6-Aryl-*as*-triazine-3,5(2*H*,4*H*)-dione——To a solution of 0.02 mole of 3-thioxotriazinone derivative dissolved in 15 ml. of *N* NaOH, 5% $K_2Mn_2O_7$ solution was added dropwise until no more color of $K_2Mn_2O_7$ disappeared, and the mixture was warmed for 15 min. on a water bath. The cooled reaction mixture was filtered, the filtrate was acidified with AcOH and the precipitate was recrystallized from EtOH.

The authors express their deepest thanks to U. S. Army Research and Development Group (Far East) for the kind support to this study.

Summary

Twelve compounds of phenylpyruvic acid thiosemicarbazone derivatives substituted with alkyl group, hydroxy group, alkoxy group or halogen atom at 2, 3- and/or 4-position in benzene ring, nine compounds of 3-thioxo-6-aryl-3,4-dihydro-*as*-triazin-5(2*H*)-one, five compounds of 3-methylthio-6-aryl-*as*-triazin-5(4*H*)-one, and five compounds of 6-aryl-*as*-triazine-3,5(2*H*,4*H*)-dione were newly synthesized.

Among these compounds, 3,4-dimethoxyphenylpyruvic acid thiosemicarbazone showed remarkable activity on the multiplication of the Mahoney strain of polio virus type 1, while 6-phenyl-, and 6-(*p*-propoxybenzyl)-3,4-dihydro-*as*-triazin-5(2*H*)-one, and 6-(*p*-chlorobenzyl)-*as*-triazine-3,5(2*H*,4*H*)-dione were slightly effective on the virus by using 100 × $TCID_{50}$ of the virus.

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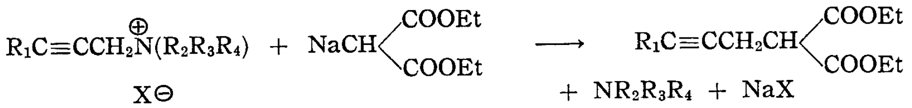
[Chem. Pharm. Bull. 11 (12) 1556 ~ 1563]

UDC 547.538.2.07

241. **Issei Iwai and Tetsuo Hiraoka**: Studies on Acetylenic Compounds. XXXIV.[*1] Rearrangement of Propargylammonium Halide Derivatives.

(*Research Laboratories, Sankyo Co., Ltd.*[*2])

In the preceding paper,[1] it was reported that propargylammonium salts derivatives react with the active methylene group to afford higher homolog of acetylenic compound involving the loss of trialkylamine.



$$\underset{X^{\ominus}}{R_1C{\equiv}CH_2\overset{\oplus}{N}(R_2R_3R_4)} + NaCH\begin{matrix}COOEt\\COOEt\end{matrix} \longrightarrow R_1C{\equiv}CH_2CH\begin{matrix}COOEt\\COOEt\end{matrix} + NR_2R_3R_4 + NaX$$

At that time, it was shown that C-N bond of propargylammonium iodide ($RC{\equiv}CCH_2\text{-}\overset{\oplus}{N}{<}$) is rather stable against cleavage than that of benzylammonium iodide ($PhCH_2\text{-}\overset{\oplus}{N}{<}$). If the cleavage reaction of propargylammonium and benzylammonium derivatives proceeds through propargyl cation ($RC{\equiv}C\overset{\oplus}{CH_2}$) and benzyl cation ($Ph\overset{\oplus}{CH_2}$), phenyl propargyl cation should be more stable than benzyl cation in accordance with the first order approximation because carbonium cation of $PhC{\equiv}C\overset{\oplus}{CH_2}$ is stabilized by the distribution

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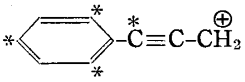
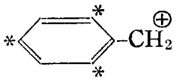
[*1] Part XXXIII This Bulletin, **11**, 1049 (1963).

[*2] Nishi-shinagawa, Shinagawa-ku, Tokyo (岩井一成, 平岡哲夫).

1) I. Iwai, T. Hiraoka: This Bulletin, **10**, 81 (1962).

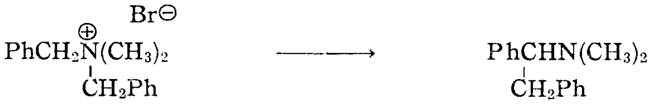
of positive charge over four carbon atoms (marked with * in the following formula), whereas benzyl cation is stabilized by that kind of distribution over three carbon atoms.





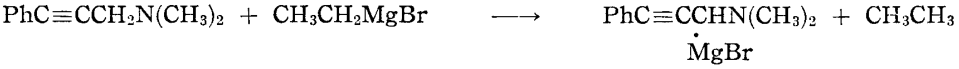
Therefore, if the reaction proceeds through Sn-1 like mechanism, the departing ability of phenylpropargyl group should be stronger than the benzyl group. Then, it is of interest to investigate the easiness of the cleavage of C-N bond of propargyl-, benzyl-, and allyl-amine.

