bined ether solution and extracts with water and drying over anhydrous sodium sulfate, removal of the solvent left 10 g. of light orange oil. This was treated with 40 ml. of 5% hydrochloric acid in which it partially dissolved. After standing for two hours the mixture was extracted with ether which yielded 2.0 g. of a brown oil from which 1.05 g. (15%) of nearly pure trimethylacetophenone was isolated by use of Girard Reagent "T."[12] The recovered redistilled ketone was a colorless oil, b.p. 219–223°, $n^{26}D$ 1.5058; reported b.p. 219–221°, $n^{19.2}D$ 1.5086. The 2,4-dinitrophenylhydrazone melted at 192.5–193.5° (reported 194–195°[13]), the oxime melted at 164.5–165° (reported 165°[14]), and the semicarbazone melted at 160–160.5° (reported 159°[15]).

When the acidic aqueous solution from the above ether extraction was made basic 6.1 g. of red oil separated. On distillation this gave 0.80 g. (15%) of N-methyl-*o*-phenylenediamine along with unreacted benzimidazole. The diamine was identified by conversion to 1,2-dimethylbenzimidazole with acetic anhydride. The m.p. and mixture m.p. with a known sample was 111–112°.[16]

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[12] A. Girard and G. Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

[13] J. H. Ford, C. D. Thompson and C. S. Marvel, THIS JOURNAL, **57**, 2619 (1935).

[14] J. U. Nef, *Ann.*, **310**, 316 (1899).

[15] P. Lucas, *Compt. rend.*, **152**, 1771 (1911).

[16] M. A. Phillips, *J. Chem. Soc.*, 2820 (1929).

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reductive Coupling and Polymerization of Unsaturated Amides. II. Effect of Substituents[1]

BY H. R. SNYDER AND ROBERT E. PUTNAM[2]

RECEIVED OCTOBER 24, 1953

The reduction of a series of N,N-disubstituted α,β-unsaturated amides with lithium aluminum hydride has been investigated. In nearly every case the major product was formed by reaction at the carbon–carbon double bond. However, the nature of this product depended on the sizes of the substituent groups. A mechanism to account for observed differences in reaction course has been postulated. Evidence for a stereospecific formation of reductively coupled products from N,N-diethylcinnamamide, N,N-diethylcrotonamide, N-methyl-N-phenylcinnamamide and cinnamic piperidide was obtained.

In the preceding paper[1] the reduction of N,N-diethylcrotonamide with lithium aluminum hydride was reported. Inverse addition of the hydride was shown to give a mixture of reductively coupled amide, N,N,N′,N′-tetraethyl-α-ethyl-β-methylglutaramide, a polymer of N,N-diethylcrotonamide and several amines. The relative amounts of these products could be controlled within limits by variation of the quantity of hydride added. Investigation of the behavior of a series of substituted acrylamides in the presence of lithium aluminum hydride now has been completed. The results indicate that the nature of the major product in each case is strongly dependent on the size of the substituent groups.

All of the successful reductions led to a major product of one of three types (II, III, IV). That the sizes of R^1, R^2 and R^3 in the α,β-unsaturated amide I should influence the course of the reaction is not at all surprising. However, the observation that the nature of R^4 is perhaps even more critical was not anticipated. It will be shown that effects of both types can be explained satisfactorily by consideration of the steric requirements of the groups involved.

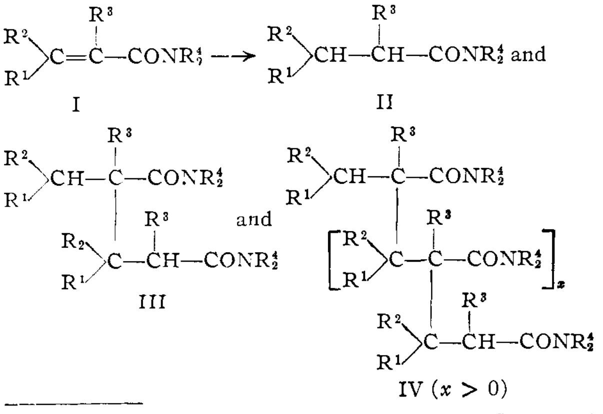

Table I lists the yields of the saturated amide II, the dimeric amide III and the polymer IV obtained when R^1, R^2 and R^3 are varied in size through the series R = hydrogen, methyl, α-furyl and phenyl, while R^4 is maintained constant at ethyl. A consideration of these data shows the strong dependence of reaction product type on the nature of the substituent group. Thus as the size of R^1 is increased ($R^2 = R^3 = H$) the degree of polymerization decreases. N,N-Diethylacrylamide (V) gives a high molecular weight polymer in nearly 100% yield. N,N-Diethylcrotonamide (VI) yields an

TABLE I

REDUCTIVE COUPLING OF SOME UNSATURATED DIETHYL AMIDES BY LITHIUM ALUMINUM HYDRIDE

Amide[a] structure	R^1	R^2	R^3	Molar ratio, hydride/amide	Yield,[b] % II	III	IV
V	H	H	H	0.25[c]	0	0	90–100
VI	CH_3	H	H	.19[d]	0	29.3	37
				.5[d]	0	10.6	17.7
VII	CH_3	CH_3	H	.26	47	12	0
VIII	CH_3	H	CH_3	.31	0	0	0
IX	α-C_4H_3O	H	H	.5	0	43–53	0
X	C_6H_5	H	H	.56	0	45–53	0

[a] For the significance of R^1 and R^2, etc., see accompanying equation. [b] For the significance of the Roman numerals, see accompanying equation. [c] This figure is based on the amount of hydride placed in the extractor thimble. Because of the rapidity of the polymerization the solution soon became very viscous and the reaction was stopped at about one-sixth of the usual reaction time; undoubtedly extraction of the hydride into the reaction solution was incomplete. [d] For results at other molar ratios see ref. 1.

