dimethylaniline in a 100-ml stoppered flask was cooled to -10° using an ice–salt bath. *n*-Butyllithium was then added and the homogeneous solution was stirred with cooling for 1 min. The alkyl halide was added all at once. The stoppered stirred solution was kept in the bath and the temperature of the bath was allowed to increase gradually for 1 hr. The bath was removed and the reaction mixture was stirred at 32 ± 2° for another hour. After the second hour, the flask was cooled in an ice–water bath. Ice was added, with stirring, until the precipitate formed during the reaction dissolved. The clear organic and aqueous layers were separated. The organic layer was used directly for product characterization and yield measurements. The products were isolated by gc and characterized by their gc retention ratios and infrared and pmr spectra. In all cases, comparisons were made with the properties of commercial or synthetic compounds.

Amines from the 1-Halobutane Reactions.—N,N-Dimethylaniline (24.4 ml, 0.20 mole) was treated with *n*-butyllithium (26 ml of 1.6 *N*, 0.040 mole) and 0.040 mole of a 1-halobutane. Samples (2 ml) were withdrawn at intervals and quenched with ice. The yield of the product, N-(*n*-pentyl)-N-methylaniline, was measured in each sample by quantitative gc using N-benzhydryldimethylamine as an internal standard, Figures 1 and 2.

The 1-iodobutane reaction was carried out using the general procedure and gave a maximum yield of product after 2.5 hr 1-Bromobutane reactions were followed under the general conditions and at room temperature because of the mildness of the reaction. In both cases with the bromide, reaction was complete after 4 hr. 1-Chlorobutane failed to give any N-(*n*-pentyl)-N-methylaniline after several days at room temperature.

Amines from the 1-Iodoalkane Reactions.—N,N-Dimethylaniline (12.2 ml, 0.10 mole) was treated with 26 ml (0.040 mole) of *n*-butyllithium and 0.020 mole of 1-iodoalkane for 2 hr as described in the general procedure.

When 1-iodopropane was used, the organic layer showed two product peaks by gc. The retention ratios of the products A and B were 0.375 and 0.518, respectively, *vs.* the benzyhydryldimethylamine standard. The product A had infrared and pmr spectra identical with those of N-(*n*-butyl)-N-methylaniline, while the product B corresponded in all properties to N-(*n*-pentyl)-N-methylaniline. Quantitative gc gave 7.6 and 16.5% as the respective yields of A and B.

Two product gc peaks were also observed when 1-iodopentane was used. These two peaks C and D had retention ratios of 0.518 and 0.760, respectively. The product C was identical with the product B from the 1-iodopropane reactions (*i.e.*, N-(*n*-pentyl)-N-methylaniline), while the product D corresponded in all properties to N-(*n*-hexyl)-N-methylaniline as prepared above. Yields of C and D were 14.3 and 8.2%, respectively.

Hydrocarbons and Amines from the 1-Halopentane Reactions.—N,N-Dimethylaniline (12.2 ml, 0.10 mole) was treated with 19 ml (0.030 mole) of *n*-butyllithium and 0.020 mole of a 1-halopentane at -10°. Instead of stopping the reaction after 2 hr as in the general procedure, the reaction was continued at 32° for 18 hr. After quenching, the organic layer was analyzed for hydrocarbon products by gc at 100° using *n*-butylbenzene as a standard. Amine yields were determined as in the preceeding experiments.

1-Iodopentane gave three gc product peaks at 100° with retention ratios of 0.217, 0.400, and 0.740. These compounds I, II, and III were identical with *n*-octane, *n*-nonane, and *n*-decane, respectively. The hydrocarbon products I, II, and III had respective yields of 16.6, 27.0, and 10.7%. Amine products as determined at 185° were C, 23.9%, and D, 15.8%.

1-Bromopentane gave the same products with yields for I, II, III, C, and D of 1.86, 32.6, 1.74, 7.0, and 6.1%, respectively.

Influence of Reactant Concentration on Amine Yields.—The reaction system, N,N-dimethylaniline, *n*-butyllithium, and 1-iodopentane, was studied by changing a single concentration variable.

