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177. Issei Iwai and Junya Ide : Studies on Acetylenic Compounds. XXXII.[1] Ring Closure of Propargyl Ethers. (2).

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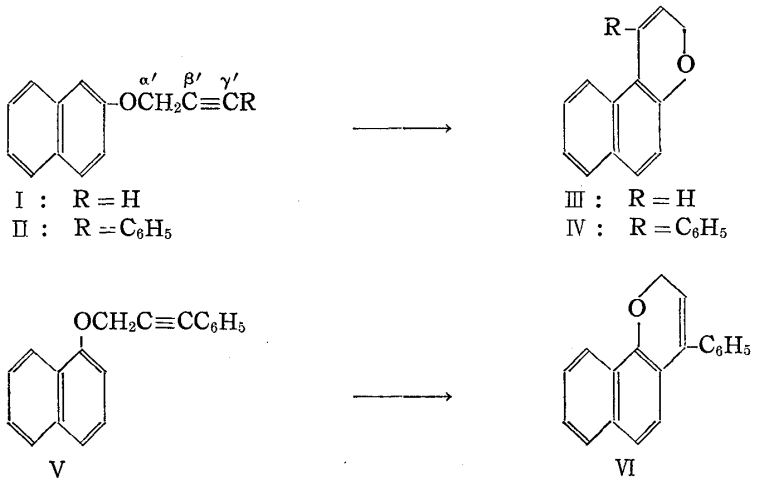
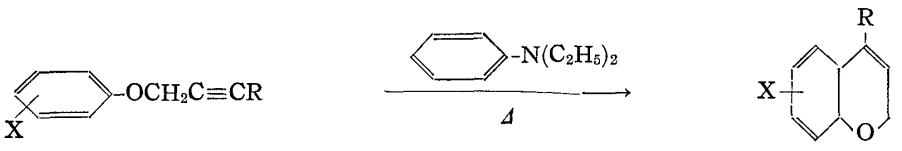
In the preceding paper,[2] the authors reported that β-naphthyl propargyl ethers, in which the double bond of β-naphthyl allyl group was replaced by a triple bond, did not undergo the Claisen rearrangement,[3] but gave naphthopyran derivatives by connecting with α-carbon atom of the naphthalene nucleus with γ′-carbon atom of triple bonds : heating of 3-(2′-naphthyloxy)-1-propyne (I) and 1′-phenyl-3-(2-naphthyloxy)-1-propyne (II) in N,N-diethylaniline gave 3*H*-naphtho[2,1-*b*]pyran (III) and 1-phenyl-3*H*-naphtho[2,1-*b*]pyran (IV), respectively. Moreover, a similar cyclization of α-naphthyl propargyl ether : 1-phenyl-3-(1′-naphthyloxy)-1-propyne (V) also occurred to give a corresponding pyran derivative (VI).



On the other hand, Iwai, *et al.*[4] reported another intramolecular ring closure of a triple bond to benzene nucleus by using polyphosphoric acid as the condensing reagent.

Expecting the same results as in the case of naphthyl propargyl ethers, this ring closure reaction was extended to study the intramolecular cyclization of phenyl propargyl ethers in this paper. Furthermore, the authors intend to clarify the reaction mechanism by the study of substituted phenyl propargyl ethers under the consideration of their electronic effects on the yields of resulting 3-chromenes.

The general experimental conditions involved heating one part of the ethers with five to ten parts of N,N-diethylaniline at 210~220° for ten to fifteen hours.



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1) Part XXXI : This Bulletin, **11**, 638 (1963).
2) I. Iwai, J. Ide : *Ibid.*, **10**, 926 (1962).
3) D.S. Tarbell : Org. Reaction **2**, chap. 1 (1944).
4) I. Iwai, T. Hiraoka : This Bulletin, **11**, 638 (1963).

Treatment of 3-phenyloxy-1-propyne with N,N-diethylaniline (b.p. 216°) for twelve hours gave a colorless oil, b.p_{14} 91~92°. Its elemental analysis agreed with C_9H_8O (B) and it showed no infrared absorptions bands for a triple bond, ethynyl group (CH≡) and terminal methylene group but showed new two absorptions; one was at 1634 cm^{-1} due to styrene type, the other was at 2841 cm^{-1}*2 which would be due to the absorption of methylene group between oxygen and double bond. The ultraviolet absorption maximum shifted to more bathochromic region comparing with that of the starting material as shown in Fig. 1.