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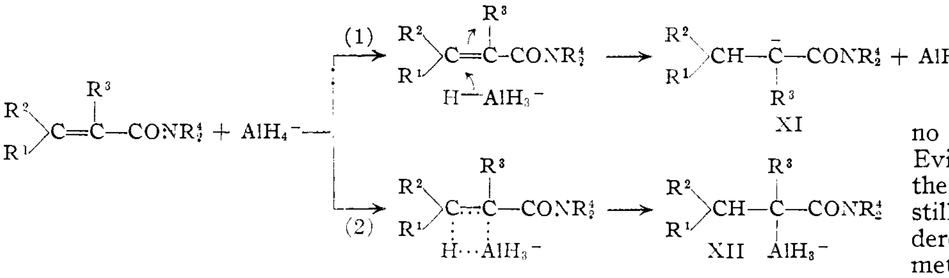
[1] For the preceding paper in this series see H. R. Snyder and Robert E. Putnam, THIS JOURNAL, **76**, 31 (1954).

[2] National Science Foundation Fellow, 1952–1953.

appreciable amount of dimer along with a low molecular weight polymer. If R^1 is quite large only the dimer is obtained. Thus N,N-diethylcinnamamide (X) and N,N-diethylfurylacrylamide (IX) give better than 50% of dimeric product and no polymer.

Even more striking is the effect of a second substituent on the reaction course. N,N-Diethyl-β-methylcrotonamide (VII), on treatment with lithium aluminum hydride, yielded 47% of N,N-diethylisovaleramide (identified by hydrolysis to isovaleric acid and conversion to isovaleranilide) and 12% of the dimeric product, N,N,N′,N′-tetraethyl-α-isopropyl-β,β-dimethylglutaramide. On the other hand two attempts to reduce N,N-diethyl-α-methylcrotonamide yielded only basic products. In addition the unsaturated amide could be recovered to the extent of 30–40%.

Undoubtedly the reactions leading to the saturated amides and the dimers and polymers all are initiated by attack of the ethylenic function by an aluminohydride anion.[3] The two most plausible modes of attack are those illustrated in the accompanying scheme.



Path 1 represents a simple hydride ion transfer from an aluminohydride ion to the unsaturated amide to give the anion XI. Hydrolysis of this anion, in the workup of the reaction mixture, would lead to the saturated amide II, and a Michael addition involving this anion and the unsaturated amide would generate a new anion which could be hydrolyzed to the dimer III or which could add to still another molecule of unsaturated amide yielding a trimer or, eventually, polymers IV. Path 2 consists in the addition of aluminohydride ion to the olefinic system yielding an organoaluminum compound XII, which by hydrolysis or addition to more of the unsaturated amide could generate saturated amide or dimer, trimer, etc.[4]

An argument against reaction as indicated by path 1 is found in the reaction of N,N-diethyl-β-methylcrotonamide. Treatment of 0.2 mole of the amide with 0.05 mole of lithium aluminum hydride gave about 0.1 mole of N,N-diethylisovaleramide along with about 0.02 mole of dimer as well as basic reduction products. The yield of the saturated amide alone was about twice the theoretical amount according to path 1, if the liberated aluminum hydride plays no further role. To account for the observed products by the stoichiometry of path 2 requires only that the primary organoaluminum hydride ion combine with more of the unsaturated amide in a reaction similar to that by which it is formed ($RAlH_3^- \rightarrow R_2AlH_2^- \rightarrow R_3AlH^-$) before the occurrence of the organometallic synthesis and hydrolysis which lead to the various products.

Reaction according to path 2 provides a satisfactory explanation of the effects of groups on the nature and yields of the products. The introduction of a single methyl group at the β-position of the acrylamide system probably does not greatly hinder the primary attack (formation of a substance of type XII), but the hindrance to organometallic synthesis by identical methyl groups in the subsequent steps reduces the extent of polymerization (compare VI and V in Table I). A second methyl group in the β-position (compound VII) exaggerates the effect. Most of the product is simple saturated amide arising by hydrolysis of addition products of type XII; only a little dimer, and no polymer, is formed. Evidently the addition of the aluminohydride ion still is not seriously hindered, but the organometallic synthesis is almost stopped. Comparison of compounds IX and X, which have as a single substituent at R^1 a bulky aromatic group, with the crotonamide derivative VI shows that the larger group is more effective in interfering with the polymerization. Finally a single methyl group in the α-position (see compound VIII, N,N-diethyl-α-methylcrotonamide) evidently blocks the primary addition; no products arising by reaction at the olefinic linkage are formed.