It is known that treatment of dibenzyldimethylammonium bromide with sodium ethoxide gives α-benzyl-N,N-dimethylbenzyl amine (Stevens rearrangement).[2]



$$\underset{\displaystyle CH_2Ph}{PhCH_2\overset{Br^{\ominus}}{\overset{\oplus}{N}}(CH_3)_2} \longrightarrow \underset{\displaystyle CH_2Ph}{PhCHN(CH_3)_2}$$

The main structural requirement for this rearrangement is that quaternary ammonium derivative has a substituent of migratory aptitude and moreover, a substituent which gives a carbanion adjacent to nitrogen (it is not a true carbanion, but a type of zwitterion in which the negative pole has carbanion character). Essential feature of this reaction is the 1,2-shift of moving group. This time, it was found that treatment of N,N-dimethyl-3-phenyl-2-propynylamine with ethylmagnesium bromide gave ethane according to the following equation :



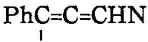
$$PhC{\equiv}CCH_2N(CH_3)_2 + CH_3CH_2MgBr \longrightarrow \underset{\displaystyle MgBr}{PhC{\equiv}CCHN(CH_3)_2} + CH_3CH_3$$

This suggests that the methylene group located between phenylacetylene and dimethylamine group acts as so-called "active methylene group." Considering these results, propargylammonium halide derivatives would undergo the Stevens type rearrangement. Practically it was found that propargyl ammonium halide derivatives afforded rearrangement products, one of which is obtained through a new type of S_{Ni}' reaction.

Treatment of benzyldimethyl-(3-phenyl-2-propynyl)ammonium iodide (II) with aqueous sodium hydroxide gave an oil of b.p$_{0.0004}$ 132~135°, whose picrate melted at 143~144°. On the basis of reaction mechanism, the structure of this oil would be one of the following substances :

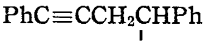
$$\underset{\displaystyle N(CH_3)_2}{PhC{\equiv}CCHCH_2Ph}$$

IV



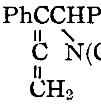
$$\underset{\displaystyle CH_2Ph}{PhC{=}C{=}CHN(CH_3)_2}$$

XX



$$\underset{\displaystyle N(CH_3)_2}{PhC{\equiv}CCH_2CHPh}$$

XXI



$$\underset{\displaystyle \underset{\displaystyle CH_2}{\|}}{PhC}\!\!\overset{\displaystyle CHPh}{\searrow N(CH_3)_2}$$

XXII

Infrared spectrum of this basic oil showed no allenic absorption at 1950 cm^{-1} region, which excludes the possibility of two structures (XX and XXII). Then, the oil obtained here, was hydrogenated over Pd-C to give an oil of b.p$_{0.0004}$ 110~115° (bath temperature), whose picrate and methyl iodide had the same melting point as those of N,N-dimethyl-1-benzyl-3-phenylpropylamine (V),[3] and the synthesis of V confirmed this structure. Thus, the oil obtained from II was identified to be as N,N-dimethyl-1-benzyl-3-phenyl-2-propynylamine (IV). Therefore, the reaction of II with aqueous sodium hydroxide is assumed to initiate by picking up of proton from the methylene group adjacent to phenylacetylene group as shown in the formula (III). The compound (II) has two

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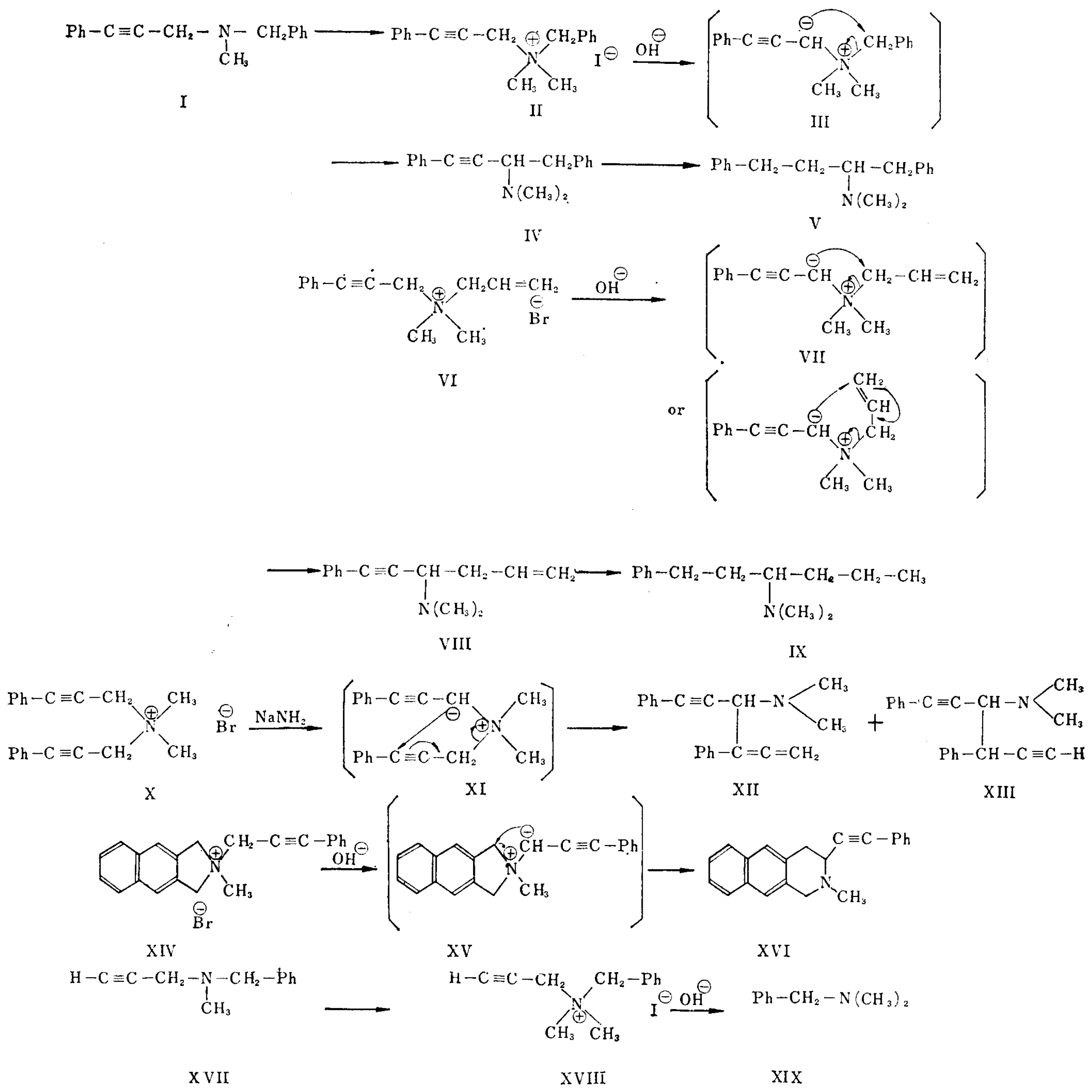
[2] T. S. Stevens, *et al.* : J. Chem. Soc, **1928**, 3193, *Ibid.*, **1932**, 1926, 1932, *Ibid.*, **1934**, 279.
[3] T. Morikawa : Yakugaku Zasshi, **80**, 475 (1960), 1932, *Ibid*, **1934**, 279.