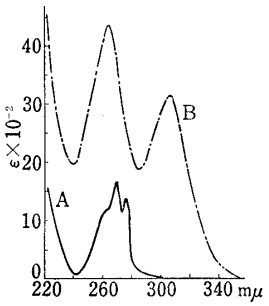
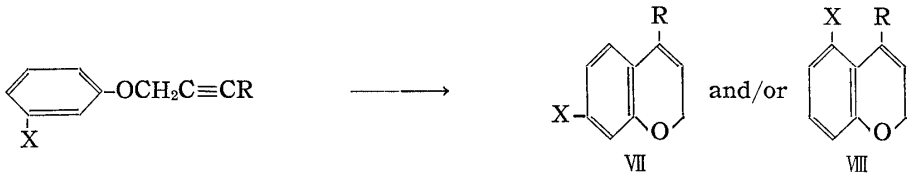


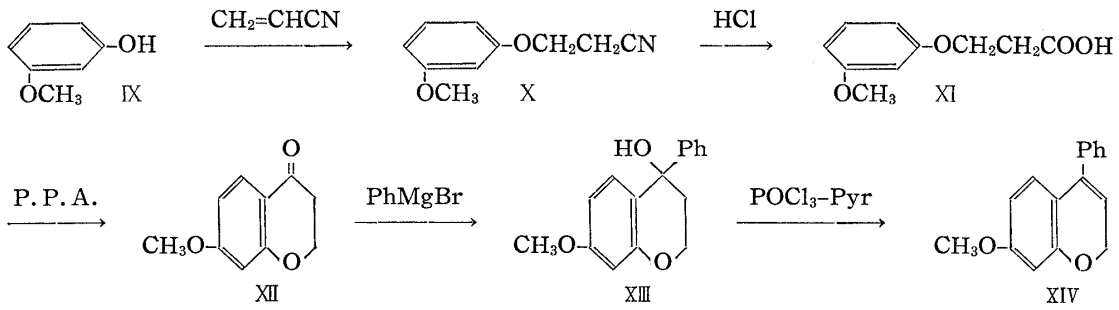
Fig. 1. Ultraviolet Absorption Spectra

A : 3-Phenyloxy-1-propyne (in EtOH)
B : 3-Chromene (in EtOH)

The dibromo derivative of B melts at 125.5~126.5°, which was identified with a compound reported by Angele, *et al.*[5] From these results, the formation of 3-chromene by intramolecular cyclization was confirmed. 4-Phenyl-3-chromene was also obtained from 1-phenyl-3-phenyloxy-1-propyne by the similar procedure. Therefore, it has been clarified that the intramolecular cyclization also occurred in the case of phenyl propargyl ether as for naphthyl propargyl ethers. The *meta*-substituted phenyl propargyl ethers would be expected to give two products : Ⅶ and Ⅷ, but practically only one product (Ⅶ) was obtained.



Heating of 1-phenyl-3-(3′-methoxyphenyloxy)-1-propyne and 3-(3′-methoxyphenyloxy)-1-propyne with N,N-diethylaniline gave pale yellow oil (C), b.$p_{0.0008}$ 170~180° and colorless oil (D), b.p_1 115~118° respectively. The former compound was synthesized by another following route :



*2 The cyclization products show the absorptions at about 2910 and 2840 cm^{-1} due to methylene group (-HC=CHCH₂-O-). The latter absorption shows rather strong intensity and shifted to lower frequency comparing with that of propargyl ethers.

5) Angele, *et al.* : Compt. rend. **235**, 1407 (1958).

Reaction of 7-methoxy-4-chromone (XII) prepared by the method of Bachman, *et al.*[6] with phenylmagnesium bromide gave XIII which on subsequent dehydration with phosphorous oxychloride was converted to 7-methoxy-4-phenyl-3-chromene (XIV). The compound (C) was identified by its boiling point, results of elemental analysis, ultraviolet and infrared spectrum with the prepared sample (XIV).

meta-Chloro substituted ethers also gave only one product, 7-chloro-3-chromene (R=Cl in VII), which showed the characteristic absorption band at 869 cm^{-1} for 1,2,4-trisubstituted benzene.

ortho-, *meta*-, and *para*-Nitrophenyl propargyl ether (R=H, X=NO_2) decomposed during the reaction to afford none of the corresponding chromene derivative. However, in the case of nitrophenyl phenylpropargyl ethers (R=C_6H_5, X=NO_2), only *para*-nitro compound gave the corrrsponding chromene derivative.