The nature of the group R^4 has a different, but equally important, effect on the course of the reaction of an unsaturated amide. Competing with the reactions discussed above are two hydrogenolytic cleavages of the amide function itself. Hydrogenolysis of the carbon–oxygen bond to yield a tertiary amine group occurred to some extent in all the reactions studied, as shown by the production of basic products, sometimes in relatively high yield. In general the basic fractions were complex mixtures of which the major components seemed to be amino amides formed by partial reduction of compounds of type III. However, when cinnamic piperidide was reduced the basic fraction was composed almost entirely of N-cinnamylpiperidine, along with some higher boiling bases. In contrast, N,N-diethylcinnamamide yielded no isolable amount of the unsaturated amine. The basic fraction from a typical reduction of this amide gave what appears to be a mixture of XIII, XIV and XV, which could not be separated by distillation. The infrared spectrum of the mixture indicated the amino amides XIV and XV to be the

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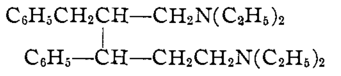
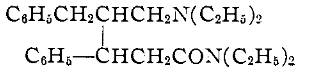
(3) For a summary of the information concerning the structure of lithium aluminum hydride and the mechanism of reduction by it see W. G. Brown in Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469; after this manuscript was prepared, V. Mićović and M. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953), reported an extensive study of the reduction of amides with this reagent.

(4) The addition of lithium aluminum hydride to an olefinic system has been observed by F. A. Hochstein and W. G. Brown [THIS JOURNAL, **70**, 3484 (1948)], and organoaluminum compounds are believed to be intermediates in the Ziegler polymerization of olefins [K. Ziegler, *Angew. Chem.*, **64**, 323 (1952)].



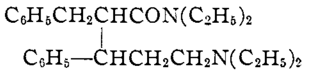
$$\begin{array}{l} C_6H_5CH_2CH{-}CH_2N(C_2H_5)_2 \\ \qquad | \\ \quad C_6H_5{-}CH{-}CH_2CH_2N(C_2H_5)_2 \end{array}$$

XIII



$$\begin{array}{l} C_6H_5CH_2CHCH_2N(C_2H_5)_2 \\ \qquad | \\ \quad C_6H_5{-}CHCH_2CON(C_2H_5)_2 \end{array}$$

XIV



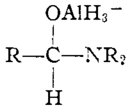
$$\begin{array}{l} C_6H_5CH_2CHCON(C_2H_5)_2 \\ \qquad | \\ \quad C_6H_5{-}CHCH_2CH_2N(C_2H_5)_2 \end{array}$$

XV

major components. Treatment of the mixture with picric acid resulted in the formation of a dipicrate having the composition expected of the salt of XIII.

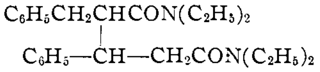
Although the structures of the basic products (XIII, XIV, XV) have not been proved, it can be stated that hydrogenolysis of the carbon–oxygen bond does not occur in the case of N,N-diethylcinnamamide until *after* the coupling reaction. In other words hydrogenolysis does not compete with the primary step (attack of the unsaturated function) in the sequence leading to the dimer. However, in the reaction of the piperidide comparable yields of dimeric amide III and unsaturated amine are formed, the two reactions being equally favored.

The initial step in the hydrogenolysis probably consists in nucleophilic attack of the amide carbonyl group by the aluminohydride ion, yielding an intermediate addition product, XVI. In this step the group NR_2 can have two effects. The first is simply steric in nature: as NR_2 becomes larger the more hindered will be the carbonyl group and consequently the less reactive. Secondly, the stronger NR_2 is in electron-donating properties the more it will cede electrons making the carbonyl group less susceptible to nucleophilic attack. The latter effect will be directly related to the base strength of the amine, R_2NH.



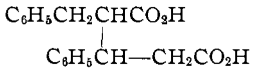
$$\begin{array}{c} OAlH_3^- \\ | \\ R{-}C{-}NR_2 \\ | \\ H \end{array}$$

XVI



$$\begin{array}{l} C_6H_5CH_2CHCON(C_2H_5)_2 \\ \qquad | \\ \quad C_6H_5{-}CH{-}CH_2CON(C_2H_5)_2 \end{array}$$

XVII



$$\begin{array}{l} C_6H_5CH_2CHCO_2H \\ \qquad | \\ \quad C_6H_5CH{-}CH_2CO_2H \end{array}$$

XVIII

The experimental results indicate that the piperidide group ($-CONC_5H_{10}$) is more susceptible to attack by aluminohydride ion than is the diethylcarbamido group [$-CON(C_2H_5)_2$]. Thus N,N-diethylcinnamamide is coupled before hydrogenolysis occurs; on the other hand, cinnamic piperidide is coupled and hydrogenolyzed at about the same rate. Since piperidine is a stronger base than diethylamine, the piperidide group should be more stable than the diethylcarbamido group toward hydrogenolysis. However, the $-NC_5H_{10}$ group is also smaller than the $-N(C_2H_5)_2$ group and so nucleophilic attack of $-CONC_5H_{10}$ is less hindered. Since cinnamic acid piperidide indeed forms amine more easily than does N,N-diethylcinnamamide, the steric effect of R^4 must overshadow in importance the electronic effect of $-N(R^4)_2$.

