

was added in 15 min. to 8.0 g. (0.027 mole) of the trichloropropeneboronic ester **2** stirred under nitrogen. After 3 hr. the slurry was treated with ether and water, and the organic phase was washed with saturated sodium chloride and dried over magnesium sulfate. Distillation yielded 5.5 g. (61%) of dibutyl 1,1-dichloro-3-butoxypropene-3-boronate (**3c**), b.p. 88–90° (0.05 mm.). A 56% yield of **3c** also was obtained by warming 5.0 g. of **2** with

10 ml. of butanol and 5 ml. of *t*-butylamine for 5 min. at 35–40°. The analytical sample was redistilled through a spinning-band column; b.p. 84–85° (0.01 mm.); strong infrared bands at 6.18, 6.72, 6.80, 7.0, 7.3–7.7, 7.95, 8.09, 8.35, 8.90, 9.1 (broad), 9.6, 9.70, 9.3–9.4, 11.17, and 11.6  $\mu$ .

*Anal.* Calcd. for  $C_{15}H_{29}BCl_2O_3$ : C, 53.13; H, 8.62; B, 3.19; Cl, 20.91. Found: C, 53.27; H, 8.81; B, 3.39; Cl, 20.99.

## Reactions of 1,1-Dichloro-2,2-diphenylethene and 1,1,1-Trichloro-2,2-diphenylethane with Nucleophilic Reagents. A New Method for Certain Allenes<sup>1</sup>

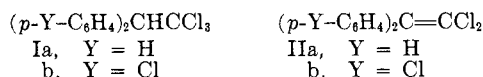
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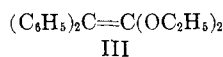
Received March 25, 1963

1,1,1-Trichloro-2,2-diphenylethane (**Ia**) underwent dehydrohalogenation with potassium amide in liquid ammonia to form 1,1-dichloro-2,2-diphenylethene (**IIa**), which reacted further with this reagent to give diphenylacetonitrile. The latter reaction presumably involved nucleophilic substitution, followed by dehydrohalogenation. Dichloroethene **IIa** and its *p*-chloro derivative **IIb** reacted with potassium diphenylmethide in liquid ammonia to afford 1,1,3,3-tetraphenylallene (**VIa**) and its *p*-chloro derivative **VIb**, respectively. These reactions also presumably involved nucleophilic substitution, followed by dehydrohalogenation. However, **IIa** was converted by potassium triphenylmethide slowly in liquid ammonia and faster in refluxing tetrahydrofuran to tolane. This product presumably arose through displacement on halogen, followed by rearrangement. **IIa** was converted to tolane by phenyllithium in ether.

It is well known that the 1,1,1-trichloro-2,2-diarylethanes (**Ia,b**) readily undergo dehydrohalogenation with refluxing, ethanolic potassium hydroxide to form the 1,1-dichloro-2,2-diarylethenes (**IIa,b**),<sup>2</sup> which are relatively stable towards this reagent.<sup>3</sup>



However, dichloroethene **IIa** has been converted to diphenylacetic acid by treatment with alcoholic potassium hydroxide at 150° (under pressure)<sup>4</sup> and by treatment with sodium ethoxide at 180° followed by hydrochloric acid.<sup>5</sup> In the latter reaction, the twofold nucleophilic substitution product **III** was assumed to be an intermediate.<sup>5</sup>



In the present investigation a study was made of the reactions of **Ia** and, especially, those of **IIa,b** with some, more strongly nucleophilic reagents.

Like potassium hydroxide and sodium ethoxide, potassium amide in liquid ammonia readily effected dehydrohalogenation of **Ia** to form **IIa**. However, in contrast to the two former nucleophiles, potassium amide reacted further with **IIa** at the same temperature to give diphenylacetonitrile (**IV**) (equation 1, Table I).