A. **Dependence on N,N-Dimethylaniline.**—*n*-Butyllithium and 1-iodopentane were used in 1:1 molar proportions; 20 mmoles of each were used in all experiments. The total solution volume was kept at 27.7 ml by changing the relative proportions of dimethylaniline and *n*-hexane. The 1.6 *N* *n*-butyllithium in hexane solution was concentrated under vacuum to allow measurements at the higher dimethylaniline concentrations. In the concentrated solutions active lithium concentrations were determined by double titration.[18] Reactions were carried out following the general procedure and amine product yields (Figure 5) were measured by the usual gc technique.

B. **Dependence on 1-Iodopentane.**—N,N-Dimethylaniline (0.10 mole) and 20 mmoles of *n*-butyllithium were used in all experiments. The total solution volume of the reaction mixture was kept at 33.1 ml by varying the relative proportions of 1-iodopentane and *n*-hexane. The standard reaction and analysis procedures were used. The results are given in Figure 3.

C. **Dependence on *n*-Butyllithium.**—N,N-Dimethylaniline and 1-iodopentane were used in 5:1 ratio, 0.10 and 0.020 mole, respectively. The reaction mixture total volume was maintained at 53.8 ml by adding varying amounts of *n*-hexane and 1.6 *N* *n*-butyllithium in *n*-hexane. Procedures were as described in A and B. The amine product distributions are given in Figure 4.

The Sodium Amide Catalyzed Rearrangement of Some Acetylenes in Ethylenediamine[1a]

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Received March 7, 1966

Any of the isomeric normal C_6 acetylenes and allenes yield the same "equilibrium" mixture when treated with sodium amide in ethylene diamine at room temperature. The required equilibration time depends on the starting substrate and amounts of sodium amide. Different quantities of sodium amide produce an "equilibrium" mixture of different composition. The novel branched dialkyl acetylenes I and II were prepared and rearranged. There was no evidence that rearrangement proceeded past the branching.

The base-catalyzed rearrangement of acetylenes is well known. In the past it was frequently accomplished in the presence of alcoholic potassium hydroxide at elevated temperatures. Thus, Jacobs[2] equilibrized the isomeric pentynes at 175° and the reaction mixture consisted of 1.3% 1-pentyne, 3.5% 1,2-pentadiene, and 95.2% 2-pentyne. Such rearrangements were frequently accompanied by side reactions such as polymerization and/or addition of solvent to the unsaturated bonds, as evidenced by the fact that not more than 70% of the hydrocarbons was recovered.[2] The rearrangement of octynes and octadienes with sodium amide in hot benzene to 2-octyne was also described.[3] Sodium and potassium *t*-butoxide in *t*-butyl alcohol near 200° were used for the rear-

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[1] (a) Presented in part at the southeastern Regional Meeting of the American Chemical Society, Charleston, W. Va., Oct 1964, and at the 40th Annual Meeting of the West Virginia Academy of Science, Fairmont, W. Va., April 1965; (b) abstracted in part from the M.S. Thesis of W. E. B., Marshall University, July 1965; (c) Abstracted in part from the M.S. Thesis of D. T. C., Marshall University, Aug 1964.

[2] T. L. Jacobs, R. I. Akawie, and R. G. Cooper, *J. Am. Chem. Soc.*, **73**, 1273 (1951).

[3] J. Bainrel, B. Wojtkowiak, and R. Romanet, *Bull. Soc. Chim. France*, 978 (1963).

rangement and equilibration of heptynes and decynes.[4] The rearrangement of macrocyclic alkadiynes with potassium *t*-butoxide in warm dimethyl sulfoxide was recently reported.[5] Moore and Ward[6] successfully equilibrated cyclic acetylenes and allenes using either sodium amide in liquid ammonia or potassium *t*-butoxide in *t*-butyl alcohol. They found that excess of sodium amide is desirable for rapid equilibrization. A rapid rearrangement without undesirable side reactions was described by Wotiz and Parsons.[7] The rearrangement was accomplished with sodium amide in liquid ammonia at room temperature. The relative amounts of the reaction products was a function of quantity of sodium amide used. It was also found that the reaction time needed for "equilibration" was dependent on the amount of sodium amide used. Thus in the rearrangement of hexynes the major product was 2-hexyne, which could be diminished in favor of 1-hexyne when the rearrangement was accomplished in the presence of higher molar quantities of sodium amide.[7]

Since the rearrangement in ammonia at its boiling point (−33°), was too slow and practically nonexistent, the reactions[7] were carried out at room temperature in a sealed autoclave. It is one of the purposes of this paper to report the successful substitution of ethylene diamine for ammonia. Reactions were carried out at room temperature and the rearrangements of isomeric normal hexynes and allenes were studied as a function of the concentration of sodium amide. Since an internal triple bond such as one in 5-decyne was also rearranged, it was of interest to ascertain whether unsaturation can be rearranged from an internal position into the terminal position and/or 2 position in an alkyne containing branching.