methylene groups. One is located in α-position of phenylacetylene group and another one is adjacent to phenyl group. The fact that picking up of proton is occurred at methylene group adjacent to phenylacetylene substituent implies its stronger acidity as compared to another methylene group. This is well agreed with the stronger electron withdrawing character of phenylacetylene group as compared to that of phenyl substituent : (σ^* value : $\sigma^*_{Ph-} = +0.60$, $\sigma^*_{PhC\equiv C-} = +1.35$[4]).

When dimethyl(2-propenyl)(3-phenyl-2-propynyl)ammonium bromide (IV), prepared from N,N-dimethyl-3-phenyl-2-propynylamine and allyl bromide, was treated with aqueous sodium hydroxide, an oily product b.p$_5$ 114~115° was obtained. This product was confirmed to be N,N-dimethyl-1-(2-phenylethynyl)-3-butenylamine (VIII) by its conversion into N,N-dimethyl-1-phenethylbutylamine (IX) which was identical with an authentic sample prepared from phenethyl bromide and butyraldehyde according to the following method :

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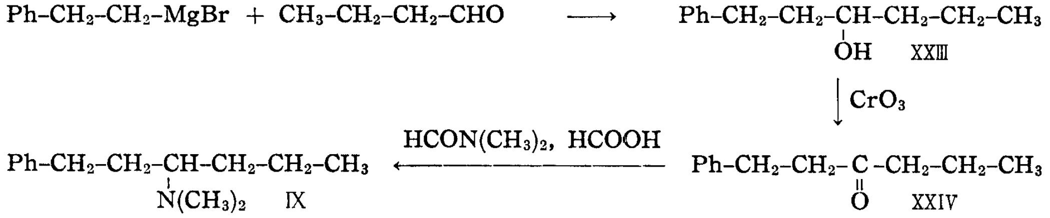
[4] M.S. Newman : "Steric Effects in Organic Chemistry," p. 619 (John Wiley and Sons, Inc.) (New York).



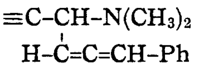
$$Ph\text{-}CH_2\text{-}CH_2\text{-}MgBr + CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO \longrightarrow Ph\text{-}CH_2\text{-}CH_2\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_2\text{-}CH_3 \quad XXIII$$

$$\downarrow CrO_3$$

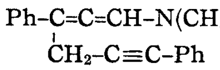
$$Ph\text{-}CH_2\text{-}CH_2\text{-}\underset{N(CH_3)_2}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_2\text{-}CH_3 \quad IX \xleftarrow{HCON(CH_3)_2,\ HCOOH} Ph\text{-}CH_2\text{-}CH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_2\text{-}CH_2\text{-}CH_3 \quad XXIV$$

As in the case of II, no allenic substance was obtained on treatment of VI with aqueous sodium hydroxide.