Table I shows that an excellent yield of **IIa** was obtained from **Ia** employing molecular equivalents of

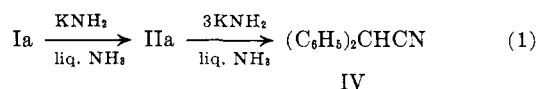


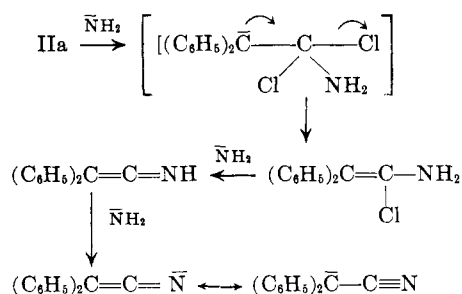
TABLE I  
REACTIONS OF HALIDES **Ia** AND **IIa** WITH POTASSIUM AMIDE IN LIQUID AMMONIA

Halide	Mol. equiv. of reagent	Mode of addition	Product	Yield, %
<b>Ia</b>	1	Inverse	<b>IIa</b>	98
<b>Ia</b>	4	Direct	<b>IIa</b>	10 <sup>a</sup>
			<b>IV</b>	87 <sup>a</sup>
<b>IIa</b>	1	Direct	<b>IV</b>	33 <sup>b</sup>
<b>IIa</b>	3	Direct	<b>IV</b>	88 <sup>c</sup>
<b>IIa</b>	3.7	Direct	<b>IV</b>	90 (98) <sup>a</sup>

<sup>a</sup> Determined by v.p.c. <sup>b</sup> 66% of **IIa** was recovered. <sup>c</sup> 10% of **IIa** was recovered (by v.p.c.).

the reactions by the inverse addition procedure, and that excellent yields of **IV** were obtained from **Ia** and **IIa** with excess of the reagent. The conversion of **IIa** to the anion of **IV** may be accounted for by nucleophilic substitution, followed by dehydrohalogenation and, finally, by ionization (Scheme A). The nucleophilic substitution presumably involves an addition-elimination mechanism.

SCHEME A



In agreement with Scheme A, three molecular equivalents of the reagent appear to be involved in the conversion of **IIa** to **IV**, since the yield was only 33% with

(1) Supported by the Army Research Office (Durham) and the National Science Foundation.

(2) See, for example, K. Brand and A. Busse-Sundermann, *Ber.*, **75**, 1819 (1942); S. J. Cristol, *J. Am. Chem. Soc.*, **67**, 1494 (1945).

(3) In contrast to trichloroethane **Ia**, the corresponding trifluoroethane is converted to diphenylacetic acid and its ethyl ester even by refluxing ethanolic potassium hydroxide; see R. Mechoilam, S. Cohen, and A. Kaluszyn, *J. Org. Chem.*, **21**, 801 (1956).

(4) F. E. Sheibley and C. F. Prutton, *J. Am. Chem. Soc.*, **62**, 840 (1940); O. Grummett, A. Buck, and A. Jenkins, *ibid.*, **67**, 156 (1945); F. Gatzl and W. Stanbach, *Helv. Chim. Acta*, **29**, 563 (1946).

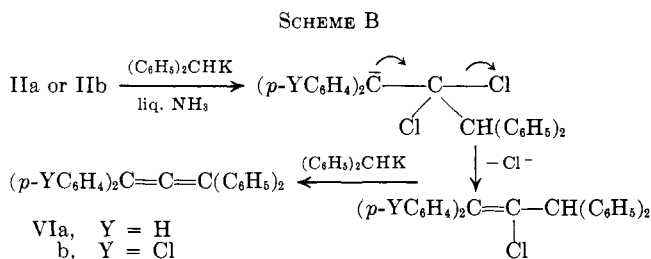
(5) E. E. Harris and G. B. Frankforter, *J. Am. Chem. Soc.*, **48**, 3144 (1926).

one equivalent, and almost the maximum yield was obtained with three equivalents (see Table I).

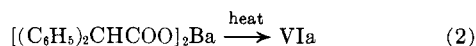
Similarly, potassium diphenylmethide effected dehydrohalogenation of trihalide Ia in liquid ammonia and then reacted further with the resulting dihalide IIa under the same conditions. However, the initial reaction was more complex than that with potassium amide. Addition of trihalide Ia to an excess of potassium diphenylmethide afforded a mixture of products, though a 75% yield of dihalide IIa was obtained from trihalide Ia when molecular equivalents of the reactants were employed by the inverse addition procedure. Only a 31% yield of IIa has been realized recently with molecular equivalents of reactions by the direct addition procedure.<sup>6</sup> The last experiment afforded also a little (3%) tetraphenylethane (V), which might possibly have arisen through displacement on halogen, followed by alkylation of unchanged potassium diphenylmethide by the resulting benzhydryl chloride.



