were carried out by Messrs. H. Higuchi, N. Higosaki, and Miss N. Sawamoto. Microanalyses were made by Dr. T. Onoe, Messrs. K. Ono, H. Nagashima, and Misses K. Saito, N. Gonda, and H. Masuda.

Summary

This is a new synthetic method for various 4-substituted-3-chromenes : phenyl propargyl ethers underwent intramolecular cyclization to give 4-chromene derivatives by heating with diethylaniline. The reaction mechanism was clarified by the study of substituted phenyl propargyl ethers under the consideration of their electronic effects on the yields of resulting 3-chromene; in general, the presence of +R group enhanced the cyclization, whereas −R group gave much lower yields of the corresponding chromenes. Therefore, this intramolecular cyclization is concluded to be an electrophilic reaction.

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178. Issei Iwai and Yasuo Yura : Studies on Acetylenic Compounds. XXXIII.*2 A New Synthetic Method for Aminoacetylenic Compounds.

(*Takamine Laboratory, Sankyo Co., Ltd.**1)

Although some synthetic methods for α-aminoacetylenes of the type $R''_2NR(R')_2C{\equiv}CR$ are known, a few of them are of general application. For the synthesis of tertiary aminoacetylenes, Mannich reaction is most frequently employed. Namely, treating an ethynyl compound with a mixture of formaldehyde and secondary amine gives the tertiary aminoacetylenes.[1]

$$RC{\equiv}CH + H_2CO + HNR_2' \longrightarrow RC{\equiv}CCH_2NR_2'$$

Besides this method, an alkylation of amines with haloacetylenes[2] or dehydrohalogenation of 2,3-dihalopropylamines[3] are also available for the synthesis. However, sometimes yields are rather low owing to side reactions.

$$RC{\equiv}CCH_2X + H_2NR' \longrightarrow RC{\equiv}CCH_2NHR' \xrightarrow{RC{\equiv}CCH_2X} (RC{\equiv}CCH_2)_2NR'$$

$$CH_2X\text{-}CHXCH_2NR_2' \xrightarrow[-2HX]{\text{Base}} HC{\equiv}CCH_2NR_2' \quad (X : \text{Halogen atom})$$

This paper describes a new synthetic method for aminoacetylenes. It has been reported that Schiff's base,[4] immonium salts,[5] aminoethers,[6] aminonitriles[7] and N,N-benzylidene bispiperidine[8] react with Grighard reagent to

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*2 Part XXXII : This Bulletin, **11**, 1042 (1963).

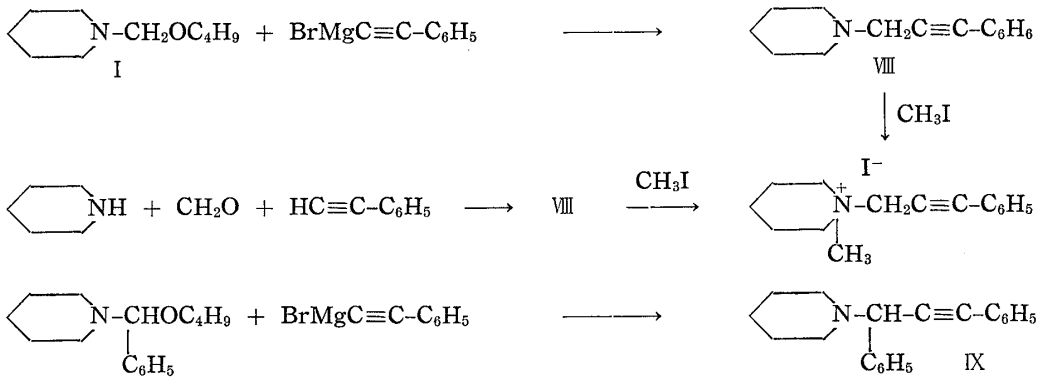
1) C. Mannich, F.T. Change : Ber., **66**, 418 (1933); I. Iwai, T. Hiraoka : This Bulletin, **10**, 81 (1962).
2) G.F. Hennion, E.G. Teach : J. Am. Chem. Soc., **75**, 1653 (1953); von V. Wolf : Ann., **576**, 35 (1952).
3) *Idem* : *Ibid.*, **592**, 222 (1955).
4) M. Busch : Ber., **37**, 2691 (1904); **38**, 1761 (1905); H. Gilman, J. Eisch : J. Am. Chem. Soc. **79**, 2150 (1957).
5) T.D. Stewart, W.E. Bradley : *Ibid.*, **54**, 4172 (1932).
6) G.M. Robinson, R. Robinson : J. Chem. Soc., **123**, 532 (1923).
7) T.S. Stevens, J.M. Cowan, J. MacKinnon : *Ibid.*, **1931**, 2568; T. Thomson, T.S. Stevens : *Ibid.*, **1932**, 2607.
8) A.T. Stewart, Jr., C.R. Hauser : J. Am. Chem. Soc., **77**, 1098 (1955).