In addition to the compounds described above, the other 3-chromene derivatives obtained by this procedure are listed in Table I.

Table I.

No.	Substituents R	Substituents X	m.p. or b.p. (mm.)	Formula	Yield (%)	n_D (°C)	Reaction time (hr.)
1	H	H	91~ 92(14)	C_9H_8O	24	1.5837(16)	12
2	〃	6-CH_3O	115~118(1)[a]	$C_{10}H_{10}O_2$	30	1.5832(18)	15
3	〃	7-CH_3O	115~118(1)[a]	〃	12.5	1.5849(18)	15
4	〃	8-CH_3O	110~115(1)[a]	〃	11.9	1.5917(16)	15
5	〃	6-Cl	80~ 85(2)[a]	C_9H_7OCl	16.6	1.5963(23)	14
6	〃	7-Cl	80~ 85(2)[a]	〃	48	1.5999(23)	14
7	〃	8-Cl	100~110(2)[a]	〃	16	1.6001(23)	14
8	C_6H_5	H	110~120(0.05)[a]	$C_{15}H_{12}O$	70	1.6271(15)	10
9	〃	6-CH_3O	69~ 70(EtOH)[b]	$C_{16}H_{14}O_2$	46.4	—	8
10	〃	7-CH_3O	170~180(8×10^{-4})[a]	〃	56.7	1.6268(15)	8
11	〃	8-CH_3O	70~ 71(MeOH)[b]	〃	26.6	—	10
12	〃	6-Cl	130~140(8×10^{-4})[a]	$C_{15}H_{11}OCl$	30	1.6309(23)	10
13	〃	7-Cl	120~125(6×10^{-4})[a]	〃	43	1.6314(23)	10
14	〃	8-Cl	135~140(8×10^{-4})[a]	〃	30	1.6318(23)	10
15	〃	6-NO_2	110~111	$C_{15}H_{11}O_3N$	15	—	10

a) Bath temperature
b) Solvent for recrystallization

From these results, the following conclusions were drawn : In the case of substituted phenyl propargyl ethers, the presence of a +R group[7] enhanced the cyclization, whereas a −R group gave much lower yields of the corresponding chromenes. Substituents such as methoxy or chloro at the *meta*-position of phenyloxy group increase the electron density at the position where a triple bond binds to form a new ring. Besides these electronic considerations, there is no steric hindrance in *meta*-substituted compounds, thus the formation of the single compound (VII) was more favoured. Therefore, such *meta*-derivatives gave the best yields as compared to *ortho*- and *para*-substituted ethers. There is no effect of *ortho*- and *para*-substituents on the yield of the cyclization products, since they do not contribute any resonance effect.

On the other hand, the electron-withdrawing nitro substituent in *meta*-position decreases electron density at the position of cyclization and therefore, none of products was obtained. However, *para*-nitro substitsted ether gave the corresponding chromene, because the electron density at the position of cyclization was not decreased so much

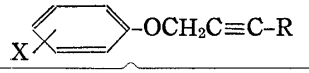
6) G. B. Bachman and H. A. Levine : J. Am. Chem. Soc., **70**, 599 (1948), J. D. Loudon, R. K. Razdan: J. Chem. Soc., **1954**, 4299 (1954).
7) E. S. Gould : Mechanism and Structure in Organic Chemistry 218. A Holt-Dryden Book Henry Holt & Co., New York.

as compared with *meta*-nitro substituted ethers. From these observations the reaction mechanism of this intramolecular cyclization is concluded to be an electrophilic reaction; namely, a triple bond attacks the δ^-— charged carbon atom adjacent to the ether linkage to form the new ring.

Experimental*2

General Procedure for the Synthesis of Phenyl Propargyl Ethers——A mixture of phenol (0.1 mol.), propargyl bromide or phenyl propargyl bromide (0.09 mol.), and anhyd. K_2CO_3 (0.12 mol.) in 40 ml. of Me_2CO was refluxed for 10 to 15 hr. The cooled mixture was filtered, and inorganic substance was dissolved in 50 ml. of H_2O and extracted with Et_2O. After concentration of filtrate, the residue was dissolved in 50 ml. of Et_2O. The combined ethereal solution was washed with 5% NaOH solution and then with H_2O until neutral and dried over anhyd. Na_2SO_4. The solvent was removed and the residues were purified either by recrystallization from a suitable solvent or distillation *in vacuo*. The phenyl propargyl ethers obtained by this method are listed in following Tables II and III.

