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Studies on Quinoline and Isoquinoline Derivatives. VIII.[1] Hydration and Hydrogenation of Ethynyl Substituents attached to the Pyridine Moiety of Quinoline and Isoquinoline Rings

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Studies were carried out on the hydration and hydrogenation of the triple bond in quinoline and isoquinoline derivatives containing an ethynyl substituent linked directly to the pyridine moiety. Fourteen kinds of ethynyl quinolines and isoquinolines such as 2-, 3-, 4-phenylethynylquinoline, 2-, 3-, 4-(1-hexynyl)quinoline, 2-(1-propynyl)quinoline, 1-, 3-, 4-phenylethynylisoquinoline, 1-, 3-, 4-(1-hexynyl)isoquinoline, and 1-(1-propynyl)-isoquinoline were converted into the corresponding acylmethyl derivatives with high selectivity, when they were heated in dilute sulfuric acid in the presence of mercuric sulfate. In all cases, no products due to reverse hydration were isolated.

Partial catalytic reduction of the ethynyl linkage of the above compounds is possible, while exhaustive reduction afforded quinolines and isoquinolines with a saturated side chain.

Keywords——ethynylquinolines; ethynylisoquinolines; hydration; acylmethylquinolines; acylmethylisoquinolines; catalytic reduction; quinolylolefins; isoquinolylolefins

In the preceding paper,[2] we showed that the orientation of hydration on phenylethynylisoxazole was strongly influenced by the position at which the phenylethynyl group was located. Namely, the addition of water to 4-phenylethynylisoxazoles under standard conditions afforded benzyl 4-isoxazolyl ketones as the main products, whereas 5-phenylethynylisoxazole was reversely hydrated under identical conditions to give 5-isoxazolylmethyl phenyl ketone predominantly. For comparison with the results mentioned above, we examined similar hydration of quinoline and isoquinoline derivatives having an ethynyl side chain at their pyridine moiety, and the results are described in the present paper. In all cases, the products thus obtained were proved to have acylmethylquinoline or acylmethylisoquinoline structures.

When 2-(1-propynyl)quinoline (**1a**) and 2-, 3-, and 4-(1-hexynyl)quinoline (**1b**, **d**, **f**)[3] were heated in dilute sulfuric acid in the presence of mercuric sulfate, the corresponding alkyl quinolylmethyl ketones (**2a**, **b**, **d**, **f**) were obtained without formation of isomeric by-products. The structures of the products (**2a**, **b**, **d**, **f**) were easily determined by taking their nuclear magnetic resonance (^{1}H-NMR) spectra, each of which showed a singlet (2H) due to an isolated methylene group. In the case of **2a** or **2b**, the presence of a tautomer was suggested by the ^{1}H-NMR spectrum. Accordingly, the quinolyl ketone structure (**4**) should be rejected.

Similarly, phenyl 2-, 3-, and 4-quinolylmethyl ketone (**2c**, **e**, **g**) were obtained by the hydration of 2-, 3-, and 4-phenylethynylquinoline (**1c**, **e**, **g**), respectively under the same conditions. The structures of these products were determined as follows. Phenyl 2-quinolylmethyl ketone (**2c**) and phenyl 4-quinolylmethyl ketone (**2g**) were identical with authentic samples prepared by the known method.[4,5] The ^{1}H-NMR spectrum of **2c** also showed the presence of an enolic tautomer (**3**). The structure (**2e**) could not be easily distinguished from the structure of type **4** by taking its ^{1}H-NMR spectrum. Thus, the product was transformed into the corresponding ketoxime by a usual method, and the resultant ketone oxime (**5**) was treated with phosphorus pentachloride in ether to give an amide (**6**). The acid hydrolysis of the amide (**6**) afforded aniline (**7**) and 3-quinolylacetic acid (**8**). The result of the above