$$RCH{=}NR' + R''MgBr \longrightarrow RR''CHNHR'$$
$$RCH{=}N^+R_2' + R''MgBr \longrightarrow RR''CHNR_2'$$
$$ROCH_2NR_2' + R''MgBr \longrightarrow R''CH_2NR_2'$$
$$NCCH_2NR' + R''MgBr \longrightarrow R''CH_2NR_2'$$
$$RCH(NC_5H_{10})_2 + R''MgBr \longrightarrow RR''CHNC_5H_{10}$$

afford corresponding amines.

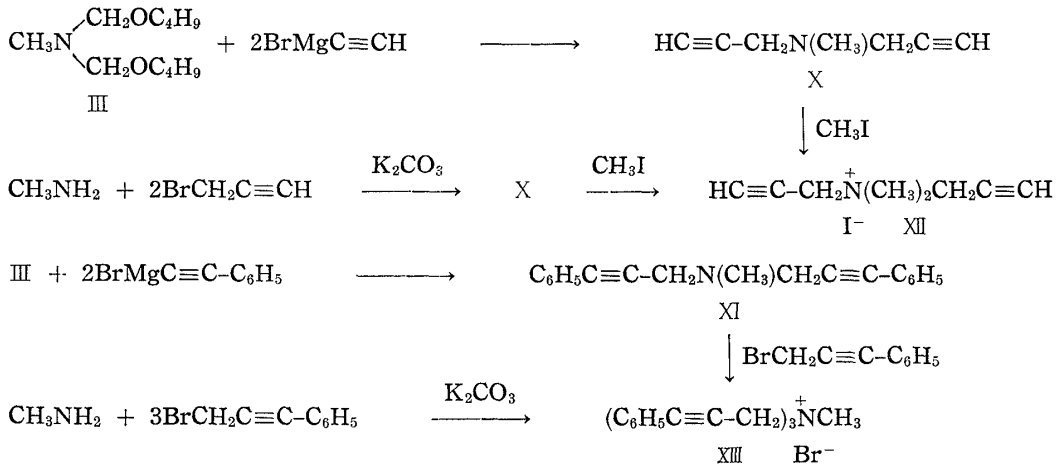
However, there is only one report on the Grignard reaction of an acetylenic compound with such nitrogen compounds. Campbell, *et al.*[9] reacted acetylenic Grignard compound with Schiff's base but they obtained neither any acetylenic amine nor a definite substance. In this laboratory it was found that acetylenic Grignard compounds were smoothly reacted with aminoethers in diethyl ether or in tetrahydrofuran to yield aminoacetylenes. It is a convenient and valuable method for the synthesis of aminoacetylenes.

Phenylethynylmagnesium bromide was reacted with piperidinomethyl butyl ether[6] (I) or α-piperidinobenzyl butyl ether[9] (II) which were prepared from piperidine, butyl alcohol and formaldehyde or benzaldehyde to give 1-phenyl-3-piperidino-1-propyne (VIII) or 3-piperidino-1,3-diphenyl-1-propyne (IX), respectively. The compounds (VIII) and (IX) showed absorptions for conjugated phenylethynyl groups in the ultraviolet spectra. The structure of VIII was further established by synthesis of the authentic sample which was prepared from piperidine, formaldehyde and phenylacetylene according to the method of Mannich and Chang.[10]