Treatment of dimethylbis(3-phenyl-2-propynyl)ammonium bromide (X), prepared from N,N-dimethyl-3-phenyl-2-propynylamine and 3-phenyl-2-propynyl bromide, with aqueous sodium hydroxide or sodium ethoxide in abs. ethanol afforded no basic substance. However, when X was reacted with sodium amide in liquid ammonia, two crystalline substances, m.p. 61~62° (major product) and m.p. 114~115° (minor product), were obtained after careful chromatographic purification on alumina. Hydrogenation of these two substances gave the same compounds. This fact showed that two crystalline substances are isomers involving multiple bond. The analytical data of both the compounds agreed with $C_{20}H_{19}N$, and in ultraviolet spectra they showed the characteristic absorptions for phenylacetylene. The former substance, m.p. 61~62°, exhibited in infrared spectrum the characteristic absorptions for an allenic bond ($>C=C=C<$) at 1950 cm^{-1} and an allenic terminal hydrogens ($>C=C=CH_2$) at 850 cm^{-1}, whereas the latter, m.p. 114~115° showed an absorption of ethynyl hydrogen at 3250 cm^{-1}. For the allenic compounds the following three compounds are possible from the reaction mechanism :

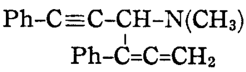
XXV


$$Ph\text{-}C\equiv C\text{-}\underset{H\text{-}C=C=CH\text{-}Ph}{\underset{|}{CH}}\text{-}N(CH_3)_2$$



XXVI

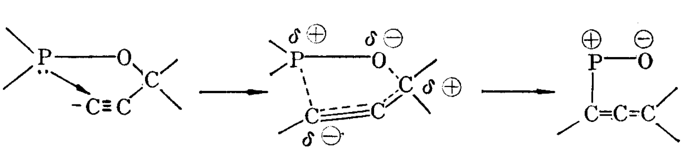
$$Ph\text{-}C=C=CH\text{-}N(CH_3)_2 \text{ with } \underset{CH_2\text{-}C\equiv C\text{-}Ph}{\underset{|}{C}}$$



XII

$$Ph\text{-}C\equiv C\text{-}\underset{Ph\text{-}C=C=CH_2}{\underset{|}{CH}}\text{-}N(CH_3)_2$$

However, the infrared spectrum absorption at 850 cm^{-1} which are characteristic for an allenic terminal hydrogens ($>C=C=CH_2$) excluded the structure of XXV and XXVI. From these results, the structure of these two compounds could be concluded to be N,N-dimethyl-2-phenyl-1-(2-phenylethynyl)-2,3-butadienylamine (XII) and N,N-dimethyl-2-phenyl-1-(2-phenylethynyl)-3-butynylamine (XIII), respectively. The reaction mechanism for the formation of XII and XIII could be described as S_{Ni}' as indicated in formula (XI), Recently, Mark[5] reported the similar S_{Ni}' mechanism in the system of $>P\text{-}O\text{-}CH_2\text{-}C\equiv C\text{-}H$ as illustrated below :



The compound (XIII) is regarded to result from XII, because such rearrangement of the unsaturated bond has been known in many cases.

$$R\text{-}CH_2\text{-}C\equiv C\text{-}H \xrightarrow[170^\circ]{KOH\text{-}EtOH} [R\text{-}CH=C=CH_2] \longrightarrow R\text{-}C\equiv C\text{-}CH_3 \text{ }^{6)}$$

$$(CH_3)_2CH\text{-}C\equiv C\text{-}H \xrightarrow[170^\circ]{KOH\text{-}EtOH} (CH_3)_2C=C=CH_2 \text{ }^{7)}$$

$$CH_3(CH_2)_4C\equiv C(CH_2)_4CH_3 \xrightarrow{NaNH_2} CH_3(CH_2)_9C\equiv CNa \text{ }^{6)}$$

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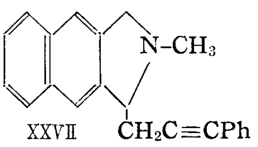
5) V. Mark : Tetrahedron Letters, **1962**, 281.
6) T. A. Jacobs, *et al.* : J. Am. Chem. Soc, **73**, 1273 (1951).
7) C. K. Ingold : "Structure and Mechanism in Organic Chemistry" p. 148 (1953) (London).

Then this propargylic rearrangement was extended to a cyclic system to cause a ring expansion reaction. 2-Methyl-2-(3-phenyl-2-propynyl)benzo[*f*]isoindolinium bromide (XIV), prepared from 2-methylbenzo[*f*]isoindoline and 3-phenyl-2-propynyl bromide, was treated with aqueous sodium hydroxide at 90° to afford a crystalline substance of m.p. 90~91°. Its analytical results agreed with $C_{22}H_{19}N$ and in ultraviolet spectrum the characteristic absorptions for phenylacetylene group at 240 and 250 mμ were observed. Since N-Me group was observed in nuclear magnetic resonance spectrum of the product, the methyl group of the starting material (XIV) took no part in this reaction. Consequently, the substance obtained here is to be either XVI, or XXVII. However, the possible structure (XXVII) is excluded by the following facts : (i) as shown in the reaction of II, VI, and X, C–N bond of phenyl propargyl ammonium group can not be cleaved with aqueous alkaline solution (ii) if phenylpropargyl group behaved as migrating group, an allenic substance should be obtained as shown in the case of the reaction of X. From these results, the crystalline substance obtained from XIV was deduced to be 2-methyl-3-(2-phenylethynyl)-1,2,3,4-tetrahydrobenzo[*g*]isoquinoline (XVI). The degradation reaction of XVI was not carried out because XVI was rather unstable and only small amount of XVI could be obtained from XIV.