Table II.



No.	Substituents R	Substituents X	IR λ_{max} μ ≡CH	IR λ_{max} μ -C≡C-	UV λ_{max}^{EtOH} mμ (log ε)
16	H	H	3.00	4.69[a]	263(3.08), 269(3.21), 276(3.14)
17	〃	2-CH_3O	2.99	4.69[a]	223(3.88), 273(3.32)
18	〃	3-CH_3O	3.01	4.70[a]	220(3.89), 273(3.33), 280(3.29)
19	〃	4-CH_3O	3.00	4.70[a]	225(3.98), 287(3.42)
20	〃	2-Cl	3.04	4.72[a]	221(3.99)(shoulder), 224.5(3.91), 273.5(3.38), 280.5(3.33)
21	〃	3-Cl	3.04	4.72[a]	268(3.16)(shoulder), 273(3.45), 280(3.32)
22	〃	4-Cl	3.04	4.72[a]	226(4.19), 279(3.31), 287(3.22)
23	〃	2-NO_2	3.02	4.70[c]	254(3.55), 312(3.39)
24	〃	3-NO_2	3.02	4.71[c]	224(4.06), 265(3.81), 318(3.33)
25	〃	4-NO_2	3.01	4.70[c]	223(4.03), 298(4.17)
26	C_6H_5	H	—	4.45[a]	240(4.38), 249(4.28)(shoulder), 270(3.42), 276(3.31)
27	〃	2-CH_3O	—	4.45[c]	240(4.36), 249(4.28)(shoulder), 265(3.66)(shoulder), 271(3.63), 278(3.52)(shoulder)
28	〃	3-CH_3O	—	4.45[a]	240(4.36), 249(4.24)(shoulder), 272(3.55), 279(3.47)
29	〃	4-CH_3O	—	4.46[c]	234(4.35)(shoulder), 239(4.37), 249(4.25)(shoulder), 271.5(3.41), 279(3.48), 283(3.49)(shoulder), 287(3.51)
30	〃	2-Cl	—	4.45[a]	240(4.32), 249(4.22)(shoulder), 272(3.39), 280.5(3.29)
31	〃	3-Cl	—	4.45[a]	234(4.26)(shoulder), 241(4.31), 249(4.20)(shoulder), 272.5(3.39), 280.5(3.29)
32	〃	4-Cl	—	4.45[c]	233(4.37), 239(4.37), 249(4.23)(shoulder), 271(3.26), 278(3.32), 287(3.15)
33	〃	2-NO_2	—	4.45[b]	240(4.21), 314(3.24)
34	〃	3-NO_2	—	4.45[b]	235(4.39)(shoulder), 239(4.41), 250(4.30)(shoulder), 318(3.34)
35	〃	4-NO_2	—	4.43[b]	228(4.45), 299(4.15)

a) in liq. film *b*) in nujol *c*) in CCl_4

3-Chromene (1)——A solution of 50 g. of 3-phenyloxy-1-propyne in 200 ml. of anhyd. N,N-diethylaniline was heated at 220~230° for 12 hr. on an oil bath. To the cooled reaction mixture was added 200 ml. of Et_2O and the ethereal solution was washed with 5% HCl until the solution showed no basisity and then washed with H_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was submitted to fractional distillation *in vacuo*: b.p_{14} 84°(1.8 g.), b.p_{14} 86~90°(4.5 g.), b.p_{14} 90~91°(15.9 g.), and b.p_{14} 91~92°(12.3 g.). The first and the second fractions showed a strong absorption of terminal ethynyl group (3344 cm^{-1}) in IR spectra, which appeared to be caused by the starting material. The third and last showed slightly the absorption. To the latter two fraction was added 5% $AgNO_3$ alcoholic solution with stirring until no precipitate appeared. After EtOH was removed under reduced pressure, the residue was extracted with Et_2O. The extracts were washed

*2 All melting points are uncorrected.

Table III.