Interestingly, the dichloroethene IIa reacted with potassium diphenylmethide in liquid ammonia to form 1,1,3,3-tetraphenylallene (VIa) in 80–90% yields. Similarly IIb reacted with this reagent to give allene VIb in 90% yield. The inverse addition procedure was employed in this case to minimize the possible benzyne type of reaction involving the chlorine in the ring. These reactions may be accounted for by nucleophilic substitution, followed by dehydrohalogenation (Scheme B).



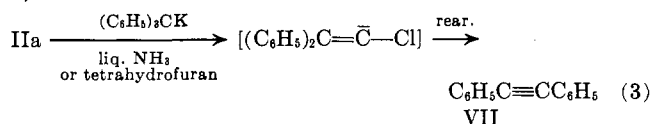
In agreement with Scheme B, about half of the original diphenylmethane used in preparing potassium diphenylmethide was regenerated (determined by v.p.c.). The identities of the products were readily established as allenes VIa,b, since they are known compounds (see Experimental). The structure of allene VIa was confirmed by an independent synthesis employing an earlier procedure (equation 2).<sup>7</sup>



The reactions indicated in Scheme B furnish a new method for the synthesis of certain allenes.<sup>8</sup> The starting dihaloethenes of type II appear best prepared from the trihalides of type I by means of alcoholic potassium hydroxide.<sup>2</sup>

In contrast to potassium diphenylmethide, potassium triphenylmethide reacted slowly with dichloroethene IIa in liquid ammonia to form toluene (VII) in 10% yield. This product was obtained in much better

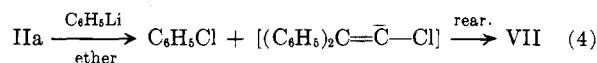
yield (67%) by effecting the reaction in refluxing tetrahydrofuran. It presumably arose through displacement on halogen followed by rearrangement (equation 3).



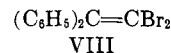
The displacement on halogen should afford also triphenylchloromethane, which could alkylate unchanged potassium triphenylmethide to give hexaphenylethane in equilibrium with triphenylmethyl. Actually there was obtained some high-melting, ether-insoluble material that appeared to be the corresponding peroxide.

The change in the course of reaction on passing from potassium diphenylmethide to potassium triphenylmethide may be ascribed to a steric factor, which might be expected to be more influential in the attack of the carbanion at the internal atom in the nucleophilic substitution than at the external atom in the displacement on halogen.

Similarly, dichloroethene IIa reacted with phenyllithium in refluxing ether to form toluene (VII) and chlorobenzene in yields of 67 and 71%, respectively (yields determined by v.p.c.). These products presumably arose through displacement on halogen (metal-halogen interchange), the resulting carbanion then undergoing rearrangement (equation 4).



This reaction appeared to occur more slowly than the similar reaction of the corresponding dibromoethene VIII with *n*-butyllithium, which has been observed by Curtin and Flynn<sup>9</sup> to afford VII in almost quantitative yield within a few minutes even at  $-35^\circ$ . This is not surprising, however, since halogen-metal interchange, which would be involved initially, is known to occur more readily with bromides than with corresponding chlorides and with *n*-butyllithium than with phenyllithium.<sup>10</sup>



Finally, in contrast to potassium amide and potassium diphenylmethide, lithium amide, potassium anilide, dipotassium phenylacetate, and dipotassium benzoylacetone failed to react appreciably with dihalide IIa in liquid ammonia. In contrast to phenyllithium, phenylmagnesium bromide failed to react with IIa in ether. The conditions employed with these apparently less nucleophilic reagents and the per cent of IIa recovered are summarized in Table II. At least certain of these reagents might be expected to react with IIa under more drastic conditions.