As indicated above there is a second possible reaction of amides with lithium aluminum hydride. It was noted that a volatile amine was produced in every reduction of an α,β-unsaturated amide. These amines could be produced only by hydrogenolysis of the carbon–nitrogen bond. In general, since they were not major products, no attempt was made to isolate them. However, when N-methyl-N-phenylcinnamamide was treated with lithium aluminum hydride the basic fraction was exclusively N-methylaniline (a 16% yield of reductively coupled amide also was obtained). The amount of amine isolated corresponded to hydrogenolysis of about 10% of the amide groups present, a far greater amount of carbon–nitrogen cleavage than occurred in any other reduction. This is especially interesting in view of the recent work of Wittig and Hornberger.[5] These workers attempted to convert N,N-dimethylcinnamamide and N-methyl-N-phenylcinnamamide to cinnamaldehyde by inverse addition of a minimum amount of hydride. The products obtained were not aldehydes and so were not investigated further. Since the diethylamide and N-methylanilide of cinnamic acid under similar conditions have been shown to give reductively coupled products it is reasonable to assume that Wittig and Hornberger obtained such products.

In no case could the other product, an aldehyde (or its reduction product), be isolated. However, evidence for its existence was obtained. The infrared spectra of all of the dimeric amides showed an absorption band characteristic of a hydroxyl-containing impurity. These compounds could arise from further reduction of the aldehyde produced. In two cases infrared spectra showed distinct aldehyde absorptions. A small, high boiling, neutral fraction from the reduction of N,N-diethyl-α-methylcrotonamide contained a high proportion of aldehyde. Likewise, a trimeric product present in the basic fraction from the reduction of N,N-diethylcrotonamide contained a small amount of aldehyde as an impurity.

With the evidence available it is not possible to state whether hydrogenolysis of the carbon–nitrogen bond occurs before or after coupling of α,β-unsaturated amides. Two generalizations are possible: 1, an amide formed from methylaniline is cleaved to aldehyde and amine more readily than one from diethylamine or piperidine[5a]; 2, a methylanilide is more susceptible to carbon–nitrogen than to carbon–oxygen cleavage. The reason for this behavior is again found in a consideration of the size of the groups involved. In order for hydrogenolysis of the carbon–oxygen bond to occur, the intermediate, XVI, must react further with some entity capable of donating a hydride ion. This entity may be aluminohydride ion or another ion of type XVI. If the NR_2 group is large enough to prevent further attack, then preferential

(5) G. Wittig and P. Hornberger. *Ann.*, **577**, 11 (1952).

(5a) NOTE ADDED IN PROOF.—Since this was written, F. Weygand, G. Eberhardt, H. Linden, F. Schäfer and O. Eigen (*Angew. Chem.*, **65**, 525 (1953)) have found the reduction of N-methylanilides with lithium aluminum hydride to be an attractive method for the preparation of aldehydes.

hydrogenolysis of the carbon–nitrogen bond will occur. Since methylaniline is considerably larger than either diethylamine or piperidine it is not surprising that carbon–nitrogen cleavage occurs while in the case of the other amides the reaction preferred is carbon–oxygen cleavage. A similar effect was noted by Mousseron, Jacquier, Mousseron-Canet and Zagdouin.[6] These authors observed that the piperidide, N-methylanilide and dibutylamide of cyclohexanecarboxylic acid undergo carbon–nitrogen hydrogenolysis by lithium aluminum hydride while the dimethylamide exhibits carbon–oxygen cleavage.

As has been shown above, the sizes of the substituent groups, R^1, R^2, R^3 and R^4, have pronounced effects on the reaction of the unsaturated amide I with lithium aluminum hydride. A second, equally interesting effect may also be attributed to the nature of these groups. In the reduction of N,N-diethylcrotonamide, N,N-diethylcinnamamide, N-methyl-N-phenylcinnamamide and cinnamic piperidide strong evidence for a stereospecific formation of the dimeric product III was obtained. Thus, in all of the above reductions only one of the two possible racemic forms of III was isolated.

The reduction of N,N-diethylcinnamamide provides the clearest example of stereospecificity. N,N,N′,N′-Tetraethyl-α-benzyl-β-phenylglutaramide (XVII), melting at 126°, was obtained in 53% yield. No other neutral product was isolated; indeed, most of the original amide not converted to XVII could be accounted for in basic products also dimeric in nature. That XVII is one racemic form only is indicated by its sharp melting point. Hydrolysis of XVII gave α-benzyl-β-phenylglutaric acid (XVIII), melting point 182–183°, which also proved to be one racemic form. This was shown by subsequent isolation of its diasteroisomeric racemate from a different source.

In an experiment with N,N-diethylcrotonamide a liquid dimer was produced in 29% yield.[1] After distillation and hydrolysis with 20% hydrochloric acid, an acid melting at 97–99° was obtained. This acid was identical with *one* of the racemic α-ethyl-β-methylglutaric acids of Michael.[7] That the isomeric amide was not produced in comparable yield can be deduced from the observation that over 85% of the unsaturated amide was accounted for in isolated products.