XXVII

Contrary to our expectation, benzyldimethyl(2-propynyl)ammonium bromide (XVIII) gave no rearrangement product by the similar procedure, but it afforded N,N-dimethylbenzylamine (XIX), which was identified as methylammonium iodide.

From these results the effectiveness of cleavage of C–N bond in this rearrangement can be illustrated by the following order :

$$\mathrm{H{-}C{\equiv}C{-}CH_2{-}\overset{\oplus}{N}{<}} \;>\; \mathrm{Ph{-}CH_2{-}\overset{\oplus}{N}{<}} \;\approx\; \mathrm{H_2C{=}CH{-}CH_2{-}\overset{\oplus}{N}{<}} \;>\; \mathrm{Ph{-}C{\equiv}C{-}CH_2{-}\overset{\oplus}{N}{<}} \;>\; {}^{\oplus}\mathrm{CH_3{-}N{<}}$$

In the case of Von Brown's reaction the order of fission of C–N bond is as follows[8] :

$$\mathrm{Ph{-}CH_2{-}N}\angle \;\approx\; \mathrm{H_2C{=}CH{-}CH_2{-}N}\angle \;>\; \mathrm{H{-}C{\equiv}C{-}CH_2{-}N}\angle \;>\; \mathrm{CH_3{-}N}\angle$$

In both cases, the tendency of the cleavage of C–N bond is similar except the propargyl group ($-CH_2-C{\equiv}C-H$). This abnormal departing character of propargyl group in basic medium would be due to the formation of a carbene :

$$\mathrm{H{-}C{\equiv}C{-}CH_2{-}\overset{\oplus}{N}{<}} \xrightarrow{\mathrm{OH}^{\ominus}} \mathrm{\overset{\ominus}{C}{\equiv}C{-}CH_2{-}\overset{\oplus}{N}{<}} \longrightarrow \mathrm{\overset{\ominus}{C}{\equiv}C{-}\overset{\oplus}{C}H_2} \longrightarrow \mathrm{:C{=}C{=}CH_2}$$

However, an attempt to trap this carbene into cyclopropane ring according to the usual carbene reaction was fruitless, because such a reaction necessitates an inert solvent, while propargyl ammonium halide derivatives are not soluble in such solvent.

Experimental[*3]

N-Benzyl-N-methyl-3-phenyl-2-propynylamine (I)——A mixture of phenylacetylene (8.1 g.), benzylmethylamine (9.6 g.), paraformaldehyde (2.9 g.) and dioxane (15 ml.) was heated on steam bath for 16 hr. The cooled reaction mixture was poured into cold aq. 10% HCl and extracted with Et_2O. The aqueous layer was made alkaline with 10% NaOH solution and extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and evaporated. Distillation of the residue gave N-benzyl-N-methyl-3-phenyl-2-propynylamine (I) of $b.p_{0.005}$ 110~111° (16 g.). *Anal.* Calcd. for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found : C, 86.41; H, 7.51; N, 5.95. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (log ε) : 240 (4.42), 250.5 (4.35)

Benzyldimethyl(3-phenyl-2-propynyl)ammonium Iodide (II)——To N-benzyl-N-methyl-3-phenyl-2-propynylamine (I) (5.7 g.) was added MeI (2 ml.) under icewater cooling. After addition the temperature

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[*3] All melting points are uncorrected.

8) H. A. Hageman : Organic Reaction Vol. VII, p. 231 (New York).

of the reaction mixture was gradually allowed to rise to room temperature. Then the resulting crystalline substance was recrystallized from abs. EtOH to give N,N-dimethyl-N-benzyl-3-phenyl-2-propynylammonium iodide (II) of m.p. 170~171° (8.5 g.). *Anal.* Calcd. for $C_{18}H_{20}NI$: C, 57.30; H, 5.34; N, 3.71. Found : C, 57.10; H, 5.43; N, 3.63.

N,N-Dimethyl-1-benzyl-3-phenyl-2-propynylamine (IV)——To benzyldimethyl (3-phenyl-2-propynyl)-ammonium iodide (II) (14 g.) in H_2O (2 L.) were added NaOH (250 g.) in H_2O (250 ml.) and benzene (250 ml.). The reaction mixture was heated on the steam bath for 3 hr. Then benzene layer was separated and the aqueous layer was extracted with benzene. The combined extracts were dried over Na_2SO_4 and evaporated to give an oil, which was distilled under reduced pressure to give N,N-dimethyl-1-benzyl-3-phenyl-2-propynylamine (IV) of b.p$_{0.0004}$ 132~135° (5 g.). *Anal.* Calcd. for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found : C, 86.16; H, 7.49; N, 5.32. UV λ_{max}^{EtOH} mμ (log ε) : 241 (4.30), 252 (4.52). Picrate of IV showed m.p. 143~144°. *Anal.* Calcd. for $C_{24}H_{22}O_7N_4$: C, 60.24; H, 4.63; N, 11.71. Found : C, 60.68; H, 4.99; N, 11.72.