The isomeric *n*-hexynes and hexadienes (1,2- or 2,3-) were treated with sodium amide in ethylenediamine. The rearrangements were followed by removing aliquots at specified time intervals and quenching them with ice–water. The products were analyzed using vapor phase chromatography and infrared and nuclear magnetic resonance spectroscopy. The reactions were allowed to proceed until no further change in composition could be determined. Such a composition was designated as "equilibrium," which in no sense intended to indicate the true thermodynamic equilibrium. However, at low catalyst concentrations such a composition should be in at least in qualitative agreement with the thermodynamic values. The "equilibrium" composition consisted of 1-, 2-, and 3-hexyne and 2,3-hexadiene. In no case did we find an infrared absorption peak near 1600 cm^{-1} characteristic of a conjugated diene. The weak absorption peak at 1950 cm^{-1} was attributed to 2,3-hexadiene rather than to 1,2-hexadiene or a mixture of the two, on the basis of the examination of its nmr spectrum in the olefinic proton region. Quantitative analytical values were obtained by vpc. Good resolution of all components was obtained in a synthetic mixture except of 1,2- and 2,3-hexadiene which had identical retention times.

A possible error in our determinations may have arisen from the fact that the reaction mixtures were heterogeneous. Attempts were therefore made to stir the reaction mixtures uniformly and to use the same lot of sodium amide and ethylenediamine. The most convenient catalyst concentration appeared to be about 15 mole % of sodium amide. At this concentration, "equilibration" was sufficiently fast and yet the system was not too viscous for efficient stirring.

All the isomeric normal hexynes and hexadienes (allenes) rearranged to give the same "equilibrium" mixture at the same sodium amide concentration. Thus a reaction mixture consisting of 0.10 mole of hexyne (1-, 2-, or 3-) or hexadiene (1,2- or 2,3-) and 0.015 mole of sodium amide in 25 ml of ethylenediamine at 25° produced an "equilibrium" mixture which consisted of about 6% of 1-, 80% of 2-, 11% of 3-hexyne, and 3% of 2,3-hexadiene. However, the absence of 1,2-hexadiene was puzzling since Moore[6] has shown from thermodynamic values that a terminal allene is slightly more stable than a terminal acetylene. We may well be dealing with a kinetic observation rather than with a thermodynamic "equilibrium." The predominance of 2-hexyne in the "equilibrium" mixture can possibly be attributed to a greater degree of stabilization of this isomer due to hyperconjugation because of its five α hydrogens. It was likely that the reaction proceeded through the prototropic base-catalyzed reaction mechanisms previously suggested by Jacobs.[2]

By removing and analyzing aliquots from the reaction mixture before "equilibrium" was established, we have established that unsaturation moves along the chain in a stepwise fashion. Thus 3-hexyne was derived from 2-hexyne *via* 2,3-hexadiene. Starting with 2,3-hexadiene, the first two components were 2- and 3-hexyne. Since 1,2-hexadiene rearranged extremely fast into 2-hexyne, it was not surprising that the rearrangement of 1-hexyne gave 2-hexyne as the first detectable rearrangement product. The first observed product of 2-hexyne was 2,3-hexadiene which was in accord with the postulated mechanism. From the study of reactions carried out under comparable conditions, it became obvious that the position of unsaturation has a large effect on the rate of rearrangement. Thus, 1-hexyne required approximately 1100 hr, whereas all the other isomers were at "equilibrium" within 0.5 hr. This we attributed to the formation of the 1-sodio derivative which is particularly stable owing to the acidity of the terminal acetylenic hydrogen. We have also established that the position of "equilibrium" was a function of catalyst concentration. An increase in sodium amide concentration increased the concentration of 1-hexyne (see Table I).

acetylene ⟶ allene ⟶ acetylene, etc.

The absence of conjugated dienes was surprising since the postulated mechanism[2] could accommodate such products. Furthermore, conjugated dienes would be more stable than the isomeric allenes and acetylenes by several kcal. The absence of conjugated dienes was not likely due to its further reaction with the solvent (amination) since we observed material balances in excess of 90%. If a path was available for the formation of conjugated dienes, then they should have been the predominant product.