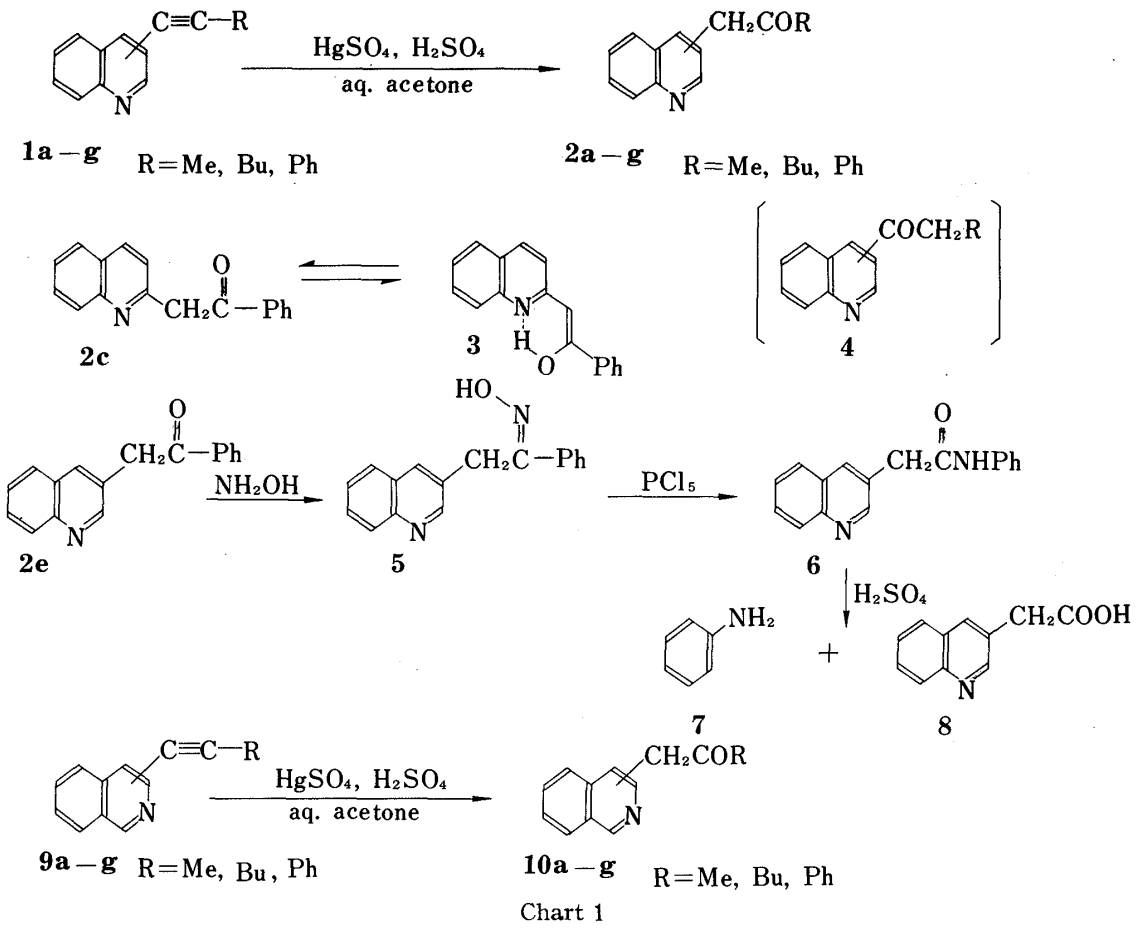
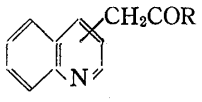


Chart 1

TABLE I. Hydration of Alkynylquinolines (**1a—g**)