The reduction of cinnamic piperidide and N-methyl-N-phenylcinnamamide also gave products each of which proved to be only one of the two possible *dl* pairs. Here, however, the failure to isolate high yields of products throws some doubt on the possibility of a stereospecific reaction. It is interesting to note that the dimer obtained from N-methyl-N-phenylcinnamamide has the same stereochemical configuration as XVII (as shown by hydrolysis to the same acid as XVII). On the other hand, the dimer from cinnamic piperidide apparently is of diastereoisomeric configuration since hydrolysis yielded the diastereoisomer (melting point 161–162°) of XVIII.

Since N,N-diethylcinnamamide, N-methyl-N-phenylcinnamamide and cinnamic acid piperidide were all prepared from *trans*-cinnamoyl chloride it is reasonable to assume that they all have the *trans* configuration. Thus the configurational differences observed in their dimeric reduction products should be due to the nature of the amide group only. It would not be reasonable to postulate an actual mechanism to explain this behavior without a knowledge of the configurations of the product amides.

Experimental[8,9]

Preparation of Amides.—All of the amides prepared were synthesized from the acids *via* the acid chlorides. The general procedure is given in reference 1. In all but one case thionyl chloride was used to convert the acid to its chloride. Acrylyl chloride was prepared by the method of Rehberg, Dixon and Fisher.[10]

Reduction of N,N-Diethyl-β-methylcrotonamide.—The following procedure is typical of the method used in the reduction of α,β-unsaturated amides.

In a flask equipped with a Soxhlet extractor and efficient reflux condenser were placed 31 g. of N,N-diethyl-β-methylcrotonamide and 600 ml. of anhydrous ether (dried over sodium hydride). The entire system was swept out with nitrogen and an ordinary paper thimble containing 2 g. of lithium aluminum hydride (Metal Hydrides, Inc.) was placed in the extractor. Refluxing was begun immediately. The initial extraction caused a violent reaction; subsequent extractions did not have as great an effect. The lithium aluminum hydride reacted with the paper thimble to some extent but not enough to cause any difficulty. Refluxing was maintained for four hours. Wet ether was added to the reaction mixture and the precipitated inorganic material was removed by filtration. The ether filtrate was extracted with 10% hydrochloric acid, dried over anhydrous sodium sulfate and the ether was removed on a steam-cone. There remained 22.5 g. of an oil with a strong menthol-like odor. The oil was fractionated under reduced pressure.

Fraction	B.p., °C.	Pressure, mm.	Wt., g.
1	49–51	0.3	2.5
2	51–54	.3	11.3
3	54–115	.3	1.0
4	115–134	.3	5.1

Fractions 1 and 2 were combined and redistilled through a modified Claisen column.

Fraction	B.p., °C.	Pressure, mm.	Wt., g.	Ref. index (20°)
1	28–104	20	0.5	1.4458
2	104–106	20	11.2	1.4455
3	106	20	1.6	1.4456

The infrared spectrum and nitrogen analysis of fraction 2 indicated it to be N,N-diethylisovaleramide (yield 47%).

Anal. Calcd. for $C_9H_{19}NO$: N, 8.90. Found: N, 8.92.

A sample of this amide was hydrolyzed with 20% sulfuric acid. The crude isovaleric acid so obtained was treated with thionyl chloride. After removal of excess thionyl chloride *in vacuo* a benzene solution of aniline was added. The crude isovaleranilide obtained melted at 98–105°. Recrystallization from cyclohexane gave pure amide of m.p. 112.5–113°. This was identical with authentic isovaleranilide (as shown by infrared spectra and mixed m.p.).

Fraction 4 was redistilled in a Holtzmann column.

Fractions 5 and 6 proved to be N,N,N′,N′-tetraethyl-α-isopropyl-β,β-dimethylglutaramide (yield 12%).

Anal. Calcd. for $C_{18}H_{36}N_2O_2$: C, 69.22; H, 11.61; N, 8.97. Found: C, 69.80; H, 11.45; N, 8.54.

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(6) M. Mousseron, R. Jacquier, M. Mousseron-Canet and R. Zagdouin, *Compt. rend.*, **235**, 177 (1952).

(7) A. Michael and J. Ross, THIS JOURNAL, **53**, 1150 (1931).

(8) All melting points are uncorrected.

(9) Microanalyses by Mrs. Lucy Chang, Mrs. Esther Fett, Mrs. Katherine Pih and Mr. Joseph Nemeth. Infrared analyses by Miss Helen Miklas.

(10) C. E. Rehberg, M. B. Dixon and C. H. Fisher, THIS JOURNAL, **67**, 208 (1945).

Fraction	B.p., °C.	Pressure, mm.	Wt., g.	Ref. index (20°)
1	28–130	1.2	0.2	1.4970
2	130–132	1.5	.4	1.4963
3	132	1.5	.5	1.4975
4	132–160	2.2	.1	1.4880
5	160–165	2.2	1.8	1.4836
6	165–172	2.2	2.0	1.4840

The poor analytical results were due to decomposition of the material during distillation. Further fractionation gave samples of even higher impurity. Since the infrared spectrum was exactly what would be expected for N,N,N',N'-tetraethyl-α-isopropyl-β,β-dimethylglutaramide, this amide was hydrolyzed and the solid acid was characterized.