No.	Substituents R	Substituents X	m.p. (°C) or b.p. (mm. Hg) (recryst. solvt.)	Yield (%)	n_D (°C)	Reaction time (hr.)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. (other)	Found C	Found H	Found (other)
16	H	H	50 ~ 51 (4)	77.5	1.5351 (16)	15	C_9H_8O	81.79	6.10	—	81.74	6.24	—
17	〃	2-CH_3O	98 ~100 (2)	60.5	1.5437 (25)	14	$C_{10}H_{10}O_2$	74.05	6.22	—	73.61	6.14	—
18	〃	3-CH_3O	97 ~ 99 (1)	67.3	1.5368 (26)	14	〃	74.05	6.22	—	73.26	6.05	—
19	〃	4-CH_3O	106 ~108 (2)	64.5	1.5357 (24)	14	〃	74.05	6.22	—	73.64	6.27	—
20	〃	2-Cl	74 ~ 76 (3)	64	1.5524 (24.5)	3	C_9H_7OCl	64.88	4.24	21.28 (Cl)	64.68	4.27	22.33 (Cl)
21	〃	3-Cl	75 ~ 76 (3)	62.7	1.5459 (24.5)	5	〃	64.88	4.24	21.28 (Cl)	64.47	4.24	21.62 (Cl)
22	〃	4-Cl	83 ~ 84 (3)	58.3	1.5457 (24.5)	6	〃	64.88	4.24	21.28 (Cl)	64.51	4.20	21.94 (Cl)
23	〃	2-NO_2	74 ~ 75.5 (EtOH)	52	—	5.5	$C_9H_7O_3N$	61.01	3.98	7.91 (N)	61.09	4.27	7.83 (N)
24	〃	3-NO_2	68 ~ 69 (EtOH)	63.2	—	7	〃	61.01	3.98	7.91 (N)	60.82	4.20	7.97 (N)
25	〃	4-NO_2	115 ~116 (EtOH)	66	—	4	〃	61.01	3.98	7.91 (N)	61.21	4.05	7.75 (N)
26	C_6H_5	H	48 ~ 49 (EtOH)	86.4	—	10	$C_{15}H_{12}O$	86.51	5.81	—	86.36	5.82	—
27	〃	2-CH_3O	43.5~ 44.5 (MeOH)	97	—	8	$C_{16}H_{14}O_2$	80.64	5.92	—	80.47	5.85	—
28	〃	3-CH_3O	155 ~156 (0.4)	65.5	—	10	〃	80.64	5.92	—	80.60	6.16	—
29	〃	4-CH_3O	80 ~ 81 (EtOH)	77.5	—	8	〃	80.64	5.92	—	80.48	5.76	—
30	〃	2-Cl	124 ~126 (4×10^{-4})	83	1.6092 (24.5)	10	$C_{15}H_{11}OCl$	74.22	4.57	14.61 (Cl)	73.70	4.57	14.49 (Cl)
31	〃	3-Cl	120 ~121 (6×10^{-4})	62.5	1.6033 (24.5)	3.5	〃	74.22	4.57	14.61 (Cl)	73.85	4.54	15.32 (Cl)
32	〃	4-Cl	59 ~ 60 (EtOH)	53	—	4	〃	74.22	4.57	14.61 (Cl)	73.46	4.64	14.57 (Cl)
33	〃	2-NO_2	89.5~ 91 (EtOH)	86.6	—	4.5	$C_{15}H_{11}O_3N$	71.14	4.37	5.53 (N)	70.98	4.65	5.65 (N)
34	〃	3-NO_2	70 ~ 70.5 (EtOH)	94	—	4	〃	71.14	4.37	5.53 (N)	71.37	4.33	5.61 (N)
35	〃	4-NO_2	77.5~ 78.5 (EtOH)	82.5	—	4	〃	71.14	4.37	5.53 (N)	71.31	4.10	5.57 (N)

with H_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was distilled *in vacuo*, to give colorless oil (11 g.), b.p_{14} 91~92° (24% of yield). *Anal.* Calcd. for C_9H_8O: C, 81.79; H, 6.10. Found: C, 80.82; H, 6.13. UV λ_{max}^{EtOH} mμ (log ε): 264 (3.64), 307 (3.49).

6-Methoxy-3-chromene (2)——A solution of 20 g. of 3-(*p*-methoxyphenyloxy)-1-propyne in 100 ml. of anhyd. N,N-diethylaniline was heated at 210~220° for 15 hr. on an oil bath. The reaction mixture was dissolved in 150 ml. of Et_2O. The solution was washed with 5% HCl until it showed no basisity, shaken with H_2O, and dried over Na_2SO_4. The solvent was removed under reduced pressure and distilled *in vacuo* to give pale yellow oil (6 g.), b.$p_{0.08}$ 110~140°. To the oily product was added 5% $AgNO_3$ alcoholic solution until no more precipitate appeared. After the precipitate was filtered off, EtOH was removed from filtration under reduced pressure. The residue was dissolved in 50 ml. of Et_2O, washed with H_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure. The distillation of the residue gave 3 g. of slight yellow oil (20% yield), b.p_1 115~118° (bath. temp.). *Anal.* Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.29; H, 6.15. UV λ_{max}^{EtOH} mμ (log ε): 223 (4.38), 260 (3.50) (shoulder), 328 (3.54).