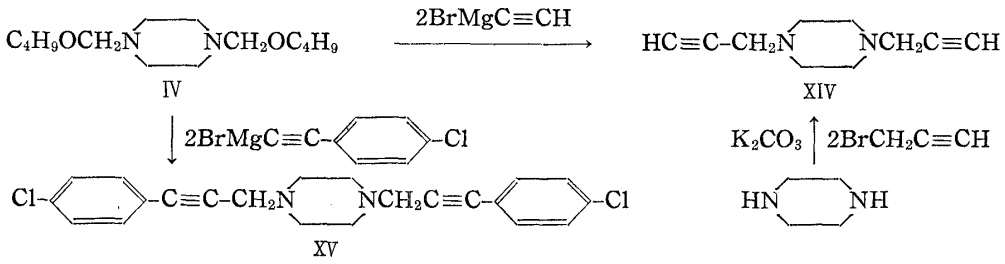


An aminoether N,N-bis(butoxymethyl)methylamine (III) was also reacted with ethynylmagnesium bromide and phenylethynylmagnesium bromide to afford N,N-di(2-propynyl)methylamine (X) and N,N-di(3-phenyl-2-propynyl) methylamine (XI), respectively. The compound X showed absorption of ethynyl group in the infrared spectrum, and the compound XI showed phenylethynyl group in the ultraviolet spectrum. The structures of X and XI were established by their independent syntheses. A methyl iodide derived from compound X showed no depression of melting point on admixture with N,N-di(2-propynyl)dimethylammonium iodide (XII), m.p. 136~137°, which was prepared by dipropynylation of methylamine followed by methylation. A quarternary ammonium bromide, obtained from compound XI and 3-phenyl-2-propynyl bromide showed no depression on the mixed melting point with tris(3-phenyl-2-propynyl)methylammonium bromide (XIII), m.p. 89~90°, which was prepared by the reaction of methylamine with 3-phenyl-2-propynyl bromide.

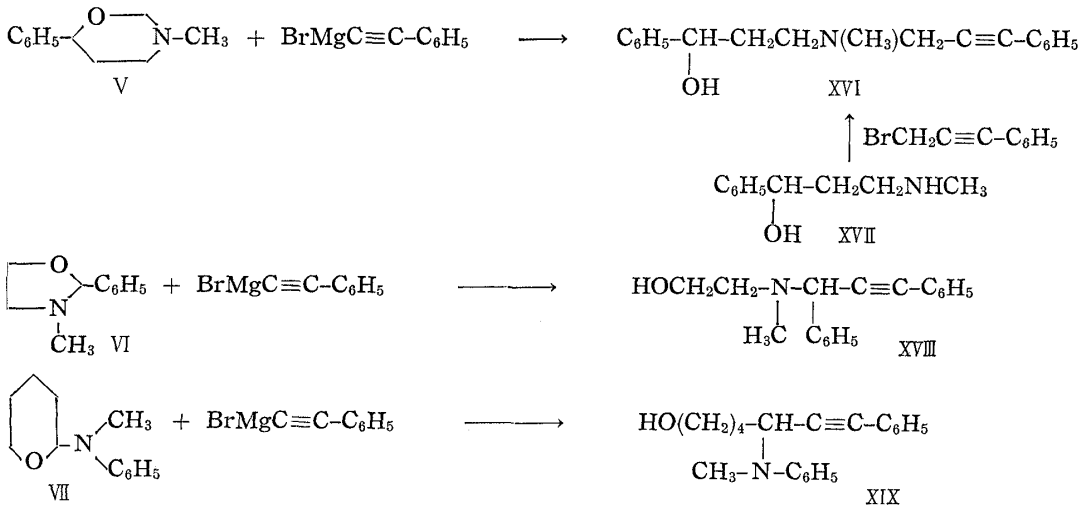
9) K.N. Campbell, C.H. Helbing, M.P. Florkowsky, B.K. Campbell: *Ibid.*, **70**, 3868 (1948).
10) C. Mannich, F.T. Chang: Ber., **66B**, 418 (1933).



Similarly, 1,4-bis(butoxymethyl)piperazine[6] (IV) yields 1,4-bispropynyl derivatives (XIV and XV). The structure of compound (XIV) was established by independent synthesis. It showed no depression in melting point on admixture with the substance, m.p. 95°, which was prepared by reaction of piperazine with 2-propynyl bromide.