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[4] W. Smadja, *Compt. Rend.*, 2426 (1963).

[5] A. J. Hubert and S. Dale, *J. Chem. Soc.*, 3118 (1965).

[6] W. R. Moore and H. R. Ward, *J. Am. Chem. Soc.*, **85**, 86 (1963).

[7] J. H. Wotiz, and C. G. Parsons, U. S. Patent 3,166,605 (1965); also, Abstracts of the 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 74P.

TABLE I

"EQUILIBRATION" OF HEXYNES AND HEXADIENES IN ETHYLENEDIAMINE AT 25°

Starting substrate	Substr/NaNH$_2$[a]	Time, hr	Product compn, %			
			$C_4C\equiv C$	$C_3C\equiv C—C$	$C_2C\equiv C—C_2$	$C_2C=C=C—C$
$C_3C\equiv C—C$	4/0.6	0.5	3	82	12	3
$C_3C\equiv C—C$	4/1.0	0.5	5	82	11	2
$C_2C\equiv C—C_2$	4/0.6	0.25	6	80	12	3
$C_2C\equiv C—C_2$	4/1.0	6.0	19	67	11	3
$C_4C\equiv C$	4/0.6	1192	6	82	10	2
$C_4C\equiv C$	4/0.2	0.5 year	4	84	12	0
$C_3C=C=C$	4/0.6	0.125	7	77	13	3
$C_2C=C=C—C$	4/0.6	0.25	6	81	11	3
$C_3C\equiv C—C$	4/0.6	0.0[b]	0	0	0	0
		0.008[b]	0	99.3	0	0.7
		0.016[b]	0	98.3	0.5	1.2
		0.024[b]	0.4	96.1	2.1	1.4
		0.33[b]	0.8	90.6	6.3	2.3
		0.50	3.1	81.8	12.2	2.3
		1.00	2.5	83.3	11.8	2.4

[a] Molar ratio, NaNH$_2$ lot A. [b] Not at "equilibrium."

TABLE II

REARRANGEMENT OF BRANCHED DIALKYL ACETYLENES IN ETHYLENEDIAMINE AT 25°

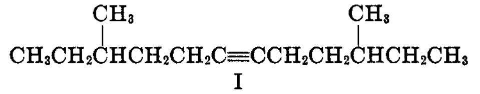
$RC_2C\equiv CC_2R$[a]

Starting substrate	Substr/NaNH$_2$	Time hr	Product compn, %				
			$RC_2C\equiv CC_2R$	$RC_2C=C=CCR$	$RC_3C\equiv CCR$	$RC_3C=C=CR$	Others[b]
R_1	5/1.0[c]	1.0	99	1	0	0	0
R_1	5/1.0[d]	1.0	99	1	0	0	0
R_1	5/2.0[c]	0.33	65	7	27	1	0
		1.0	39	4	50	6	0
		1.5[e]	32	4	55	9	0
		26.0	33	3	56	8	0
R_1	5/2.9[c]	15.0	10	0	0	0	90
R_1	5/3.8[d]	6.0[e]	38	4	5.3	5	0
R_1	5/4.8[c]	5.0	1	0	0	0	99.0
R_2	5/1.1[d]	1.0	98	2	0	0	0
R_2	5/2.6[d]	5.0[e]	62	6	29	3	0
		25.0[e]	60	5	31	4	0
R_2	5/3.2[e,d]	26.5	15	0	0	0	85

[a] $R_1 = CH_3CH_2CHCH_3$ and $R_2 = CH_3CH_2CH_2CHCH_3$. [b] Amination products and polymers. [c] Molar ratio, NaNH$_2$ lot B. [d] Molar ratio, NaNH$_2$ lot C. [e] "Equilibrium."

The internal triple bond in 5-decyne was also rearranged under the influence of sodium amide in ethylenediamine. After 12 hr the reaction mixture contained five new components, one of which was 1-decyne. The mixture also contained allenes as evidenced by the infrared absorption peak at 1950 cm^{-1}. There was no infrared evidence for the presence of conjugated dienes or olefins. The identification of the other products was not attempted.

In order to ascertain whether an internal triple bond can be rearranged into a terminal position in compounds containing a methyl group between the triple bond and the terminal carbon atoms, two branched dialkylacetylenes were prepared and treated with sodium amide. 3,10-Dimethyl-6-dodecyne (I) and 4,11-dimethyl-7-tetradecyne (II) were prepared by the dialkylation of sodium acetylide in liquid ammonia at −33°. The reaction products were spectroscopically and vaporchromatographically pure.