### Experimental<sup>11</sup>

**Reactions of Halides Ia and IIa with Potassium Amide.** Table I. (A) Reactions of Trihalide Ia.—To a stirred suspension of 7.28 g. (0.025 mole) of 1,1,1-trichloro-2,2-diphenylethane (Ia)<sup>12</sup>

(6) W. G. Kofron and C. R. Hauser, *J. Org. Chem.*, **28**, 577 (1963).

(7) D. Vorlaender and C. Siebert, *Ber.*, **39**, 1024 (1906).

(8) For a recent method of synthesis of VIa and other allenes, see H. Gilman and R. A. Tomasi, *J. Org. Chem.*, **27**, 3647 (1962).

(9) D. Y. Curtin and E. W. Flynn, *J. Am. Chem. Soc.*, **81**, 4714 (1959).

(10) See R. G. Jones and H. Gilman, *Org. Reactions*, VI, 342 (1951).

(11) Melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord by the potassium bromide pellet method.

(12) A. Baeyer, *Ber.*, **8**, 1098 (1872).

TABLE II  
REAGENTS THAT FAILED TO REACT WITH DIHALIDE IIa

Reagent	Mol. equiv.	Solvent (reflux)	Reaction time, hr.	Recovered IIa, %
LiNH <sub>2</sub>	4	Liq. NH <sub>3</sub>	2	98 <sup>a</sup>
KNHC <sub>6</sub> H <sub>5</sub> K	2	Liq. NH <sub>3</sub>	5	86 <sup>b,c</sup>
C <sub>6</sub> H <sub>5</sub> CHCOOK K	2	Liq. NH <sub>3</sub>	1.5	95
C <sub>6</sub> H <sub>5</sub> COCHCOCH <sub>2</sub> K	2	Liq. NH <sub>3</sub>	2	91
C <sub>6</sub> H <sub>5</sub> MgBr	3	Ether	17	88 <sup>b</sup>

<sup>a</sup> A vapor phase chromatogram showed only one peak, that of IIa; no peak for toluene or diphenylacetonitrile was observed. <sup>b</sup> Indicated by v.p.c. <sup>c</sup> A 94% recovery of aniline was indicated by v.p.c.

in 250 ml. of commercial, anhydrous liquid ammonia was added, through the stop-cock of an inverse addition flask, a solution of 0.025 mole of potassium amide in 350 ml. of liquid ammonia. After 1 hr., a small quantity (1 g.) of ammonium chloride was added and the ammonia was evaporated on the steam bath. Ether and water were added and the two layers were separated. The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. A vapor phase chromatogram of a sample of this ethereal solution showed only one peak, which corresponded to 1,1-dichloro-2,2-diphenylethene (IIa), and no detectable quantity of diphenylacetonitrile (see next experiment). The solvent was removed from the ethereal solution under reduced pressure to leave 6.25 g. (98%) of IIa, m.p. 75–77°. One recrystallization from 95% ethanol raised the melting point to 77–78.5°, which was undepressed on admixture with an authentic sample of IIa.<sup>13</sup>

In another experiment, a solution of 7.15 g. (0.025 mole) of Ia in dry ether was added to a stirred solution of 0.10 mole of potassium amide in 400 ml. of liquid ammonia. After stirring for 1 hr., the reaction mixture was worked up as described previously. A vapor phase chromatogram of a sample of the dried ethereal solution of the product indicated, by comparison of retention times with those of authentic samples, the presence of IIa (10%) and diphenylacetonitrile (87%).

(B) **Reactions of Dihalide IIa.**—To a stirred solution of 0.059 mole of potassium amide in 400 ml. of liquid ammonia was added 4.0 g. (0.016 mole) of 1,1-dichloro-2,2-diphenylethene (IIa) dissolved in 50 ml. of dry ether. After stirring for 3 hr., the reddish brown reaction mixture was neutralized with 5 g. of ammonium chloride. The ammonia was removed (steam bath) as an equal volume of ether was added. The resulting ethereal suspension was shaken with 200 ml. of water and the two layers were separated. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, and most of the solvent removed under reduced pressure. A vapor phase chromatogram of a small sample of the remaining solution indicated that less than 1% of the starting halide IIa was present; the chromatogram showed a single peak, the retention time of which corresponded to that of authentic diphenylacetonitrile (IV) (98%). The remaining solvent was removed and the residue was recrystallized from 95% ethanol to give 2.72 g. (90%) of IV, m.p. 72–74°, which was not depressed on admixture with an authentic sample of IV. The infrared spectra of the two samples were identical.