An oxazine compound *i.e.* 3-methyl-6-phenyltetrahydro-1,3-oxazine (V),[11] which is considered to be other type of aminoether, was reacted with phenylethynylmagnesium bromide to give oily product (XVI), which showed characteristic absorption of hydroxy group (3300 cm^{-1}) in the infrared spectrum and phenylethylnyl group (UV : λ_{max} 239.5, 249.5 mμ) in the ultraviolet spectrum. The compound (XVI) was identified as N-(1,3-diphenyl-2-propynyl)-N-(3-hydroxy-3-phenylpropyl)methylamine, by independent synthesis. Therefore, during the reaction, it is shown that the oxazine ring is cleaved to



11) H.D. Hartough, J.J. Dickert, Jr. : U.S.P., 2,647,117 (1953); C.A., 48, 8265 (1954).

afford acetylenic alcohol. Likewise, on the Grignard reaction of 2-phenyl-3-methyloxazolidine (VI),[12] the ring of the oxazolidine was opened to give an acetylenic aminoalcohol 3-[N-(2-hydroxyethyl)methylamino]-1,3-diphenyl-2-propyne (XVII). Moreover, 2-aminotetrahydropyranyl derivative *i.e.* 2-[(N-methyl)phenylamino]tetrahydropyran[13] (VII) also was reacted with phenylethynylmagnesium bromide has been shown to give the corresponding acetylenic aminoalcoholy (XIX).

It was shown that acetylenic Grignard compounds reacted with aminoethers to cleave the ether linkage and afforded aminoacetylenes. Furthermore, in the ring compound such as oxazine, oxazolidine and tetrahydropyran compounds, the ether linkages were cleaved by this reaction to afford acetylenic aminoalcohol derivatives. Accordingly, acetylenic derivatives of β-, γ-, and δ-aminoalcohols, which are expected to have a biological activities, have become readily available by this reaction from acetylenic Grignard compound and oxazine, oxazolidine and tetrahydropyran compounds, respectively.

Table I.

Amino-ether	Grignard reasent	Product	Formula	Yield (%)	b.p. (°C) (mm.)	m.p. (°C)
I	PhC≡CMgBr	VIII	$C_{14}H_{17}N$	76	95 (0.025)	167[a]
II	〃	IX	$C_{20}H_{21}N$	30	105 (3×10^{-4})	—
III	HC≡MgBr	X	C_7H_9N	44	66.5 (65)	136.5～137[a]
III	PhC≡CMgBr	XI	$C_{19}H_{17}N$	55	136 (2×10^{-4})	89 ～ 90[b]
IV	HC≡CMgBr	XIV	$C_{10}H_{14}N_2$	52	—	95
IV	*p*-ClC_6H_4-C≡CMgBr	XV	$C_{22}H_{20}N_2Cl_2$	61	—	155
V	PhC≡CMgBr	XVI	$C_{19}H_{21}ON$	33	150 (10^{-4})	—
VI	〃	XVIII	$C_{18}H_{19}ON$	53	145 (3×10^{-4})	—
VII	〃	XIX	$C_{20}H_{23}ON$	26	155～165 (1.5×10^{-4})	—

a) Melting point of the methiodide of the corresponding tertiary amines
b) Melting point of the 3-phenyl-2-propynyl bromide of XI

Experimental

Materials——Piperidinomethyl butyl ether (I),[6] α-piperidinobenzyl butyl ether (II),[9] N,N-bis(butoxymethyl) methylamine (III),[6] 1,4-bis (butoxymethyl) piperazine (IV),[6] 3-methyl-6-phenyltetrahydro-1,3-oxazine (V),[11] 2-phenyl-3-methyloxazolidine (VI)[12] and 2-[(N-methyl)phenylamino]tetrahydropyran (VII)[13] were prepared as described in the literature, respectively.

Reaction of Acetylenic Grignard Reagents with Aminoether.

1-Phenyl-3-piperidino-1-propyne (VIII)——To EtMgBr solution prepared from 9.55 g. of EtBr and 2.05 g. of Mg in 100 ml. of anhyd. tetrahydrofuran, a solution of 8.94 g. of phenylacetylene in 10 ml. of anhyd. tetrahydrofuran was added dropwise over a period of 30 min. The mixture was stirred at 50° for 2 hr. To the mixture, a solution of 10 g. of piperidinomethyl butyl ether (I) in 10 ml. of anhyd. tetrahydrofuran was added and stirred under reflux for 3 hr. The mixture was decomposed with 10% aq. HCl under ice-cooling, and extracted with Et_2O to remove unchanged material. The acidic aqueous solution was made alkaline with K_2CO_3, and filtered off to remove $MgCO_3$. The filtrate was extracted with Et_2O and dried over K_2CO_3. The residue was distilled *in vacuo* to give 8.8 g. of pale yellow oil, $b.p._{0.025}$ 90～95°. *Anal.* Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.38; H, 8.56; N, 6.90. UV λ_{max}^{EtOH} mμ (log ε): 239.5 (4.32), 250 (4.25).