α-Isopropyl-β,β-dimethylglutaric Acid.—A solution of 2 g. of N,N,N',N'-tetraethyl-α-isopropyl-β,β-dimethylglutaramide in 50 ml. of 20% hydrochloric acid was refluxed for 24 hours. The solution was cooled and extracted with four 20-ml. portions of ether. The ether extract was washed with 5% sodium hydroxide; the aqueous layer was separated and then was acidified with 10% hydrochloric acid. The acid solution was extracted with three 20-ml. portions of ether, the ether layer was dried over anhydrous sodium sulfate and the ether was evaporated under an air jet. There remained 327 mg. (25%) of an oil which solidified on standing (m.p. 86–89°). Two recrystallizations from cyclohexane gave white crystals of α-isopropyl-β,β-dimethylglutaric acid, m.p. 88–90°.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.44; H, 9.11.

Polymerization of N,N-Diethylacrylamide.—The reaction was run in the usual way. The quantities used were as follows: 20 g. of amide, 600 ml. of anhydrous ether and 1.5 g. of lithium aluminum hydride. The first extraction caused an extremely violent reaction and an immediate copious precipitate formed. Refluxing was continued for 30 min. The reaction mixture was carefully decomposed with water and the precipitate was filtered with the aid of a filter dam. After air drying, the mixed polymer and inorganic material weighed 21 g. The ether filtrate was extracted with 10% hydrochloric acid and the ether layer was dried over anhydrous sodium sulfate. Evaporation of the ether yielded a negligible amount of viscous oil (0.3 g.). The hydrochloric acid extract was made basic with 5% sodium hydroxide. A white, gummy, basic polymer of N,N-diethylacrylamide separated which, after drying in a vacuum desiccator at 20 mm., weighed 2 g. This was not further investigated.

An 8-g. sample of the mixed polymer and inorganic matter was placed in the cup of a Soxhlet extractor and extracted with benzene for 70 hr. At this time there remained in the cup 1.5 g. of white solid which was evidently alumina and lithium hydroxide since it was almost completely soluble in cold 20% hydrochloric acid. Evaporation of the benzene and drying in a vacuum desiccator at 0.03 mm. gave 6 g. of a rubber-like polymer. This was only slightly soluble in organic solvents (including benzene). Its slight solubility in benzene with the production of a gel was interpreted as the result of cross-linking, perhaps by means of aluminum-carbon bonds.

Attempted Reduction of N,N-Diethyl-α-methylcrotonamide.—The quantities used were as follows: 25 g. of amide, 600 ml. of anhydrous ether and 1.9 g. of lithium aluminum hydride. The reduction was run in the usual way; refluxing was maintained for 4 hr. Wet ether was cautiously added to the mixture, causing a violent reaction. The precipitated inorganic material was removed by filtration and the filtrate was washed with 10% hydrochloric acid. The ether layer was dried over anhydrous sodium sulfate. Evaporation of the ether and fractionation of the residual oil gave 7.3 g. of N,N-diethyl-α-methylcrotonamide (shown by identity of infrared spectrum with that of an authentic sample), b.p. 76–80° (2.7 mm.), 29.4% recovery. A higher boiling material (129–131° (2.7 mm.)) was also obtained (1.3 g.). An infrared spectrum indicated a mixture of compounds containing alcohol, aldehyde and amide groups. This was not further investigated because of the poor yield.

The hydrochloric acid extract was made basic and worked up in the usual way. Five grams of a foul smelling oil was obtained. This was not investigated further.

Reduction of N,N-Diethylcinnamamide.—The reduction was run in the usual fashion. The quantities used were as follows: 35.8 g. of amide, 500 ml. of anhydrous ether and 3.8 g. of lithium aluminum hydride. Refluxing was maintained for 3.5 hr. The initial extraction caused a violent reaction and the appearance of a bright orange color. This color was gradually discharged by subsequent extractions. The reaction mixture was decomposed with wet ether, filtered to remove inorganic material and allowed to stand overnight. N,N,N',N'-Tetraethyl-α-benzyl-β-phenylglutaramide (13.05 g.) separated in long white needles, m.p. 121–124°. After removal of the precipitate the ether filtrate was extracted with 1 *N* hydrochloric acid. The ether layer was dried over calcium chloride, concentrated and cooled to 8°. In this way an additional 2.7 g. of crude amide (m.p. 108–116°) was obtained. Extraction of the inorganic precipitate with ether and evaporation of the ether gave 3.55 g. of crude amide (m.p. 109–115°). The total yield of amide was 19.3 g. (52.5%). In two other experiments yields of 45 and 46% were obtained. Two recrystallizations from ether gave pure white needles, m.p. 126°.

Anal. Calcd. for $C_{26}H_{36}N_2O_2$: C, 76.42; H, 8.88; N, 6.86. Found: C, 76.57; H, 8.85; N, 6.57.

The hydrochloric acid extract was made basic with 10% sodium hydroxide and extracted with ether. The ether layer was dried over anhydrous sodium sulfate and the ether was distilled. The residual oil weighed 6.4 g. and had a strong amine odor. On standing for two weeks at 8° the amine fraction deposited 2.7 g. of white crystals which melted at room temperature. These were separated by decantation. The liquid amine was distilled under reduced pressure, the main fraction boiling over a 50° range (150–200°) at 0.4 mm. An infrared spectrum indicated a mixture containing at least one compound with an amide carbonyl.