N,N-Dimethyl-1-benzyl-3-phenylpropylamine (V)——N,N-Dimethyl-1-benzyl-3-phenyl-2-propynylamine (IV) (0.6 g.) in EtOH (10 ml.) was hydrogenated over Pd-C (5%) (0.3 g.). 126 ml. of H_2 gas was absorbed (room temperature : 26°). The solid substance was filtered off and washed well with EtOH. The combined filtrate was evaporated under reduced pressure. The oily residue was dissolved in aq. 10% HCl and extracted with Et_2O. The aqueous solution was made alkaline with 10% NaOH solution and again extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and evaporated. Distillation of the residue gave N,N-dimethyl-1-benzyl-3-phenylpropylamine (V) of b.p$_{0.0004}$ 110~115° (bath temperature) (0.4 g.). *Anal.* Calcd. for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53. Found : C, 85.18; H, 9.01; N, 5.41. Picrate of V showed m.p. 142~143° (reported m.p. 143°[3]). *Anal.* Calcd. for $C_{24}H_{26}N_4O_7$: C, 59.74; H, 5.43; N, 11.61. Found : C, 59.72; H, 5.60; N. 11.39. Methylammonium iodide of V showed m.p. 192~194° (reported m.p. 193-194$_{\circ}$[3]) *Anal.* Calcd. for $C_{19}H_{26}NI$: C, 57.72; H, 6.63; N, 3.54. Found : C, 57.47; H, 65. 4; N, 3.64.

Dimethyl(2-propenyl)(3-phenyl-2-propynyl)ammonium bromide (VI)——To N,N-dimethyl-3-phenyl-2-propynylamine (15.7 g.) in abs. EtOH (100 ml.) was added allyl bromide (11.9 g.) under ice-water cooling. After addition the reaction mixture was stirred at room temperature overnight. Then, EtOH was evaporated under reduced pressure and the residual oil was dissolved in H_2O, and extracted with Et_2O. The aqueous layer was evaporated under reduced pressure to give an oil, which crystallized after long standing, m.p 93~95.5° (27 g.). Recrystallization from Me_2CO gave pure dimethyl(2-propenyl)(3-phenyl-2-propynyl)ammonium bromide of m.p. 96~97°. *Anal.* Calcd. for $C_{14}H_{18}NBr$: C, 60.01; H, 6.48; N, 4.99. Found : C, 59.98; H, 6.49; N, 4.96.

N,N-Dimethyl-1-(2-phenylethynyl)-3-butenylamine (VIII)——To dimethyl(2-propenyl)(3-phenyl-2-propynyl)ammonium bromide (VI) (26 g.) in H_2O (500 ml.) were added NaOH (60 g.) in H_2O (100 ml.) and benzene (200 ml.). The reaction mixture was heated on the water bath (90°) for 4 hr. Benzene layer was separated and the aqueous layer was extracted with Et_2O. The combined organic solution was extracted with cold aq. 10% HCl and the extracts were made alkaline with 10% NaOH solution under ice-water cooling. The solution was again extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and evaporated. Distillation of the residue gave N,N-dimethyl-1-(2-phenylethynyl)-3-butenylamine (VIII) of b.p$_5$ 114~115° (4 g.). *Anal.* Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.14; H, 8.63; N, 6.96. UV λ_{max}^{EtOH} mμ (log ε) : 240 (4.34), 251 (4.29). IR λ_{max}^{Liquid} μ : 10.04, 10.9 ($-CH=CH_2$). Picrate of VIII showed m.p. 117~118°. *Anal.* Calcd. for $C_{20}H_{20}N_4O_7$: C, 56.07; H, 4.71; N, 13.08. Found : C, 55.95; H, 4.95; N, 13.13.

N,N-Dimethyl-1-phenethylbutylamine (IX) from N,N-dimethyl-1-(2-phenylethynyl)-3-butenylamine (VIII)——N,N-dimethy-1-(2-phenylethynyl)-3-butenylamine (VIII) (0.5 g.) in EtOH (10 ml.) was hydrogenated over Pd-C (5%) (350 mg.). After absorption of H_2 gas the solid substance was filtered and washed well with EtOH. The combined filtrate was evaporated under reduced pressure. Distillation of the residue gave slightly impure N,N-dimethyl-1-phenethylbutylamine (IX) of b.p$_{2.5}$ 90~95° (bath temperature). This substance was contaminated with a small amount of an amine which was not completly hydrogenated. This contamination was confirmed by gas chromatography. Therefore it was purified and identified as methyl ammonium iodide. Methyl ammonium iodide of IX showed m.p. 150~152° and on admixture with an authentic sample no depression in melting point was observed. *Anal.* Calcd. for $C_{15}H_{26}NI$: C, 51.88; H, 7.55; N, 4.03. Found : C, 51.31; H,7.66; N,4.21.

1-Phenyl-3-hexanol (XXIII)[9]——Phenethylmagnesium bromide was prepared from phenethyl bromide (51.5 g.), Mg (6.8 g.), abs. Et_2O (200 ml) and abs. tetrahydrofurane (100 ml.) as usual. To this solution was added butylaldehyde (20 g.) in abs. Et_2O (30 ml.) under ice-water cooling. After addition the reaction mixture was stirred at 40° for 2 hr. After standing at room temperature overnight the solution was decomposed with 10% H_2SO_4 solution. The aqueous layer was extracted with Et_2O. The combined extracts were washed with $NaHCO_3$ solution and H_2O until neutral to litmus, dried over Na_2SO_4 and

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9) I. N. Nazarov, A. I. Kakhniashvili : Sbornik Statei Obshchei Khim, 2, 919 (1954).

evaporated. Distillation of the residue gave 1-phenyl-3-hexanol (XXIII) of b.p$_2$ 99~101° (21 g.). *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found : C, 80.26; H, 10.23.