A mixture of 1 g. of VIII, 0.72 g. of CH_3I and 1 ml. of anhyd. EtOH was allowed to stand for 5 hr. at room temperature. After removal of EtOH, the solid residue was recrystallized from EtOH to give colorless needles of m.p. 167°. A mixed melting point with the authentic sample, m.p. 167°, prepared by the method of Mannich and Chang,[10] showed no depression. *Anal.* Calcd. for $C_{15}H_{20}NI$: C, 52.78; H, 5.86; N, 4.10. Found: C, 52.70; H, 5.99; N, 3.98. IR: ν_{max}^{Nujol} 2231 cm^{-1}(-C≡C-).

3-Piperidino-1,3-diphenyl-1-propyne (IX)——α-Piperidinobenzyl butyl ether (II; 10 g.) was heated with phenylethynylmagnesium bromide (prepared from 4.13 g. of phenylacetylene, 4.4 g. of EtBr and 0.98 g. of Mg in tetrahydrofuran) as above and the crude product was distilled *in vacuo*, b.p. 105°/3×10^{-4}.

12) M. Senkus: J. Am. Chem. Soc., **67**, 1515 (1945).
13) C. Glacet: Bull. soc. chim. France, **21**, 575 (1954).

Yield, 3.07 g. (30%). *Anal.* Calcd. for $C_{20}H_{21}N$: C, 87.22; H, 7.69; N, 5.09. Found: C, 87.12; H, 7.60; N, 5.19. UV λ_{max}^{EtOH} mμ (log ε): 241.0 (4.31), 251.5 (4.24).

N,N-Di(2-propynyl)methylamine (X)——a) To a solution of ethynylmagnesium bromide in tetrahydrofuran prepared from 43.6 g. of EtBr, 9.6 g. of Mg, 400 ml. of anhyd. tetrahydrofuran and acetylene by the method of Jones, *et al.*,[14] a solution of N,N-bis(butoxymethyl)methylamine (III; 40.6 g.) in 50 ml. of anhyd. tetrahydrofuran was added and stirred at 50° for 15 hr. The mixture was treated as above, and the residue was distilled *in vacuo* to give 9.4 g. of colorless oil, b.p_{70} 69~70°. *Anal.* Calcd. for C_7H_9N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.06; H, 8.46; N, 12.98. IR ν_{max}^{liquid} cm^{-1}: 3300 (≡CH), 2215, 2200 (-C≡C-). A methiodide of X melted at 136.5~137° which was recrystallized from EtOH. A mixed melting point with the corresponding methiodide (XII), m.p. 136~137°, which was prepared from methylamine and 2-propynyl bromide, showed no depression. *Anal.* Calcd. for $C_8H_{12}NI$: C, 38.55; H, 4.81; N, 5.62. Found: C, 38.65; H, 4.91; N, 5.66. IR ν_{max}^{Nujol} cm^{-1}: 3190 (≡CH), 2130 (-C≡C-).
b) A mixture of 4.2 g. of CH_3NH_2, 16 g. of 2-propynyl bromide, 24 g. of K_2CO_3 and 20 ml. of EtOH was allowed to stand for one week at room temperature. The mixture was diluted with H_2O, and extracted with Et_2O. After removal of Et_2O the basic residue was distilled at reduced pressure, b.p_{70} 69~70°. It gave a methiodide of m.p. 136~137°. *Anal.* Calcd. for $C_8H_{12}NI$: C, 38.55; H, 4.81; N, 5.62. Found: C, 38.72; H, 4.80; N, 5.71. IR ν_{max}^{Nujol} cm^{-1}: 3190 (≡CH), 2130 (-C≡C-).

N,N-Bis(3-phenyl-2-propynyl)methylamine (XI)——To a solution of phenylethynylmagnesium bromide in tetrahydrofuran (prepared from 11.6 g. phenylacetylene, 12.4 g. of EtBr, 2.38 g. of Mg and 130 ml. of anhyd. tetrahydrofuran), a solution of 11.5 g. of N,N-bis-(butoxymethyl)methylamine (III) and 20 ml. of tetrahydrofuran was added and stirred on a steam bath for 15 hr. The reaction mixture was treated as above. b.p. 136°/2×10⁻4. Yield, 8.1 g. (55%). *Anal.* Calcd. for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.52; H, 6.60; N, 5.34. UV λ_{max}^{EtOH} mμ (log ε): 240.0 (4.57), 251.0 (4.53).

