst were added. The hydrogenation was then carried out at a slightly positive pressure for 19 hr. After removing most of the acid at reduced pressure the reaction mixture was taken in ether and washed successively with dilute sodium bicarbonate solution, dilute hydrochloric acid, and water. After drying the ether layer over anhydrous magnesium sulfate, the solvent was evaporated which yielded 0.6 g. (crude) of XII. Evaporative distillation gave a viscous oil; $n^{25}D$ 1.4906, λ_{max} 5.6 μ (1786 cm.$^{-1}$, β-lactam carbonyl).

Anal. Calcd. for $C_{17}H_{26}BrNO_5$: C, 50.50; H, 6.48; N, 3.46; Br, 19.77. Found: C, 50.30; H, 6.73; N, 3.47; Br, 19.46.

N-Benzylacryloylamide (XVI). To a solution of 2.4 g. of *N*-benzyl-β-bromopropionamide[9] in 25 ml. of benzene was added 2 g. (excess) of triethylamine. The contents were allowed to stand at room temperature for 3 days and then washed with dilute hydrochloric acid and water. Removal of the solvent and the crystallization of the residue from ligroin gave a colorless solid, m.p. 67–68° (15.5% yield); $\lambda_{max}^{CHCl_3}$ 5.95 μ (1681 cm.$^{-1}$, amide), 6.1 μ (1639 cm.$^{-1}$, double bond).

Diethyl N-acryloylanilinomalonate (XVIII). A solution of 2.5 g. of diethyl anilinomalonate in 25 ml. of benzene, 3 g. (excess) of acryloylchloride,[10] and a trace of hydroquinone were heated under reflux for 4 hr. The reaction mixture was worked up as described for the preparation of IV, to give a colored, viscous liquid in theoretical yield; λ_{max} 5.97 μ (1675 cm.$^{-1}$, amide), 6.12 μ (1634 cm.$^{-1}$, conjugated double bond).

Diethyl *N*-acryloylanilinomalonate was heated under reflux for 4 hr. with an equivalent proportion of triethylamine in benzene solution. The reaction mixture was then washed successively with dilute hydrochloric acid and water. Removal of the solvent after drying yielded a material which on the basis of its infrared spectrum was found to be identical with the starting diethyl *N*-acryloylanilinomalonate (XVI). The same lack of reaction was observed on carrying out the reaction at room temperature for 3 days.

Bromination of diethyl N-acryloylanilinomalonate. A solution of 1.6 g. of XVI in 20 ml. of carbon tetrachloride and 0.8 g. of bromine in 20 ml. of carbon tetrachloride were mixed with constant stirring at room temperature. Removal of the solvent gave 1.8 g. (75%) of a pale yellow solid residue, m.p. 88–91°. Filtration of this product in methylene chloride solution through acid-washed alumina and crystallization from benzene–petroleum ether mixture gave colorless crystals, m.p. 96–97° (80% yield). The NMR spectrum showed the presence of IV and a small quantity of impurity.

Anal. Calcd. for $C_{16}H_{19}Br_2NO_5$: C, 41.31; H, 4.12; N, 3.01. Found: C, 38.30; H, 3.93; N, 3.00.

Diethyl N-(α-methyl)acryloylanilinomalonate (XIX). Using the same reaction conditions as in the preparation of XVI, 4.9 g. (78%) of a viscous liquid [λ_{max} 6 μ (1667 cm.$^{-1}$, amide)] was obtained by the acylation of 5 g. of III with 6 g. (excess) of methacryloyl chloride.[11]

A benzene solution of XIX containing an equivalent amount of triethylamine was kept at room temperature for 4 days. After working up the reaction mixture in the usual way, there was obtained a product which showed an infrared spectrum which was identical with that of the starting material XIX.

Diethyl N-(β-phenyl)acryloylanilinomalonate (XX). A solution of 2.5 g. of diethyl anilinomalonate in 25 ml. of benzene was heated under reflux with 1.5 g. of cinnamic acid and 2 ml. of phosphorus trichlroide for 4 hr. After the usual work-up, there was obtained a viscous, pale yellow liquid (84% yield) which solidified on keeping. It crystallized as colorless needles, m.p. 64–65°, from a mixture of benzene and petroleum ether (70% recovery) and showed satisfactory infrared and NMR spectra.

Anal. Calcd. for $C_{23}H_{24}NO_5$: C, 69.27; H, 6.07; N, 3.67. Found: C, 69.48; H, 6.03; N, 4.08.

To a benzene solution of XX was added a base and the mixture stored at room temperature for 4 days. Triethylamine, piperidine, and sodium hydride were used as bases in parallel experiments. From the infrared spectrum, the product in each experiment was found to be the unchanged starting material XX.