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2C\equiv CCH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$$

I

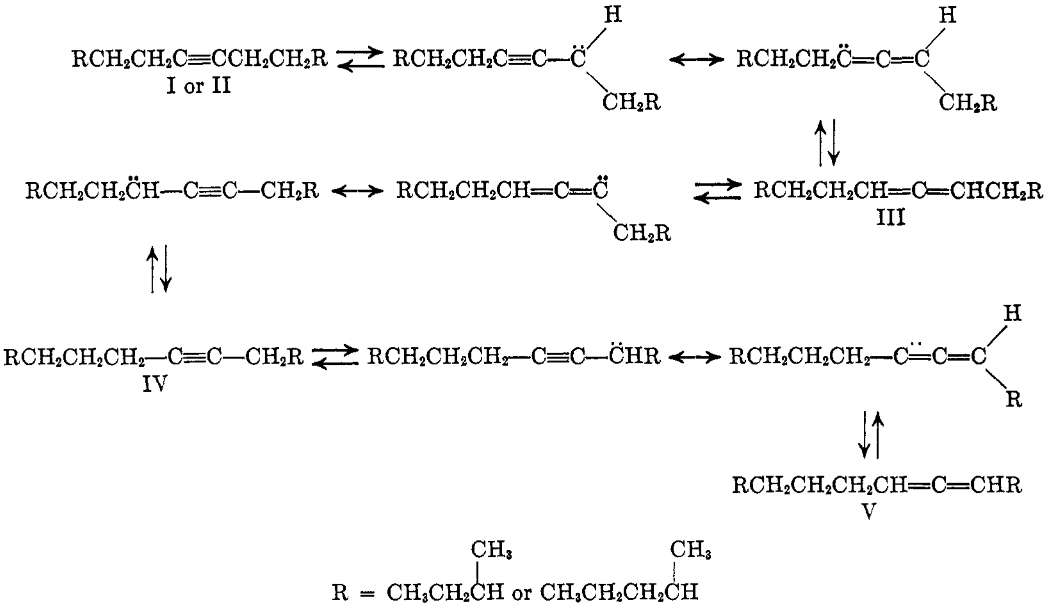
$$CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_2C\equiv CCH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_3$$

II

Compounds I and II were treated with sodium amide at room temperature in ethylenediamine. In the range of NaNH$_2$ to substrate of 1 to 2.5–5 two internal allenes and one new internal alkyne were formed, but no terminal alkyne (see Table II). In line with previously suggested mechanism,[2] the rearrangement proceeded as outlined in Scheme I.

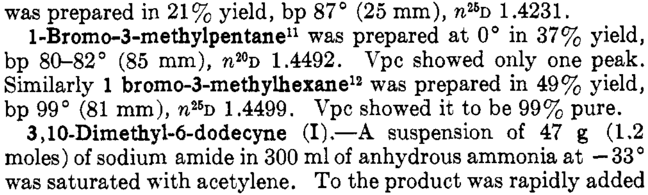
The two new allenes were compounds III and V and acetylene compound IV. It would seem that another acetylene (VI, $RCH_2CH_2CH_2CH_2C\equiv C—R$) and another allene (VII, $RCH_2CH_2CH_2CH_2\overset{\overset{H}{|}}{C}=C=\overset{\overset{CH_3}{|}}{C}—CH_2CH_2CH_3$) also could be formed. Furthermore, the absence of acetylene VI could be attributed to its lower stability compared with acetylenes I or II and IV which have four α hydrogens. Compound VI has only three α hydrogens and is therefore not stabilized so much by hyperconjugation. Higher sodium amide concentrations produced polymerization and amination reactions, the products of which were not characterized. Thus, if compounds VI and VII were formed, they could have undergone further isomerization between the methyl groups to some conjugated dienes. Traces of such unknown dienes were detected spectroscopically.