1-Phenyl-3-hexanone (XXIV)⑽——To 1-phenyl-3-hexanol (XXIII) (18 g.) in AcOH (50 ml.) was added CrO_3 (7.2 g.) in AcOH (230 ml.) and H_2O (90 ml.) at 25~30° over a period of 3 hr. After addition the reaction mixture was stirred at room temperature for 2 hr. and then it was left at room temperature overnight. A small amount of oxalic acid was added and the green colored solution was submitted to steam distillation. About 3 L. of distillate was collected and it was extracted with Et_2O. The combined extracts were washed with $NaHCO_3$ solution and H_2O until neutral to litmus, dried over Na_2SO_4 and evaporated. Distillation of the residue gave 1-phenyl-3-hexanone (XXIV) of b.p$_7$ 122~124° (14 g.). 2,4-dinitrophenylhydrazone of (XXIV) showed m.p. 166~167°. *Anal.* Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66; N, 15.72. Found : C, 60.30; H, 5.69; N, 15.87.

N,N-Dimethyl-1-phenethylbutylamine (IX) from 1-Phenyl-3-hexanone (XXIV)——A mixture of 1-phenyl-3-hexanone (XXIV) (7 g.), dimethylformamide (11.6 g.) and formic acid (98%) (7.3 g.) was heated at 170~180° (bath temperature) for 37 hr. The cooled reaction mixture was poured into aq. 10% HCl and extracted with Et_2O. The aqueous layer was made alkaline with 10% NaOH solution and again extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and evaporated. Distillation of the residue gave N,N-dimethyl-1-phenethylbutylamine (IX) of b.p$_{3.5}$ 107~110° (bath temperature) (1.65 g.). Methyl ammonium iodide of IX showed m.p. 151~152.5° after recrystallization from abs. EtOH. *Anal.* Calcd. for $C_{15}H_{26}NI$: C, 51.88; H, 7.55; N, 4.03. Found : C, 51.67; H, 7.67; N, 3.91.

Dimethylbis(3-phenyl-2-propynyl)ammonium Bromide (X)——To N,N-dimethyl-3-phenyl-2-propynylamine (15.9 g.) in abs. EtOH (20 ml.) was added 3-phenyl-2-propynyl bromide (19.5 g.) in abs. EtOH (8 ml.) under ice-water cooling. Then the reaction mixture was allowed to stand at room temperature for 2 days. The resulting crystalline substance was collected by filtration and recrystallized from abs. EtOH to give dimethylbis(3-phenyl-2-propynyl)ammonium bromide (X) of m.p. 179~180° (22 g.). *Anal.* Calcd. for $C_{20}H_{20}NBr$: C, 67.80; H, 5.69; N, 3.95. Found : C, 67.77; H, 5.74; N, 4.01.

N,N-Dimethyl-2-phenyl-1-(2-phenylethynyl)-2,3-butadienylamine (XII) and N,N-Dimethyl-2-phenyl-1-(2-phenylethynyl)-3-butynylamine (XIII)——$NaNH_2$ was prepared from Na (334 mg.), liquidNH_3 (150 ml.) and a small amount of $Fe(NO_3)_3$ as usual. To this solution was added dimethylbis(3-phenyl-2-propynyl)ammonium bromide (X) (2.56 g.) and the reaction mixture was stirred at −50° for 3 hr. Then NH_4Cl (1.6 g.) was added and NH_3 was evaporated at room temperature with continuous mechanical stirring. To the residue was added H_2O and Et_2O, and Et_2O layer was separated, the aqueous layer was extracted with Et_2O. The combined extracts were washed three times with H_2O, dried over Na_2SO_4 and evaporated. The oily residue (1.9 g.) was dissolved in benzene (4 ml.) and adsorbed in Al_2O_3 (60 g.) (Woelm, grade III). Elution with hexane gave crystalline N,N-dimethyl-2-phenyl-1-(2-phenylethynyl)-2,3-butadienylamine (XII) (1.29 g.). Recrystallization from 95% EtOH gave prisms of m.p. 61~62° (0.61 g.). Picrolonate showed m.p. 153~154° after recrystallization from 95% EtOH. *Anal.* Calcd. for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found : C, 87.71; H, 7.06; N, 4.97. UV λ_{max}^{EtOH} mμ (log ε) : 241.5 (4.49), 251 (4.48). IR $\nu_{max}^{CS_2}$ μ : 5.15 ($>C=C=C<$), 11.76 ($>C=C=CH_2$).

Elution with hexane-benzene (1:1) gave N,N-dimethyl-2-phenyl-1-(2-phenylethynyl)-3-butynylamine (XIII) (409 mg.). Recrystallization from hexane afforded needles of m.p. 111~113°. One more recrystallization from the same solvent gave a sample of m.p. 114~115° (130 mg.). *Anal.* Calcd. for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found : C, 87.91; H, 6.94; N, 4.95. UV λ_{max}^{EtOH} mμ (log ε) : 241.5 (4.37), 252.2 (4.31). IR ν_{max}^{Nujol} μ : 3.09 ($-C\equiv C-H$).