A solution of 1 g. of XI and 0.66 g. of 3-phenyl-2-propynyl bromide in EtOH (5 ml.) was allowed to stand over-night at room temperature. After removal of EtOH the solid was recrystallized from 50% EtOH to give III as needles of m.p. 89~90°. UV λ_{max}^{EtOH} mμ (log ε): 231.5 (3.90), 289 (2.88). IR ν_{max}^{Nujol} cm^{-1}: 2245 (-C≡C-).

A mixture of 2.8 g. of CH_3NH_2, 17.6 g. of 3-phenyl-2-propynyl bromide, 32 g. of K_2CO_3 and 30 ml. of EtOH was heated under reflux for 3 hr. The mixture was treated with H_2O and Et_2O, and insoluble solid was collected. The solid was recrystallized from 50% EtOH to give colorless needles of m.p. 89~90°. It showed no depression on admixture with XIII.

1,4-Di(2-propynyl)piperazine (XIV)——a) To a solution of ethynylmagnesium bromide (prepared from 8.45 g. of EtBr, 1.87 g. Mg, 100 ml. of anhyd. tetrahydrofuran and acetylene), 10 g. of 1,4-bis-(butoxymethyl)piperazine (IV) was added and stirred at 50° for 5 hr. The mixture was treated with aq. HCl and then made alkaline with 20% NaOH. A basic material was extracted with Et_2O and the extract was evaporated. The residue was crystallized from Et_2O to give 3.3 g. pale yellow needles, m.p. 93.5~95.0°. *Anal.* Calcd. for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 73.97; H, 8.68; N, 17.15. IR ν_{max}^{Nujol} cm^{-1}: 3200 (≡CH), 2200 (-C≡C-).
b) A solution of 2-propynyl bromide (27.6 g.), piperazine hydrate (25 g.) and K_2CO_3 (23.8 g.) in EtOH (150 ml.) was heated on the steam bath for 10 hr. After evaporation of EtOH the residue was treated with H_2O and Et_2O. The ethereal solution was dried and evaporated, and the solid was recrystallized from Et_2O to give a pale yellowish needles of m.p. 94~95°. It showed no depression on admixture with the sample obtained by Grignard reaction. *Anal.* Calcd. for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 73.89; H, 8.69; N, 17.20.

1,4-Bis[3-(*p*-chlorophenyl)-2-propynyl]piperazine (XV)——To a solution of *p*-chlorophenylethynylmagnesium bromide (prepared from 10.6 g. of *p*-chlorophenylacetylene, 8.45 g. of EtBr, 1.87 g. of Mg and 100 ml. of dehyd. tetrahydrofuran), a solution of 1,4-bis(butoxymethyl)piperazine (IV; 10 g.) in tetrahydrofuran (20 ml.) was added and stirred at 50° for 5 hr. The mixture was treated with 10% HCl and insoluble HCl-salts were filtered. The salt was treated with 20% NaOH and tetrahydrofuran, and the organic layer was dried over K_2CO_3 and evaporated. The residue was crystallized from benzene to give 9.03 g. of colorless needles, m.p. 154~155°. *Anal.* Calcd. for $C_{22}H_{20}N_2Cl_2$: C, 68.93; H, 5.22; N, 7.31. Found: C, 68.99; H, 5.17; N, 7.34. UV λ_{max}^{EtOH} mμ (log ε): 246.5 (4.73), 257.0 (4.70).

N-(1,3-Diphenyl-2-propynyl)-N-(3-hydroxy-3-phenylpropyl)methylamine (XVI)——a) To a solution of phenylethynylmagnesium bromide (prepared from 6.0 g. of phenylacetylene, 6.4 g. of EtBr, 1.14 g. of Mg and 70 ml. of tetrahydrofuran), a solution of 10.4 g. of 3-methyl-6-phenyltetrahydro-1,3-oxazine (V) in tetrahydrofuran (15 ml.) was added and heated at 50° for 3 hr. The mixture was treated as above and the residue was distilled *in vacuo* to give 5.8 g. of viscous oil, b.p. 150°/10^{-4}. *Anal.* Calcd. for $C_{19}H_{21}ON$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.18; H, 7.59; N, 5.12. UV λ_{max}^{EtOH} mμ (log ε): 239.5 (4.34), 249.5 (4.28). IR: ν_{max}^{Liquid} 3300 cm^{-1} (OH).