2a—g

Compd. No.	Position R	Reaction time (h)	Yield (%)	bp(°C) (mm Hg)	mp (°C)	Appearance (recrystn. solv.)	Formula	Analysis (%) Calcd (Found) C	H	N
2a	2-Me	24	88		68—69 (Lit.[6] 68—69)	Yellow needles (ether–*n*-hexane)	*a*)			
2b	2-Bu	37	70	165—170 (2)		Yellow liquid	$C_{15}H_{17}NO$	79.26 (79.28)	7.54 (7.84)	6.16 (6.18)
2c	2-Ph	36	81		116—117 (Lit.[4] 119—120)	Yellow needles (AcOEt)	*a*)			
2d	3-Bu	20	46		77—78	Colorless needles (acetone–*n*-hexane)	$C_{15}H_{17}NO$	79.26 (79.33)	7.54 (7.62)	6.16 (5.87)
2e	3-Ph	18	89	230—240 (3)	74—75	Colorless needles (ether–*n*-hexane)	$C_{17}H_{13}NO$	82.57 (82.27)	5.30 (5.29)	5.66 (5.39)
2f	4-Bu	72	88	147—151 (2)		Yellow liquid	$C_{15}H_{17}NO$	79.26 (79.51)	7.54 (7.62)	6.16 (5.94)
2g	4-Ph	64	86	180—185 (2)	117—118 (Lit.[5] 114)	Colorless needles (acetone–*n*-hexane)	*a*)			

a) These compounds (**2a, c, g**) have appeared in the literature.

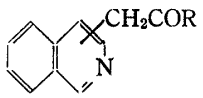
Beckmann rearrangement provides definitive support for the phenyl 3-quinolylmethyl ketone structure (**2e**).

Like ethynylquinolines, the corresponding ethynylisoquinolines were readily converted selectively into the products having an acylmethyl group. Namely, 1-, 3-, and 4-phenylethynylisoquinoline (**9c, e, g**) were hydrolyzed into isoquinolylmethyl phenyl ketones (**10c, e, g**) without the formation of the corresponding isomers. In the mass spectra of **10c, e, g**, a peak due to the $(M\text{-}PhCO)^+$ ion was commonly observed together with a molecular ion peak (m/e=247). The presence of the $(M\text{-}PhCO)^+$ ion peak with medium intensity was also recognized in the mass spectra of **2c, e, g**. Although chemical elucidation of **10c, e, g** was not attempted, the above spectral data supported the isoquinolylmethyl phenyl ketone structures of the products (**10c, e, g**).

Since the hydration of 1-(1-propynyl)isoquinoline (**9a**) and 1-, 3-, and 4-(1-hexynyl)-isoquinoline (**9b, d, f**) giving alkyl isoquinolylmethyl ketones was simple and similar to that of **10a, b, d, f**, the results thus obtained are listed in Table II without further explanation.

Based on the above experiments, the hydration of ethynylquinolines and ethynylisoquinolines is concluded to give the same type of methylene ketones, regardless of the substituted position.

TABLE II. Hydration of Alkynylisoquinolines (**9a—g**)



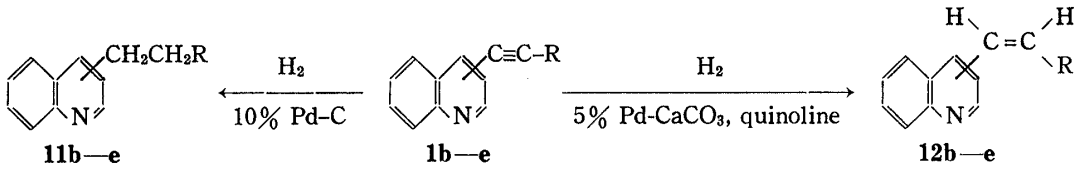
10a—g

Compd. No.	Position R	Reaction time(h)	Yield (%)	bp(°C) (mmHg)	mp (°C)	Appearance (recrystn.solv.)	Formula	Analysis (%) Cacld (Found) C	H	N
10a	1-Me	21	85	117—120(2) (Lit.[8] 120—130(1))	91—92.5	Yellow needles (ether–*n*-hexane)	*a*)			
10b	1-Bu	49	75	140—145(1)	54—55	Yellow needles (AcOEt)	$C_{15}H_{17}NO$	79.26 (79.08)	7.54 (7.37)	6.16 (5.87)
10c	1-Ph	48	66	198—200(1)	88—89 (Lit.[7] 85—86)	Yellow needles (acetone–*n*-hexane)	*a*)			
10d	3-Bu	20	90	145—149(2)		Yellow liquid	$C_{15}H_{17}NO$	79.26 (79.15)	7.54 (7.50)	6.16 (5.88)
10e	3-Ph	25	78	165—175(1)	117—117.5	Yellow needles (AcOEt)	$C_{17}H_{13}NO$	82.57 (82.84)	5.30 (5.25)	5.66 (5.41)
10f	4-Bu	45	88	150—152(1)		Yellow liquid	$C_{15}H_{17}NO$	79.26 (78.98)	7.54 (7.44)	6.16 (6.07)
10g	4-Ph	66	62		125—126	Colorless needles (acetone–*n*-hexane)	$C_{17}H_{13}NO$	82.57 (82.34)	5.30 (5.35)	5.66 (5.66)