Similar experiments were performed (reaction time, 1 hr.) with 0.025 mole of dihalide IIa and 0.075 mole of potassium amide and with 0.025 mole each of IIa and potassium amide. The yields of IV and recovered IIa, which were determined by v.p.c., are given in Table I.

**Reaction of Trihalide Ia with Potassium Diphenylmethide.**—To a stirred suspension of 7.28 g. (0.0255 mole) of 1,1,1-trichloro-2,2-diphenylethane (Ia) in 200 ml. of liquid ammonia was added a solution of 0.0255 mole of potassium diphenylmethide in 300 ml. of liquid ammonia. The orange-red color of the reagent was discharged immediately. After 1 hr., the reaction mixture was worked up to give dihalide IIa in approximately 75% yield (determined by v.p.c.) along with unidentified products.

**Reactions of Dichloroethenes IIa,b with Potassium Diphenylmethide to Form Allenes.** (A) **Reaction of IIa.**—To a stirred

solution of 0.02 mole of potassium amide in 150 ml. of liquid ammonia was added 3.36 g. (0.02 mole) of diphenylmethane in 50 ml. of dry ether. The resulting orange-red solution of potassium diphenylmethide (0.02 mole) was stirred for 10 min. and a solution of 2.5 g. (0.01 mole) of 1,1-dichloro-2,2-diphenylethene (IIa) was added. The reaction mixture darkened and a precipitate formed. The mixture was stirred until the ammonia had evaporated and the residue was stirred with water and hexane. The insoluble material was removed by filtration and recrystallized from chloroform-methanol to give 1,1,3,3-tetraphenylallene (VIa) in 90% yield, melting at 164°. The melting point was undepressed on admixture with an authentic sample of VIa prepared in 24% yield by dry distillation of barium diphenylacetate.<sup>7</sup> Infrared spectra of the two samples were identical, and identical with the published spectrum.<sup>14</sup> The hexane solution was shown by v.p.c. to contain diphenylmethane (54%), identified by comparison of its retention time with that of an authentic sample.

**Reaction of IIb.**—To a stirred solution of 3.18 g. (0.01 mole) of 1,1-bis(4-chlorophenyl)-2,2-dichloroethene (IIb)<sup>2,15</sup> in 40 ml. of dry ether was added slowly 0.02 mole of potassium diphenylmethide in 75 ml. of liquid ammonia employing an inverse addition flask. The ammonia was replaced with ether and the resulting ethereal suspension was shaken with water. After filtering, the ethereal layer was separated and dried over Drierite. The solvent was removed and the residue recrystallized from methylene chloride-methanol to give 1,1-bis(4-chlorophenyl)-3,3-diphenylallene (VIb) in 90% yield, melting at 92°; reported m.p. 93–95°. <sup>16</sup>

*Anal.*<sup>17</sup> Calcd. for C<sub>27</sub>H<sub>18</sub>Cl<sub>2</sub>: C, 78.45; H, 4.39; Cl, 17.16. Found: C, 78.40; H, 4.35; Cl, 17.20.

**Reaction of Dichloroethene IIa with Potassium Triphenylmethide.** (A) **Reaction in Liquid Ammonia.**—To a stirred solution of 0.064 mole of potassium amide in 800 ml. of liquid ammonia was added 0.065 mole of triphenylmethane. The resulting red solution of potassium triphenylmethide (0.064 mole) was stirred for 25 min. and a solution of 7.96 g. (0.032 mole) of 1,1-dichloro-2,2-diphenylethene (IIa) in 50 ml. of dry ether was added. After 10 hr., 5 g. of ammonium chloride was added and the ammonia was replaced by ether. The resulting ethereal suspension was filtered, and a vapor phase chromatogram determined on a sample of the ethereal filtrate indicated a 10% yield of toluene (VII) and an 85% recovery of dihalide IIa.