SCHEME I



Experimental Section

Hydrocarbons.—The isomeric hexynes were purchased from the Farchan Chemical Co., Cleveland, Ohio, and **5-decyne** from the Columbia Organic Chemicals Co., Columbia, S. C. **Hexadienes** (1,2-, and 2,3-) were prepared by the procedures of Moore and Ward.[8] The branched dialkyl acetylenes I and II were prepared by the following sequence of reactions. The starting branched alcohols were prepared from the appropriate secondary bromides *via* the Grignard reagent and ethylene oxide.



$$\mathrm{ROH} \xrightarrow{\mathrm{PBr_3}} \mathrm{RBr} \xrightarrow[-33^\circ]{\mathrm{NaC{\equiv}C{-}H}} \mathrm{R{-}C{\equiv}C{-}H} \xrightarrow[-33^\circ]{\mathrm{NaC{\equiv}C{-}H\ or\ NaNH_2}} \mathrm{R{-}C{\equiv}C{-}Na} \xrightarrow{\mathrm{RBr}} \mathrm{R{-}C{\equiv}C{-}R}$$

$$\mathrm{R} = \mathrm{CH_3CH_2}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{CH_2CH_2}\ (\mathrm{I})\ \text{or}\ \mathrm{CH_3CH_2CH_2}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{CH_2CH_2}\ (\mathrm{II})$$

3-Methyl-1-pentanol[9] was formed in 34% yield, based on starting bromide, bp 93–95° (35 mm), $n^{20}\mathrm{D}$ 1.4224. **3-Methyl-1-hexanol**[10] was prepared in 21% yield, bp 87° (25 mm), $n^{25}\mathrm{D}$ 1.4231.

1-Bromo-3-methylpentane[11] was prepared at 0° in 37% yield, bp 80–82° (85 mm), $n^{20}\mathrm{D}$ 1.4492. Vpc showed only one peak. Similarly **1 bromo-3-methylhexane**[12] was prepared in 49% yield, bp 99° (81 mm), $n^{25}\mathrm{D}$ 1.4499. Vpc showed it to be 99% pure.

3,10-Dimethyl-6-dodecyne (I).—A suspension of 47 g (1.2 moles) of sodium amide in 300 ml of anhydrous ammonia at −33° was saturated with acetylene. To the product was rapidly added 99 g of 1-bromo-3-methylhexane and stirred for 8 hr. Upon addition of water the formed organic layer was washed with dilute iced hydrocloric acid. Distillation yielded 5.8 g (9.5% yield) of 5-methyl-1-heptyne, bp 118° (752 mm), $n^{25}\mathrm{D}$ 1.4175, infrared bands near 3310 (≡C—H) and 2120 cm^{-1} (—C≡C—H). Further distillation produced 58.1 g (39% yield) of I, bp 122–124° (18 mm), $n^{25}\mathrm{D}$ 1.4443, weak infrared band near 2220 cm^{-1} (—C≡C—), no bands near 3310 or 2120 cm^{-1}. The product was 99% pure by vpc analysis. *Anal.* Calcd for $C_{14}H_{26}$: C, 86.7; H, 13.4. Found: C, 85.8; H, 13.4. Catalytic hydrogenation of 400.0 mg of I (2.06 mmoles) over platinum catalyst resulted in the uptake of 92.2 ml (STP) corresponding to 4.12 mmoles of hydrogen. The product, **3,10-dimethyldodecane**, $n^{20}\mathrm{D}$ 1.4308, was vapor chromatographically pure with a retention time shorter than I.

4,11-Dimethyl-7-tetradecyne (II).—Following the procedure used for the preparation of I, 26.4 g (0.676 mole) of sodium amide and 60.5 g (0.338 mole) of 1-bromo-3-methylhexane produced 17.8 g (42.5% yield) of **5-methyl-1-octyne**, bp 84–85° (118 mm), $n^{25}\mathrm{D}$ 1.4205, and 6.1 g (8% yield) of II.

Larger quantities of II were prepared by suspending 10.9 g of (0.288 mole) sodium amide in 1800 ml of anhydrous ammonia, adding 22.2 g (0.124 mole) of 5-methyl-1-octyne and refluxing for 24 hr. Fractionation of the product yielded 12.6 g (45.8% yield) of II, bp 116–118° (2.4 mm), $n^{25}\mathrm{D}$ 1.4469, weak infrared band near 2220 cm^{-1}. *Anal.* Calcd for $C_{16}H_{30}$: C, 86.5; H, 13.5. Found: C, 85.6; H, 13.8.

1-Decyne.—Using the general procedure described for the preparation I, 9.2 g (0.40 g-atom) of sodium was converted to sodium amide, saturated with acetylene, and treated with 38.6 g (0.20 mole) 1-bromooctane. 1-Decyne,[13] bp 81–82° (34 mm), $n^{25}\mathrm{D}$ 1.4245, was produced in 56.7% yield. There was no evidence of the formation of dioctylacetylene.