a) These compounds (**10a, b**) have appeared in the literature.

The stepwise reduction of these acetylenes was also investigated. These acetylenes were reduced to the quinoline and isoquinoline derivatives with a saturated side chain by the use of a palladium-charcoal catalyst. However, when they were hydrogenated in the presence of a palladium-calcium carbonate catalyst and quinoline, the absorption of hydrogen stopped at the stage of one equivalent of hydrogen absorption, and the corresponding olefins (**12b—e, 14b, c, f, g**) were obtained, as expected. In the ^{1}H-NMR spectra of all the products, the coupling constants of two olefin protons on the side chain ranged from 11.0 Hz to 12.0 Hz, which demonstrated the *cis* configuration of the side chains. Since the condens-

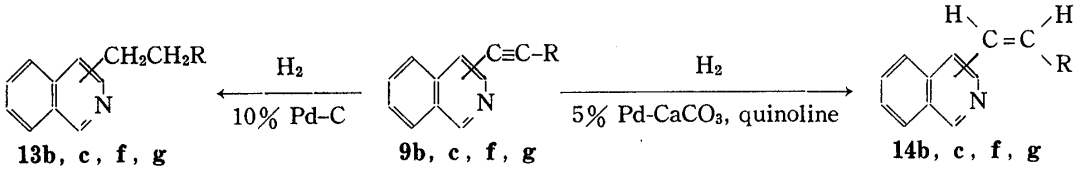
TABLE III. Catalytic Reduction of Alkynylquinolines (**1b—e**)



11b—e **1b—e** **12b—e**

Compd. No.	Position R	Yield (%)	bp(°C) (mmHg) [mp(°C)]	Appearance (recrystn.solv.)	Formula	Analysis (%) Calcd (Found) C	H	N
11b	2-Bu	70	105—110(1)	Yellow liquid	$C_{15}H_{19}N$	84.45 (84.19	8.98 9.16	6.57 6.48)
11c	2-Ph	60	150—165(1)	Yellow liquid	$C_{17}H_{15}N$	87.51 (87.41	6.48 6.46	6.00 6.06)
11d	3-Bu	59	160—164(5)	Yellow liquid	$C_{15}H_{19}N$	84.45 (84.21	8.98 9.07	6.57 6.63)
11e	3-Ph	66	152—154(4)	Yellow liquid	$C_{17}H_{15}N$	87.51 (87.33	6.48 6.49	6.00 5.98)
12b	2-Bu	71	143—145(1)	Yellow liquid	$C_{15}H_{17}N$	85.26 (85.26	8.11 8.49	6.63 6.72)
12c	2-Ph	65	165—170(3) [91—92]	Colorless needles (ether–*n*-hexane)	$C_{17}H_{13}N$	88.28 (88.23	5.67 5.88	6.06 6.34)
12d	3-Bu	76	155—160(6)	Yellow liquid	$C_{15}H_{17}N$	85.26 (85.16	8.11 8.12	6.63 7.00)
12e	3-Ph	79	196—200(3)	Yellow liquid	$C_{17}H_{13}N$	88.28 (88.10	5.67 5.93	6.06 6.43)

TABLE IV. Catalytic Reduction of Alkynylisoquinolines (**9b, c, f, g**)