(B) **Reaction in Tetrahydrofuran.**—A solution of 0.05 mole of potassium triphenylmethide in 600 ml. of liquid ammonia was prepared and the ammonia was evaporated (steam bath) as 300 ml. of tetrahydrofuran was added. The resulting solution was refluxed gently under a nitrogen atmosphere as a solution of 6.23 g. (0.025 mole) of 1,1-dichloro-2,2-diphenylethene (IIa) in 50 ml. of tetrahydrofuran was added slowly. After refluxing gently for 0.5 hr., the reaction mixture was cooled and a solution of 4 ml. of glacial acetic acid in ether was added. The mixture was filtered and the filtrate was analyzed by v.p.c. The chromatogram indicated the presence of 2.9 g. (67%) of toluene (VII) and some unchanged dihalide IIa. A small sample of VII was collected at the chromatograph exit port and recrystallized from ethanol to give crystals, m.p. 59–60°, undepressed on admixture with an authentic sample of VII. The infrared spectra of the two samples were identical.

**Reaction of Dihalide IIa with Phenyllithium.**—To a stirred solution of 0.05 mole of phenyllithium in 150 ml. of ether (under nitrogen) was added a solution of 4.97 g. (0.05 mole) of 1,1-dichloro-2,2-diphenylethene (IIa) in 50 ml. of ether. The reaction mixture was heated on the steam bath for 1 hr. and stirred for 3 hr. Ethanol (10 ml.) and water were added and the layers were separated. The ethereal layer was dried over anhydrous magnesium sulfate. A vapor phase chromatogram of a sample of the ethereal solution indicated 66% conversion of IIa to toluene (VII) and the presence of chlorobenzene (71% based on the yield of VII). A small sample of VII was collected from the chromatograph exit port and recrystallized from 95% ethanol to give crystals melting at 60–61°, undepressed on admixture with an authentic sample of VII. The infrared spectra of the two samples were identical.

(14) W. Otting, *Ber.*, **87**, 611 (1954).

(15) See A. I. Vogel, "Practical Organic Chemistry," 2nd Ed., Longmans, Green and Co., New York, N. Y., 1951, p. 877.

(16) E. Bergmann, H. Hoffmann, and H. Meyer, *J. prakt. Chem.*, [2] **135**, 245 (1932).

(17) Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(13) Ref. 12, **6**, 223 (1873).

**Treatment of Dihalide IIa with Other Reagents.** (Table II).—The experiments listed in Table II with lithium amide, potassium anilide, dipotassio phenylacetate, and dipotassiobenzoylacetone in liquid ammonia were carried out in a manner similar to that described with potassium amide and potassium diphenylmethide. The experiment with phenylmagnesium bromide in ether was carried out in a manner similar to that with phenyllithium. Potassium anilide was prepared by adding aniline to a molecular

equivalent of potassium amide in liquid ammonia. Dipotassio phenylacetate<sup>18</sup> and dipotassiobenzoylacetone<sup>19</sup> were prepared by adding phenylacetic acid and benzoylacetone, respectively, two molecular equivalents of potassium amide in liquid ammonia.

(18) See C. R. Hauser, D. Lednicer, and W. R. Brasen, *J. Am. Chem. Soc.*, **80**, 4345 (1958).

(19) See C. R. Hauser and T. M. Harris, *ibid.*, **80**, 6360 (1958).

## Reactions of Cyclohexylisonitrile and Isobutyraldehyde with Various Nucleophiles and Catalysts

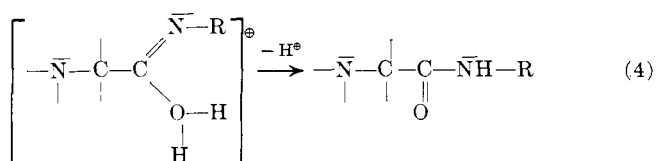
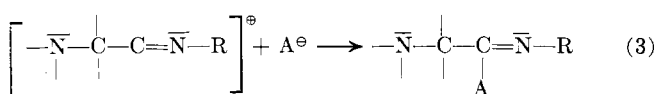
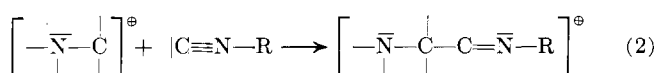
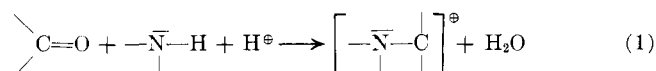
JAMES W. MCFARLAND