Rearrangements.—The hydrocarbons were rearranged in a flask provided with a Teflon-encased magnetic stirring bar. The flask was fitted with a serum cap through which samples were withdrawn with the aid of a hypodermic syringe. Usually 0.1 mole of the hydrocarbon was mixed with 25 ml of ethylene diamine (Union Carbide Chemicals Co.), redistilled, and stored over Linde 4A Molecular Sieve, 100% assay, and appropriate amount of sodium amide (Robert's Chemical Co.) in a nitrogen-purged drybox. Samples were kept at 25° and withdrawn at specific time intervals, quenched with 2 to 3 ml of iced water. The organic layer was dried over anhydrous sodium sulfate. The infrared analyses of hexynes and hexadienes were obtained from neat samples using a Beckman IR-5 spectrophotometer and 0.025-mm cells. Gas chromatograms were obtained with a Beckman GC-5 gas chromatograph using a 12 ft × 0.25 in. column packed with 12–18% mixture of Carbowax 4M and silicone 550-150 on Chromosorb W (30–60 mesh). Areas under the peaks were measured by an Instron Model A-30 integrator. Nmr spectra were obtained on a Varian A-60 spectrometer.[14] The higher molecular weight hydrocarbons were analyzed using a Perkin-Elmer Model 237 grating infrared spectrophotometer and a F & M Model 500 programmed-temperature gas chromatograph using columns packed with 20% (by weight on 60–80 Chromosorb P) Carbowax 20 M of 15- and 28-ft length.

Experiments were usually allowed to proceed until no further change in the composition could be detected. This value was designated as "equilibrium." In case of the C_6 hydrocarbons such a mixture contained also a slight infrared peak at 1950 cm^{-1} which we attributed to 2,3-hexadiene rather

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(8) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962).

(9) R. C. Huston and A. H. Agett [*ibid.*, **6**, 123 (1941)] reported bp 151–152° (740 mm), $n^{23}\mathrm{D}$ 1.4112.

(10) R. C. Huston and A. H. Agett[9] report bp 80° (25 mm), $n^{23}\mathrm{D}$ 1.4213.

(11) P. A. Levene and R. E. Marker [*J. Biol. Chem.*, **91**, 77 (1931)] reported bp 80° (85 mm), $n^{25}\mathrm{D}$ 1.4415.

(12) Lit.[11] bp 65° (20 mm), $n^{20}\mathrm{D}$ 1.4496.

(13) B. B. Elsner and P. F. M. Paul [*J. Chem. Soc.*, 893 (1951)] reported bp 170° (761 mm), $n^{22}\mathrm{D}$ 1.4269.

(14) We wish to thank the Union Carbide Corp., Olefin Division, especially Dr. W. T. Pace, for the use of its nmr facilities.

than 1,2-hexadiene or a mixture of the two. The two allenes had identical retention times, but the nmr spectrum in the olefinic proton region clearly differentiated between the two allenes.

Efforts were made to agitate the reactions at a uniform rate and good and reproducible values were found. Some variations were noticed when different lots of sodium amide were used. This could have been caused by differences in the particle size of the sodium amide or by qualitative differences caused by deteriation during preparation and/or storage. Within a given lot the values were consistent and reproducible.

Reactions of Enamines. VIII. The Reaction of Eniminium Salts with Trichloroacetate[1]

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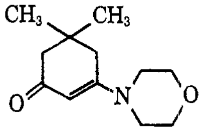
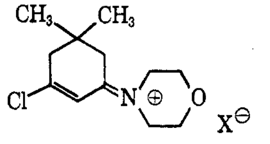
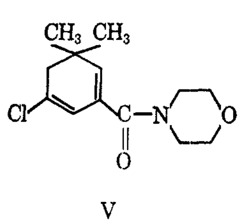
Received February 7, 1966

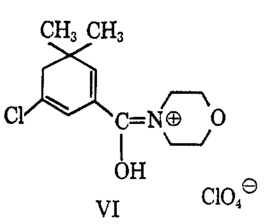
The relatively unstable compound isolated from the reaction of trichloroacetyl chloride with 5,5-dimethyl-3-N-morpholinylcyclohex-2-en-1-one has been shown to be N-1-(1-trichloromethyl-3-chloro-5,5-dimethylcyclohex-2-enyl)morpholine. The mechanism of formation of the latter from N-(3-chloro-5,5-dimethylcyclohex-2-en-1-ylidene)morpholinium trichloroacetate is discussed. The generality of this reaction of eniminium trichloroacetates is demonstrated.