To 1 g. of the mixture of liquid amines in 10 ml. of alcohol was added a saturated solution of picric acid in ethanol. A yellow oil precipitated immediately. This oil eventually crystallized on standing in the ethanol solution. Several recrystallizations from ethanol gave a pure yellow solid of melting point 178–180°. Its analysis indicated a dipicrate of N,N,N',N'-tetraethyl-2-benzyl-3-phenyl-1,5-pentanediamine.

Anal. Calcd. for $C_{38}H_{46}N_8O_{14}$: C, 54.41; H, 5.53; N, 13.36. Found: C, 54.62; H, 5.24; N, 13.19.

Thus the liquid amine is perhaps a mixture of N,N,N',N'-tetraethyl-2-benzyl-3-phenyl-1,5-pentanediamine and at least one amine containing an amide group. The solid amine undoubtedly contains amide groups also. Since attempts at the preparation of derivatives (methiodide and picrate) were unsuccessful the solid amine was not investigated further.

α-Benzyl-β-phenylglutaric Acid, 183° Isomer.—A mixture of 7.4 g. of N,N,N',N'-tetraethyl-α-benzyl-β-phenylglutaramide and 100 ml. of 1:1 hydrochloric acid was refluxed for 7 hr. The oil initially formed gradually solidified during the reaction. The mixture was cooled to room temperature and filtered. The filtrate was extracted with ether and the ether layer was used to dissolve the solid previously obtained. The ether solution was extracted with 10% sodium hydroxide. The aqueous layer was acidified with 20% hydrochloric acid and extracted with ether. The ether layer was dried over anhydrous sodium sulfate; evaporation of the ether on a steam-cone gave 5.1 g. of crude acid of melting point 160–175°. This crude product was exhaustively extracted with hot benzene. α-Benzyl-β-phenylglutaric acid, insoluble in benzene, was obtained as a white powder, m.p. 178–180° (3.3 g.). On concentration and cooling the benzene solution deposited 1.5 g. of white crystals, m.p. 155–165°. This was assumed to be a mixture of α-benzyl-β-phenylglutaric acid and its two isomeric half-amides. Hydrolysis of this mixture with 1:1 hydrochloric acid and work-up as before yielded 1 g. of α-benzyl-β-phenylglutaric acid, m.p. 172–183°. The total yield of crude acid was 81%. Recrystallized from 10% ethanol it melted at 182–183°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.45; H, 6.25.

Reduction of N-Methyl-N-phenylcinnamamide.—The reduction was run in the usual way. The quantities used were as follows: 23.7 g. of amide, 500 ml. of anhydrous ether and 2 g. of lithium aluminum hydride. Refluxing was maintained for 3 hr. The initial extraction caused the appearance of a bright yellow color which was discharged by subsequent extractions. The reaction mixture was decomposed with wet ether and the precipitated inorganic material was removed by filtration. The ether filtrate was extracted with 100 ml. of 0.5 *N* hydrochloric acid. The ether layer was separated, dried over anhydrous sodium sulfate and the ether was removed on a steam-cone leaving a colorless oil. High-boiling petroleum ether was added and a white crystalline solid (2.8 g.) separated; it melted at 141–143.5°. After standing for one month the solution deposited an additional 1 g. of crystals, m.p. 138–147°. The total yield of N,N′-dimethyl-N,N′-diphenyl-α-benzyl-β-phenylglutaramide was 16%. Recrystallization from high-boiling petroleum ether gave white needles; m.p. 146–146.5°.

Anal. Calcd. for $C_{32}H_{32}N_2O_2$: C, 80.64; H, 6.77; N, 5.86. Found: C, 80.94; H, 6.81; N, 6.13.

The petroleum ether was removed from the filtrate *in vacuo*. The resulting oil could not be induced to crystallize nor could it be distilled without extensive decomposition. It was not investigated further.

The hydrochloric acid extract was made basic with 10% sodium hydroxide and the resulting oil was taken up in ether. The ether layer was dried over anhydrous sodium sulfate and the ether was removed on a steam-cone leaving 0.95 g. of a light brown oil with the odor of methylaniline.

The oil was dissolved in 15 ml. of pyridine and a solution of 2.5 g. of benzenesulfonyl chloride in 5 ml. of pyridine was added. The reaction mixture became warm and turned light brown. It was allowed to stand at room temperature for 24 hr. It was then poured into 75 ml. of 20% hydrochloric acid and the red oil which precipitated was allowed to stand in the solvent till solidification occurred. The solid was filtered and air-dried; it weighed 1.05 g. (47%). Several recrystallizations from 80% ethanol gave pure white needles of N-methylbenzenesulfonanilide of melting point 78–79°. Admixture with an authentic sample of N-methylbenzenesulfonanilide (m.p. 78–80°) failed to depress the melting point (78–80°).