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(9) S. Kushner, R. I. Cassell, J. Morton, and J. H. Williams, *J. Org. Chem.*, 16, 1283 (1951).

(10) G. H. Stempel, Jr., R. P. Cross, and R. P. Mariella, *J. Am. Chem. Soc.*, 72, 2300 (1950).

(11) Methacryloyl chloride, b.p. 90°, was prepared in 17% yield by the method described for acryloyl chloride.[10]

Acknowledgment. Grateful acknowledgment is made of a research grant (MY-3930) from the National Institute of Mental Health of the U. S. Public Health Service for partial support of this work. Thanks are due to Dr. E. R. Malinowski for NMR spectra and their interpretation.

HOBOKEN, N. J.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Alkali Salts of 2,2-Diphenyl-1-picrylhydrazine[1]

JOHN A. WEIL AND GAILE A. JANUSONIS

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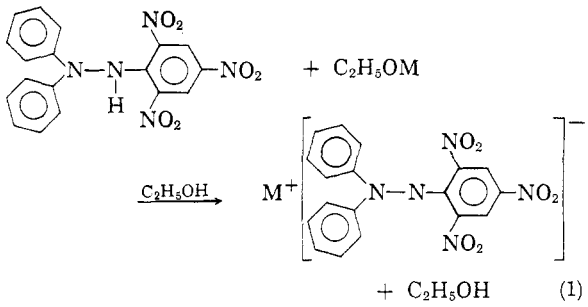
Several monoalkali salts, as well as a quaternary ammonium salt, of 2,2-diphenyl-1-picrylhydrazine have been prepared. They have been characterized by elemental analysis, acid-base titrimetric analysis, and by use of proton high resolution magnetic resonance. The intense optical absorptions of solutions of these salts have been measured.

The dark coloration generated by addition of bases to solutions of 2,2-diphenyl-1-picrylhydrazine was first reported several decades ago,[2] and in fact optical studies of such solutions have been published.[3,4] The latter authors[3] attribute the color to ionization, for example as in the reaction:



(1)

where M is an alkali metal atom. It appears, however, that no further studies of the chemical changes involved have been made. We wish to report such studies, which have led to the synthesis (*via* reaction 1) and characterization of various salts of diphenylpicrylhydrazine including those of lithium, sodium, potassium, rubidium, and also of a quaternary ammonium ion.

The elemental analyses listed in the Experimental section show that the product is essentially the one given by Equation 1. The product is independent of the alcohol used. The black crystalline salts are sensitive to moisture, hydrolyzing to regenerate the diphenylpicrylhydrazine and the corresponding alkali hydroxide, but exhibit no particular tendency to explode. The product is diamagnetic as indicated by the absence of electron paramagnetic resonance (EPR) absorption in the powder or in solution. However, solutions of the salts in acetone shaken with lead dioxide give the typical purple color and EPR hyperfine structure of 2,2-diphenyl-1-picryl hydrazyl (DPPH).

We found it possible to make quantitative molecular weight determinations by carrying out titrations of both the acidic diphenylpicrylhydrazine and its basic salts. With the hydrazine, we followed the procedure given by Fritz *et al.*[5] for titration of nitroaromatic amines, using triethyl-*n*-butylammonium hydroxide as the titrant in a reaction completely analogous to reaction 1; the quaternary ammonium salt produced was isolated and characterized (see Experimental section). Alternatively, titrations with alkali alkoxide solutions were feasible. Similarly, quantitative titrations of the salts of diphenylpicrylhydrazine were carried out by potentiometric titrations with trichloroacetic acid. The molecular weights of the alkali salts thus obtained are reported in the Experimental section; the titrations were accurate to 1–2%. The end product of the titrations of the salts was diphenylpicrylhydrazine, as judged by color and melting temperature (176°).

In general, the salts are soluble in polar organic solvents (acetone, ethanol) and insoluble in the nonpolar ones (benzene, ether). To arrive at some feeling for the relative polarity of the alkali salts, estimates were made of their solubility in 1,4-dioxane (lithium and sodium: 10^{-2} mole $l.^{-1}$ potassium and rubidium: 10^{-4} mole $l.^{-1}$). For comparison, the solubility of diphenylpicrylhydrazine itself was measured and was found to be 0.6 mole $l.^{-1}$.

High resolution NMR results of the salts in acetone, using tetramethylsilane as internal standard,[6] gave additional information. Two proton peaks are observed, with areas in the ratio of 5:1. The larger, occurring at $\tau = 2.90$, arises from the protons on the two phenyl rings, and is little shifted

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission

(2) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

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