7-Methoxy-3-chromene (3)——A solution of 20 g. of 3-(*m*-methoxyphenyloxy)-1-propyne in 100 ml. of anhyd. N,N-diethylaniline was heated at 210~220° for 15 hr. on an oil bath. The same procedure as in the case of 6-methoxy-3-chromene gave 2.5 g. of a pale yellow oil, b.p_1 115~118° (bath temp.) (12.5% yield). *Anal.* Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.34; H, 6.10. UV λ_{max}^{EtOH} mμ (log ε): 222 (4.24), 279 (3.88).

8-Methoxy-3-chromene (4)——Starting from a solution of 23.5 g. of 3-(*o*-methoxyphenyloxy)-1-propyne in 120 ml. of dehyd. N,N-diethylaniline, 2.8 g. of a pale yellow oil of b.p_1 110~115° (bath temp.) was given in yield of 11.9% by the same procedure as in the case of 6-methoxy-3-chromene. *Anal.* Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.30; H, 6.30. UV λ_{max}^{EtOH} mμ (log ε): 223 (4.23), 269 (3.84), 277 (3.75) (shoulder), 310 (3.21).

6-Chloro-3-chromene (5)——A solution of 3 g. of 3-(*p*-chlorophenyloxy)-1-propyne in 25 ml. of anhyd. N,N-diethylaniline was heated at 210~220° for 14 hr. on an oil bath. The reaction mixture was dissolved in 100 ml. of Et_2O. N,N-Diethylaniline was removed by shaking with 5% HCl. The ethereal solution was washed with H_2O and dried over Na_2SO_4. The solvent was removed *in vacuo* and the distillation of the residue *in vacuo* gave a pale yellow oil (0.7 g.), b.p_1 75~79° (bath temp.). Its IR spectra showed a weak absorption of a terminal ethynyl group at 3400 cm^{-1}. The redistillation of the oil *in vacuo* gave a colorless oil, b.p_2 80~85° (bath temp.) (16.6% yield). *Anal.* Calcd. for C_9H_7OCl: C, 64.80; H, 4.15; Cl, 21.24. Found: C, 63.90; H, 4.35; Cl, 21.54. UV λ_{max}^{EtOH} mμ (log ε): 224 (4.50), 265 (3.50), 318 (3.46).

7-Chloro-3-chromene (6)——A solution of 3 g. of 3-(*m*-chlorophenyloxy)-1-propyne in 25 ml. of anhyd. N,N-diethylaniline was heated at 210~220° for 14 hr. on an oil bath. The same procedure as in case of 6-chloro-3-chromene, gave 1.44 g. of colorless oil (48% yield), b.p_2 80~85° (bath temp.). *Anal.* Calcd, for C_9H_7OCl: C, 64.80; H, 4.15; Cl, 21.24. Found: C, 64.20; H, 4.36; Cl, 21.03. UV λ_{max}^{EtOH} mμ (log ε): 227 (4.39), 270 (3.74), 311 (3.50).

8-Chloro-3-chromene (7)——Heating a solution of 3 g. of 3-(*o*-chlorophenyloxy)-1-propyne in 25 ml. of anhyd. N,N-diethylaniline at 210~220° for 14 hr. on an oil bath, 0.45 g. of colorless oil (15% yield), b.p_2 100~110° (bath temp.) was given by the same procedure as in the case of 6-chloro-3-chromene. *Anal.* Calcd. for C_9H_7OCl: C, 64.80; H, 4.15; Cl, 21.24. Found: C, 64.35; H, 4.25; Cl, 21.28. UV λ_{max}^{EtOH} mμ (log ε): 225 (4.35), 231.5 (4.20) (shoulder), 268 (3.64), 276 (3.57) (shoulder), 312 (3.35).