14) E. R. H. Jones, L. Skatteböl, M. C. Whiting: J. Chem. Soc., **1956**, 4765.

b) To a solution of 1 g. of 3-(N-methylamino)-1-phenyl-1-propanol in 16 ml. of anhyd. Et_2O was added 0.54 g. of 3-phenyl-2-propynyl bromide, and the mixture was stirred for 4 hr. at room temperature. The Et_2O layer was decanted from the precipitated salt and the ethereal solution was evaporated to give a pale viscous oil distilling at $150°/10^{-4}$. Yield, 0.88 g. (52%). Its IR and UV absorption spectra were superimposable with those of XVI. *Anal.* Found : C, 81.55; H, 7.56; N, 5.02.

3-(N-Methylamino)-1-phenyl-1-propanol (XVII)——To a solution of 2.45 g. of 2-(N-methylamino)-propiophenone[15] in 10 ml. of 95% EtOH, a solution of 1.36 g. of $NaBH_4$ in 30 ml. of EtOH was added and the reaction mixture was allowed to stand for 24 hr. at room temperature. The solvent was then removed under reduced pressure, and the residue was decomposed with 10% HCl and filtered. The filtrate was made alkaline with aq. NaOH, and extracted with Et_2O. After removal of solvent the residue was distilled to give a colorless oil of $b.p_2$ 109°. Yield, 2 g. (84%). *Anal.* Calcd. for $C_{10}H_{15}ON$: C, 72.69; H, 9.15; N, 8.48. Found : C, 72.49; H, 9.01; N, 8.43. Its IR spectrum showed no absorption of a carbonyl group.

1,3-Diphenyl-3-[N-(2-hydroxyethyl)methylamino]-1-propyne (XVIII)——To a solution of phenylethynylmagnesium bromide (prepared from 5.5 g. of phenylacetylene, 5.87 g. of EtBr, 1.3 g. of Mg and 60 ml. anhyd. tetrahydrofuran), a solution of 2-phenyl-3-methyloxazolidine (VI; 8.8 g.) in tetrahydrofuran (10 ml.) was added and heated for 3 hr. The mixture was treated an above and the residue was distilled *in vacuo* to give 7.58 g. of yellow viscous oil, b.p. $145°/3\times10^{-4}$. *Anal.* Calcd. for $C_{18}H_{19}ON$: C, 81.47; H, 7.22; N, 5.28. Found : C, 81.01; H, 7.19; N, 4.99. UV λ_{max}^{EtOH} mμ (log ε): 241.0 (4.33), 251.5 (4.28). IR : ν_{max}^{Liquid} 3440 cm^{-1}(OH).

5-[(N-Methyl)phenylamino]-7-phenyl-7-heptyn-1-ol (XIX)——To a solution of phenylethynylmagnesium bromide (prepared from 3.9 g. of phenylacetylene, 4.17 g. EtBr, 0.92 g. of Mg and 40 ml. of tetrahydrofuran), a solution of 2-[(N-methyl) phenylamino]tetrahydropyran (VII; 7.3 g.) in tetrahydrofuran (10 ml.) was added and heated for 6 hr. The mixture was treated as VIII and the residue was distilled *in vacuo* to give 2.91 g. of pale yellowish oil, b.p. $155\sim165°/1.5\times10^{-4}$. *Anal.* Calcd. for $C_{20}H_{23}ON$: C, 81.87; H, 7.90; N, 4.77. Found : C, 81.22; H, 7.79; N, 4.82. UV λ_{max}^{EtOH} mμ (log ε) : 239.5 (4.41), 251.0 (4.47). IR : ν_{max}^{Liquid} 3420 cm^{-1}(OH).

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Summary

A new and convenient route for the synthesis of various kinds of aminoacetylenes has been devised with Grignard reaction of aminoethers using acetylenemagnesium bromide. In the various cases examined, the yields range was 26~76%. Both N,N-di(2-propynyl)amine- an 1,4-di(2-propynyl)piperazine derivatives could be produced by this reaction, but in latter N,N-di(2-propynyl)methylamine derivative due to low reactivity of N,N-bis(butoxymethyl)methylamine (III) the reaction time was prolonged. Furthermore, by this reaction acetylenic aminoalcohols were obtained from cyclic aminoethers.

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15) C. Mannich, G. Heilner, Ber., **55**, 356 (1922).