13b, c, f, g **9b, c, f, g** **14b, c, f, g**

Compd. No.	Position R	Yield (%)	bp(°C) (mmHg) [mp(°C)]	Appearance (recrystn.solv.)	Formula	Analysis (%) Calcd (Found) C	H	N
13b	1-Bu	71	115—119(1)	Yellow liquid	$C_{15}H_{19}N$	84.45 (84.61	8.98 8.61	6.57 6.56)
13c	1-Ph	76	115—118(1)	Yellow liquid	$C_{17}H_{15}N$	87.51 (87.64	6.48 6.47	6.00 5.87)
13f	4-Bu	84	125—130(3)	Colorless liquid	$C_{15}H_{19}N$	84.45 (84.31	8.98 9.04	6.57 6.44)
13g	4-Ph	63	160—165(1)	Colorless liquid	$C_{17}H_{15}N$	87.51 (87.46	6.48 6.45	6.00 6.07)
14b	1-Bu	80	133—135(1)	Yellow liquid	$C_{15}H_{17}N$	85.26 (85.31	8.11 8.07	6.63 6.54)
14c	1-Ph	91	165—167(1) [106—107]	Colorless needles (AcOEt)	$C_{17}H_{13}N$	88.28 (88.36	5.67 5.91	6.06 6.08)
14f	4-Bu	76	130—135(1)	Yellow liquid	$C_{15}H_{17}N$	85.26 (84.92	8.11 8.46	6.63 6.49)
14g	4-Ph	60	200—205(6)	Yellow liquid	$C_{17}H_{13}N$	88.28 (88.10	5.67 5.86	6.06 6.20)

ation of methylquinoline and methylisoquinoline with aldehydes[9] as well as the cross-coupling reaction of haloquinolines and haloisoquinolines with olefins,[10] has severe limitations, the reduction of the acetylenes to the olefins is a simple and potentially very useful procedure for the preparation of quinolyl and isoquinolylolefins.

Experimental

All melting points and boiling points are uncorrected. Infrared (IR) spectra were measured with a JASCO IRA-1 spectrometer. ^{1}H-NMR spectra were taken at 60 MHz with Hitachi-Perkin-Elmer R-20 spectrometer and a JEOL JNM-PMX60 spectrometer. Chemical shifts are expressed as ppm downfield from tetramethylsilane (TMS) as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet, and b=broad. Mass spectra (MS) were taken on a Hitachi M-52G spectrometer.

2-(1-Propynyl)quinoline (1a)——2-Iodoquinoline (2.50 g, 0.01 mol) was dissolved in Et_3N (40 ml) with a catalytic amount of $Pd(PPh_3)_2Cl_2$ (80 mg) and CuI (40 mg). Propyne, generated from 1,2-dibromopropane (25 g, 0.12 mol) with KOH (23.0 g, 0.45 mol) in *n*-BuOH (50 ml), was introduced into the reaction mixture with stirring for 14 h at room temperature. The reaction mixture was concentrated to dryness under reduced pressure. Water (40 ml) was added to the residue, and the aqueous layer was made alkaline with K_2CO_3 and extracted with benzene. The benzene extract was passed through a short Al_2O_3 column. After removal of the solvent, the residual oil was purified by vacuum distillation, and recrystallized from ether–*n*-hexane to give colorless scales. Yield 1.30 g (79%). bp 110—116°C (1 mmHg). mp 68—69°C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2200. ^{1}H-NMR ($CDCl_3$): 2.10 (3H, s), 7.23—8.65 (6H, m). *Anal.* Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.32; H, 5.36; N, 8.19.

1-(1-Propynyl)isoquinoline (9a)——In a manner similar to that described above, a mixture of 1-iodoisoquinoline (2.50 g, 0.01 mol), $Pd(PPh_3)_2Cl_2$ (100 mg), CuI (50 mg), Et_3N (60 ml), and propyne generated from 1,2-dibromopropane (25.0 g, 0.12 mol) was stirred for 22 h at room temperature to give a pale yellow liquid. Yield 1.50 g (92%). bp 105—110°C (1 mmHg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2220. *Anal.* Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 85.95; H, 5.28; N, 8.27.