4-Phenyl-3-chromene (8)——A solution of 3 g. of 3-phenyloxy-1-propyne in 45 ml. of anhyd. N,N-diethylaniline was heated at 240~250° for 10 hr. on an oil bath. N,N-Diethylaniline was removed under reduced pressure and the residue was dissolved in 60 ml. of Et_2O. The ethereal solution was washed successively with 5% HCl, sat. $NaHCO_3$ and H_2O, and dried over Na_2SO_4. After the evaporation of the solvent under reduced pressure, the residue was distilled *in vacuo* to give a 2.2 g. of pale yellow oil, b.$p_{0.05}$ 110~120° (bath temp.) (70% yield). *Anal.* Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.63; H, 5.70. UV λ_{max}^{EtOH} mμ (log ε): 221.5 (4.47) (shoulder), 248 (3.94) (shoulder), 269 (3.59), 274 (3.56) (shoulder), 306 (3.36).

4-Phenyl-6-methoxy-3-chromene (9)——A solution of 3.5 g. of 1-phenyl-3-(*p*-methoxyphenyloxy)-1-propyne in 35 ml. of anhyd. N,N-diethylaniline was heated at 240~250° for 8 hr. on an oil bath. N,N-Diethylaniline was removed under reduced pressure and the distillation of the residue *in vacuo* gave 1.623 g. of pale yellow oil, b.p. 140~150°/6×10^{-4} mm. Hg (bath temp.), which solidified on standing overnight at room temperature. Recrystallization of it from 95% EtOH gave colorless plates, m.p. 69~70° (46.6% yield). *Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.46; H, 5.90. UV: λ_{max}^{EtOH} 330 mμ (log ε 3.58).

4-Phenyl-7-methoxy-3-chromene (10)——A solution of 3 g. of 1-phenyl-3-(*m*-methoxyphenyloxy)-1-propyne in 45 ml. of anhyd. N,N-diethylaniline was heated at 240~245° for 8 hr. on an oil bath. After the basic solvent was removed under reduced pressure, the residue was distilled *in vacuo* to yield 1.7 g.

of a pale yellow oil, b.p. 170~180°/8×10^{-4} mm. Hg (56.7% yield). *Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.48; H, 5.83. UV: λ_{max}^{EtOH} 280 mμ (log ε 3.90).

4-Phenyl-8-methoxy-3-chromene (11)——A solution of 3 g. of 1-phenyl-3-(*o*-methoxypyhenyloxy)-1-propyne in 30 ml. of anhyd. N,N-diethylaniline was heated at 240~245° for 10 hr. on an oil bath. N,N-Diethylaniline was removed under reduced pressure. The viscous brown residue was dissolved in 99% EtOH and treated with active charcoal. After EtOH was removed under reduced pressure, the residue was distilled *in vacuo* to give 0.8 g. of a pale yellow oil, b.p. 160~170°/4×10^{-4} mm. Hg (bath temp.) which solidified on standing overnight at room temperature. The recrystallization of it from MeOH for three times gave colorless plates, m.p. 70~71° (26.6%). *Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: c, 80.44: H, 5.91. UV λ_{max}^{EtOH} mμ (log ε): 222 (4.57), 268 (3.84) (shoulder), 273 (3.85), 311 (3.14)

4-Phenyl-6-chloro-3-chromene (12)——A solution of 2 g, of 1-phenyl-3-(*p*-chlorophenyloxy)-1-propyne in 25 ml. of anhyd. N,N-diethylaniline was heated at 230~240° for 10 hr. on an oil bath. After N,N-diethylaniline was removed under reduced pressure, the residue was distilled *in vacuo* to give a pale yellow oil, b.p. 125~135°/4×10^{-4} mm. Hg (bath temp.), IR spectrum of which showed a slight absorption at 2230 cm^{-1} caused by a triple bond. The redistillation of the oil gave 0.6 g. of an oil, b.p. 130~140°/8×10^{-4} mm. Hg (bath temp.) (30% yield). *Anal.* Calcd. for $C_{15}H_{11}OCl$: C, 74.21; H, 4.57; Cl, 14.61. Found: C, 73.86; H, 4.36; Cl, 14.66. UV λ_{max}^{EtOH} mμ (log ε): 226 (4.46), 270 (3.50) (shoulder), 319 (3.35).

4-Phenyl-7-chloro-3-chromene (13)——Starting from a solution of 2 g. of 1-phenyl-3-(*m*-chlorophenyloxy)-1-propyne in 30 ml. of anhyd. N,N-diethylaniline, 0.86 g. of a pale yellow oil of b.p. 120~125°/6×10^{-4} mm. Hg (bath temp.) by the same procedure as in the case of 4-phenyl-6-chloro-3-chromene was given in a yield of 43%. *Anal.* Calcd. for $C_{15}H_{11}OCl$: C, 74.21; H, 4.57; Cl, 14.61. Found: C, 74.38; H, 4.64; Cl, 14.09. UV λ_{max}^{EtOH} mμ (log ε): 223 (4.32), 272.5 (3.55), 280 (3.49) (shoulder), 310 (3.18).