In a previous paper in this series[2] it was shown that reaction of the enamino ketone I with trichloroacetyl chloride gave the chloroeniminium salt II (X = Cl). A second major product, a somewhat unstable oil, was induced to crystallize from aqueous acetone. Elemental analysis indicated the empirical formula $C_{13}H_{19}Cl_4NO$. Dimers were excluded by a molecular weight determination. In contrast to the starting material and II, the compound showed only end absorption in the ultraviolet so that the chromophores present cannot be in conjugation. The nuclear magnetic resonance (nmr) spectrum showed the presence of one vinyl hydrogen, and the presence of a carbon–carbon double bond was confirmed by a band at 6.10 μ in the infrared spectrum. On the basis of this evidence structure III may be assigned to the compound. The formation of III could proceed by the series of reactions I → IV → III (Scheme I). Initial O-acylation is followed by addition of chloride ion to give the intermediate IV which can collapse by loss of trichloroacetate ion to the chloroeniminium cation, which is precipitated in part as II (X = Cl). Under the reaction conditions, the trichloroacetate anion undergoes decarboxylation to the trichloromethyl anion, which adds[1] to the chloroeniminium cation to produce the observed product III. Further evidence for structure III was provided by degradation. Heating III with aqueous acetone or ethanol effected its conversion to an oil, the morpholide V. The nmr spectrum of V showed the presence of two vinyl protons at τ 4.10 and 4.30. Bands at 6.05 and 6.12 μ in the carbonyl region of the infrared spectrum may be assigned to amide carbonyl and carbon–carbon double bonds, respectively. The presence of a cross-conjugated diene acid chromophore was confirmed by the ultraviolet absorption at 279 mμ. The morpholide V formed a crystalline perchlorate, which had the correct elemental analysis and spectral data compatible with structure VI.[3]

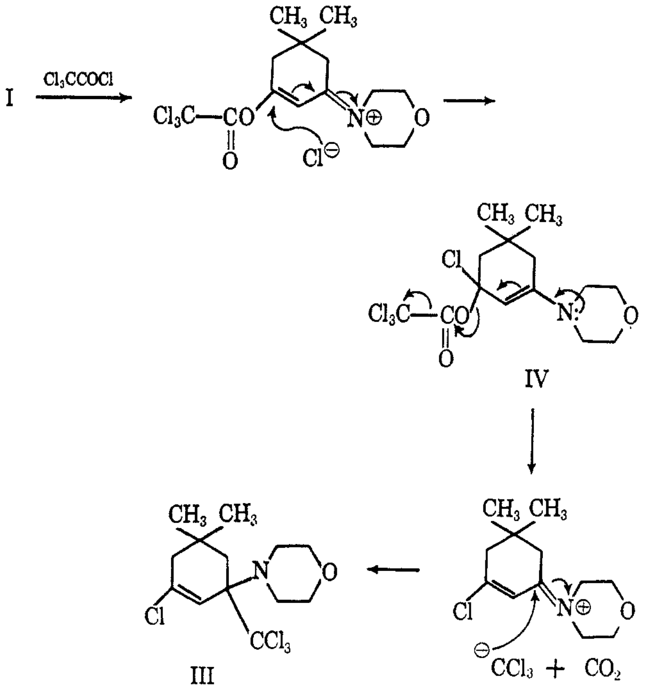

I


II

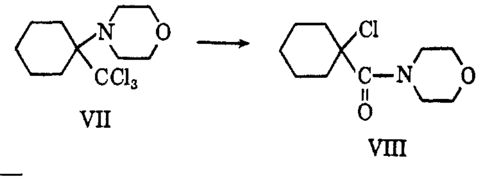

V


VI

Scheme I



The formation of V from III must have taken place by a mechanism similar to that involved in the rearrangement of the trichloromethyl derivative VII to



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(1) Part VII: G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **31**, 1340 (1966).

(2) G. H. Alt and A. J. Speziale, *ibid.*, **29**, 794 (1964).

(3) See G. H. Alt and A. J. Speziale, *ibid.*, **30**, 1407 (1965), and references there cited for the site of protonation of amides.