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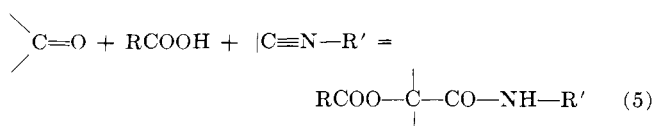
Received March 11, 1963

Cyclohexylisonitrile, isobutyraldehyde, and dimethylammonium acetate react to give N-cyclohexyl- $\alpha$ -dimethylaminoisovaleramide (I). By making slight variations in the reaction conditions one also can obtain N-cyclohexyl- $\alpha$ -hydroxyisovaleramide (II), N'-cyclohexyl-N,N-dimethyl- $\alpha$ -dimethylaminoisovaleramide (III), and  $\alpha$ -acetoxy-N-cyclohexylisovaleramide (IV). The Ugi and Passerini reactions are discussed.

In recent years Ugi and his co-workers have reported the results of a new reaction which gives great versatility to isonitriles as intermediates in organic syntheses.<sup>1-4</sup> This reaction serves usefully in the syntheses of such varied structures as  $\alpha$ -aminoamides, dipeptides,  $\beta$ -lactams, thioamides, and tetrazoles. The ensuing reaction scheme was suggested by Ugi, and fairly well explains the observed facts. One may imagine an aldehyde or ketone to react with an amine, an isonitrile, and a nucleophile ( $A^\ominus$ ) in the following way.



In reaction 3 the imino product is most often a reactive intermediate, and a further reaction occurs to give a stable product. For example, when the nucleophile  $A^\ominus$  is water the loss of a proton leads to an  $\alpha$ -aminoamide (reaction 4). Nearly forty years prior to this work Passerini discovered that isonitriles, carbonyl compounds, and carboxylic acids react slowly to give  $\alpha$ -acyloxyamides.<sup>5</sup>

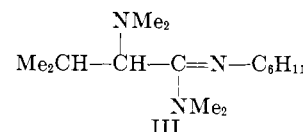
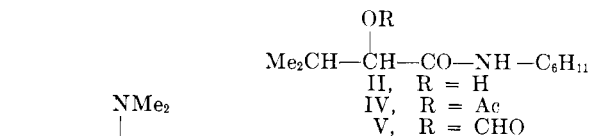
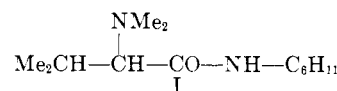


As part of a larger research program in these laboratories it was desired to synthesize N-cyclohexyl- $\alpha$ -dimethylaminoisovaleramide (I), and it seemed convenient to use the Ugi reaction for this purpose. At the beginning of this project only the preliminary report of this reaction had been published,<sup>1</sup> and it was not clear what the optimum conditions for the synthesis of I would be. To establish this point isobutyraldehyde, dimethylamine, and cyclohexylisonitrile were allowed to react under a set of varying conditions. The results of these studies are summarized in Table I.

TABLE I  
UGI REACTIONS<sup>a</sup>

Expt.	Catalyst	Moles	Me <sub>2</sub> NH, moles	Products (yield, %)
1	None	...	0.02	None
2	Me <sub>2</sub> NH·HCl	0.01	None	I (32 <sup>b</sup> ); II (32 <sup>b</sup> )
3	Me <sub>2</sub> NH·HCl	.01	.01	III (70)
4	AcOH	.02	.02	I (94); IV (6 <sup>b</sup> )
5	AcOH	.01	.01	I (35); IV (41)

<sup>a</sup> Reaction of 0.01 mole of isobutyraldehyde and 0.01 mole of cyclohexylisonitrile in 25.0 cc. of absolute methanol at room temperature. <sup>b</sup> Crude material.



It is evident from these studies that I is best obtained when a twofold excess of dimethylammonium acetate is used (experiment 4). Surprisingly, however, three other products were obtained in substantial yield when the nature of the catalyst was only slightly modified.

Experiment 1 illustrates the necessity of an acid catalyst for the reactions presently under investigation. However, since acids react directly with isonitriles to

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