4-Phenyl-8-chloro-3-chromene (14)——Starting from a solution of 2 g. of 1-phenyl-3-(*o*-chlorophenyloxy)-1-propyne in 40 ml. of anhyd. N,N-diethylaniline, 0.6 g. of an pale yellow oil, b.p. 135~140°/8×10^{-4} mm. Hg (bath temp.) was given by the same procedure as in the case of 4-phenyl-6-chloro-3-chromene. *Anal.* Calcd. for $C_{15}H_{11}OCl$: C, 74.21; H, 4.57; Cl, 14.61. Found: C, 74.53; H, 4.42; Cl, 14.03. UV λ_{max}^{EtOH} mμ (log ε): 272 (3.64), 312 (3.31).

4-Phenyl-6-nitro-3-chromene (15)——A solution of 2 g. of 1-phenyl-3-(*p*-nitrophenyloxy)-1-propyne in 30 ml. of anhyd. N,N-diethylaniline was heated at 230~240° for 10 hr. on an oil bath. After most of all N,N-diethylaniline was removed under reduced pressure, the product was dissolved in 60 ml. of EtOH and an insoluble substance was filtered off. The ethereal solution washed with H_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue solidified which was recrystallized from 99% EtOH to give 0.3 g. of pale yellow needles, m.p. 110~111°. *Anal.* Calcd. for $C_{15}H_{11}O_3N$: C, 71.14; H, 4.37; N, 5.53. Found: C, 71.14; H, 4.48; N, 5.52. UV: λ_{max}^{EtOH} 251 mμ (log ε 4.35).

3,4-Dibromochromane——A solution of 3.2 g. (0.02 mol.) of Br_2 in 10 ml. of CCl_4 was added dropwise to a solution of 2.6 g. (0.02 mol.) in 8 ml. of CCl_4 with stirring under cooling with ice-water. After the addition of Br_2, stirring was continued for additional 30 min. The CCl_4 was removed under reduced pressure and the residue was recrystallized from CCl_4 to give 4 g. of colorless plates, m.p. 125.5~126.5° (69% yield). *Anal.* Calcd. for $C_9H_8OBr_2$: C, 37.01; H, 2.72; Br, 54.73. Found: C, 36.86; H, 2.66; Br, 54.92.

7-Methoxy-4-chromone (XII)——15 g. of 3-(*m*-methoxyphenyloxy)-propionic acid was added in small pieces to polyphosphoric acid prepared from 90 g. of P_2O_5 and 40 ml. of H_3PO_4 under stirring at 100° for 2 hr. Reaction mixture was poured into ice-water with stirring, stirred for additional 1 hr. and extracted with Et_2O. The extracts were washed with H_2O and dried over Na_2SO_4. After removal of the solvent, the residue solidified, recrystallized from petr. ether to give 3 g. of colorless needles, m.p. 56~57° (20% yield).

4-Phenyl-7-methoxy-3-chromene from XII——To the Grignard solution prepared from 0.136 g. of Mg and 0.882 g. of PhBr in 10 ml. of anhyd. Et_2O was added dropwise 1.0 g. of XII in 10 ml. of anhyd. Et_2O during 10 min. and the reaction mixture was stirred for 3 hr. and decomposed with sat. NH_4Cl solution and extracted with Et_2O. The ethereal solution was washed and dried over Na_2SO_4. The removal of the solvent gave 1.5 g. of a crude substance (XIII). To a solution of 1.5 g. of crude (XIII) in 25 ml. of anhyd. pyridine was added dropwise 7 ml. of $POCl_3$ with stirring under ice-cooling. The reaction mixture was allowed to stand for 2 days, poured into crushed ice, and extracted with Et_2O. The ethereal solution was washed successively with 5% HCl and H_2O, and dried over Na_2SO_4. After the removal of Et_2O, the residue was submitted to *vacuo* distillation to give a pale yellow oil, b.p. 140~150°/4×10^{-4} mm. Hg (bath temp.) (0.3 g.). *Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.11; H, 5.80. UV: λ_{max}^{EtOH} 280 mμ (log ε 3.85).

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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.

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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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