A sample of the N,N′-dimethyl-N,N′-diphenyl-α-benzyl-β-phenylglutaramide described above was hydrolyzed with 20% hydrochloric acid. The acid obtained was identical with the 183° isomer of α-benzyl-β-phenylglutaric acid obtained from N,N,N′,N′-tetraethyl-α-benzyl-β-phenylglutaramide.

Reduction of Cinnamic Piperidide.—The reduction was run in the usual way. The quantities used were as follows: 21.5 g. of amide, 600 ml. of ether and 1 g. of lithium aluminum hydride. Refluxing was maintained for two hours. The initial extraction caused the appearance of a bright yellow color which was never completely discharged. Wet ether was added cautiously and the resulting precipitate of inorganic material was removed by filtration. A strong odor of piperidine was noted, indicating hydrogenolysis of the amide group had taken place to some extent. The ethereal filtrate was cooled in an ice-box. In this way a white solid (A) of melting point 141–146° separated (2.2 g.). This was removed by filtration and the filtrate was extracted with 10% hydrochloric acid. The ether layer was dried over anhydrous sodium sulfate and the ether was evaporated on a steam-cone. There remained 9.0 g. of a colorless oil. A little ether and a few crystals of the previously obtained solid were added. The mixture was cooled to 8° and was kept at this temperature for several days. Another 2.1 g. of amide (B) (m.p. 129–137°) was obtained. To the residual oil was added 10 ml. of cyclohexane and the solution was allowed to stand for several months during which time 4.1 g. of a solid (C) of melting point 105–120° separated.

Solids A and B were combined and recrystallized three times from high-boiling petroleum ether giving a pure product melting at 147–148°. This was α-benzyl-β-phenylglutaric dipiperidide (yield 20%).

Anal. Calcd. for $C_{28}H_{36}N_2O_2$: C, 77.74; H, 8.39; N, 6.48. Found: C, 77.94; H, 8.33; N, 6.37.

Recrystallization of C from ethanol gave cinnamic piperidide, m.p. 118–120° (19% recovery).

The hydrochloric acid extract of the crude reaction product was made basic with 10% sodium hydroxide and was extracted with ether. The ether layer was dried over anhydrous sodium sulfate and the ether was evaporated on a steam-cone. There remained 4.2 g. of an oil with a strong piperidine odor. This was combined with 5.8 g. of the corresponding oil from a similar reduction of cinnamic acid piperidide. The combined amine fractions were distilled through a Holtzmann column at reduced pressure.

Fraction	B.p., °C.	Pressure, mm.	Wt., g.
1	88–107	0.6	1.0
2	107–108	.6	1.2
3	108	.6	4.5
4	108	.6	0.9
5	Pot residue	.6	

The infrared spectrum of a sample of fraction 3 was nearly identical with that of diethylcinnamylamine indicating that fractions 2, 3 and 4 were probably N-cinnamylpiperidine.

Anal. (Fraction 3) Calcd. for $C_{14}H_{19}N$: C, 83.54; H, 9.50; N, 6.96. Found: C, 83.30; H, 9.55; N, 7.27.

α-Benzyl-β-phenylglutaric Acid, 161° Isomer.—A mixture of 1.1 g. of α-benzyl-β-phenylglutaric dipiperidide and 25 ml. of 20% hydrochloric acid was refluxed for 20 hr. The reaction mixture was cooled, extracted with ether till all solid had dissolved and the ether layer was decanted and extracted with 5% sodium hydroxide. The basic layer was acidified with 10% hydrochloric acid and cooled to 0°. The light brown precipitate was filtered and dried; it weighed 0.65 g. (83%), m.p. 142–155°. Three recrystallizations from benzene gave a pure white powder, m.p. 160–161°. Its infrared spectrum indicated a dibasic acid and was slightly different from that of the 182–183° isomer of α-benzyl-β-phenylglutaric acid. Thus it is probably the diastereoisomer of the 182–183° acid.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.73; H, 5.98.

Reduction of N,N-Diethylfurylacrylamide.—The reduction was run in the usual fashion. The quantities used were as follows: 19.3 g. of amide, 500 ml. of anhydrous ether and 1.9 g. of lithium aluminum hydride. Refluxing was maintained for three hours. The initial extraction caused a bright yellow color which was discharged by subsequent extractions. Wet ether was added and the precipitated inorganic material was removed by filtration. The ether filtrate was washed with 10% hydrochloric acid and dried over anhydrous sodium sulfate. Evaporation of the ether left 10.8 g. of a colorless oil. This oil was distilled through a short path apparatus. N,N,N′,N′-Tetraethyl-α-furfuryl-β-furylglutaramide distilled at 195° (0.5 mm.) and weighed 9.8 g. (53%). A second experiment gave a yield of 43.5%.

Anal. Calcd. for $C_{22}H_{32}N_2O_4$: C, 68.01; H, 8.17; N, 7.21. Found: C, 68.21; H, 8.37; N, 7.10.

On treatment with water N,N,N′,N′-tetraethyl-α-furfuryl-β-furylglutaramide formed a monohydrate which recrystallized from cyclohexane in large plates of melting point 59–61°.

Anal. Calcd. for $C_{22}H_{34}N_2O_5$: C, 65.02; H, 8.63; N 7.06. Found: C, 65.47; H, 8.47; N, 6.85.

Urbana, Illinois