2-Methyl-2-(3-phenyl-2-propynyl)benzo[*f*]isoindolinium Bromide (XIV)——To 2-methylbenzo[*f*]isoindoline (650 mg.) in abs. EtOH (8 ml.) was added 3-phenyl-2-propynyl bromide (695 mg.) in abs. EtOH (2 ml.) and the reaction mixture was stirred at room temperature for 12 hr. The resulting crystalline substance was collected by filtration and recrystallized from EtOH (99%) to give 2-methyl-2-(3-phenyl-2-propynyl)benzo[*f*]isoindolinium bromide (XIV) as needles of m.p. 196~197° (800 mg.). *Anal.* Calcd. for $C_{22}H_{20}NBr$: C, 69.85; H, 5.33; N, 3.70. Found : C, 69.68; H, 5.21; N, 3.76.

2-Methyl-3-(2-phenylethynyl)-1,2,3,4-tetrahydrobenzo[*g*]isoquinoline (XVI)——To 2-methyl-2-(3-phenyl-2-propynyl)benzo[*f*]isoindolinium bromide (XIV) (670 mg.) in H_2O (200 ml.) were added NaOH (22 g.) in H_2O (20 ml.) and benzene (20 ml.). Then the reaction mixture was heated on a water bath (90°) for 2 hr. Benzene layer was separated and the aqueous layer was extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and evaporated to give an oily substance (400 mg.), which was dissolved in hexane-benzene (1:1) (4 ml.) and was adsorbed on Al_2O_3 (20 g.) (Woelm, grade III). Elution with hexane-benzene (1:1) gave a crystalline substance (190 mg.), which was recrystallized from hexane to give 2-methyl-3-(2-phenylethynyl)-1,2,3,4-tetrahydrobenzo[*g*]isoquinoline (XVI) as prisms of m.p. 90~91°. One more recrystallization from the same solvent did not alter the melting point. *Anal.* Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found : C, 88.42; H, 6.23; N, 4.47. UV λ_{max}^{EtOH} mμ (log ε) : 222.5 (4.90),

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10) H. Rupe, H. Hirschman : Helv. Chim. Acta., **14**, 687 (1931).

239.6 (4.50), 251 (4.41), 266 (3.80), 278 (3.77), 287 (3.50). Picrate of XVI showed m.p. 172～173° after recrystallization from 95% EtOH. *Anal.* Calcd. for $C_{28}H_{22}N_4O_7$: C, 63.87; H, 4.21; N, 10.64. Found: C, 63.72; H, 4.15; N, 10.67.

N-Benzyl-N-methyl-2-propynylamine (XVII)——A mixture of benzylmethylamine (82 g.), Na_2CO_3 (140 g.), 2-propynyl bromide (80 g.) and EtOH (1400 ml.) was heated under reflux for 6.5 hr. The solid substance was filtered and washed with EtOH. The combined filtrate was evaporated under reduced pressure to give about 200 ml. of a liquid, which was poured into H_2O and extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and evaporated. Distillation of the residue gave N-benzyl-N-methyl-2-propynylamine (XVII) of b.p$_7$ 89～91° (60 g.). *Anal.* Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found : C, 82.16; H, 8.17; N, 8.61. Picrolonate showed m.p. 159～160°.

Benzyldimethyl(2-propynyl)ammonium Iodide (XVIII)——To N-benzyl-N-methyl-2-propynylamine (XVII) (10 g.) was added methyl iodide (10.7 g.) under ice-water cooling. After addition the temperature of the reaction mixture was allowed to rise to room temperature. The resulting crystalline substance was recrystallized from EtOH to give benzyldimethyl(2-propynyl)ammonium iodide (XVIII) of m.p. 148～149° (11.5 g.). *Anal.* Calcd. for $C_{12}H_{16}NI$: C, 47.85; H,5.36; N, 4.65. Found : C, 47.83; H, 5.38; N, 4.73.

N,N-Dimethylbenzylamine (XIX) from Benzyldimethyl(2-propynyl)ammonium Iodide (XVIII)——To benzyl dimethyl(2-propynyl)ammonium iodide (XVIII) (9.1 g.) in H_2O (700 ml.) was added NaOH (80 g.) in H_2O (100 ml.). Then the reaction mixture was heated on the water bath (90°) for 4 hr. The cooled solution was extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and evaporated. The residue was distilled under reduced pressure to give an oil of b.p$_4$ 43～45° (1.6 g). IR spectrum of this substance was identical with that of N,N-dimethylbenzylamine. This compound was converted into trimethylbenzylammonium iodide, which showed m.p. 178～179° after recrystallization from EtOH, no depression in melting point was observed on admixture with the authentic sample. *Anal.* Calcd. for $C_{10}H_{16}NI$: C, 43.34; H, 5.82; N, 5.05. Found : C, 43.31; H, 5.76; N, 5.34.

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Summary

The Stevens type rearrangement of phenylpropargylammonium halide derivatives was carried out. This rearrangement usually consists of 1,2-shift of migratory group, however, it was found that bis phenylpropargylammonium halide derivative underwent the 1,4-shift to give an allenic compound. The rearrangement was extended to a ring expansion reaction.

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