General Procedure for the Hydration of Alkynylquinoline and Alkynylisoquinoline——An alkynylquinoline (0.005 mol) and $HgSO_4$ (1.50 g, 0.005 mol) were dissolved in 70—80% aqueous acetone (20 ml). Conc. H_2SO_4 (1.0 g) was added to this solution slowly with stirring.

The mixture was concentrated to dryness under reduced pressure, then a suitable quantity of water (40—50 ml) was added to the residue and the aqueous layer was made alkaline with K_2CO_3 and extracted with chloroform. The chloroform extract was passed through a short Al_2O_3 column. After removal of the solvent, the crude product was purified by vacuum distillation and (or) recrystallization.

Beckmann Rearrangement of Phenyl 3-Quinolylmethyl Ketone Oxime (5)——A solution of KOH (2.80 g, 0.05 mol) in MeOH (50 ml) was added to a solution of $NH_2OH \cdot HCl$ (3.4 g, 0.05 mol) in H_2O (35 ml). The

Table V. IR, Mass, and ^{1}H-NMR Spectral Data for **2a—g**

Comp. No.	IR $\nu_{max}^{CHCl_3}$ cm^{-1}	Mass (*m/e*) M$^+$, (M-PhCO)$^+$	^{1}H-NMR δ ($CDCl_3$)
2a	1710, 1645		2.11 (2.31H, s), 2.26 (0.69H, s), 4.11 (0.45H, s) 5.30 (0.77H,s), 6.64 (0.77H, s), 6.95—7.80 (4.77H, m), 7.94—8.23 (0.45H, m), 14.60—15.30 (0.77H, b)
2b	1720, 1640		0.20—1.18 (3H, m), 1.18—2.10 (4H, m), 2.20—2.87 (2H, m), 4.12 (0.35H, s), 5.33 (0.82H, s), 6.63 (0.82H, d, J=9.5 Hz), 6.85—8.46 (6H, m)
2c	1640	247, 142	6.08 (1H, s), 6.83(1H, d, J=9.0 Hz), 7.00—7.80 (8H,m), 7.80—8.30 (2H, m), 15.50—16.00 (1H, b)
2d	1720		0.60—1.08 (3H, m), 1.08—1.91 (4H, m), 2.50 (2H, t, J=6.4 Hz) 3.87 (2H, s), 7.20—8.48 (5H, m), 8.79 (1H, d, J=2.0 Hz)
2e	1700	247, 142	4.28 (2H, s), 6.80—8.23 (10H, m), 8.82 (1H, d, J=2.0 Hz)
2f	1720		0.57—1.03 (3H, m), 1.03—1.95 (4H, m), 2.47 (2H, t, J=7.0 Hz), 4.10 (2H, s), 7.28 (1H, d, J=4.4 Hz), 7.50—8.30 (4H, m), 8.85 (1H, d, J=4.4 Hz)
2g	1700	247, 142	4.65 (2H, s), 7.20 (1H, d, J=4.2 Hz), 7.21—8.30 (9H, m),8.83 (1H, d, J=4.2 Hz)

TABLE VI. IR, Mass, and ^{1}H-NMR Spectral Data for **10a—g**

Compd. No.	IR $\nu_{max}^{CHCl_3}$ cm^{-1}	Mass (*m/e*) M$^+$, (M-PhCO)$^+$	^{1}H-NMR δ ($CDCl_3$)
10a	1715, 1620		2.19 (3H, s), 4.39 (0.3H, s), 6.00 (0.85H, s), 6.65 (0.85H, d, J=7.0 Hz), 7.23 (0.85H, d, J=7.0 Hz), 7.00—7.48 (4H, m), 7.48—8.18 (0.85H, m), 8.32—8.58 (0.3H, m)
10b	1720, 1620		0.30—1.11 (3H, m), 1.11—2.00 (4H, m), 2.10—2.70 (2H, m), 4.38 (0.34H, s), 6.00 (0.83H, s), 6.61 (0.83H, d, J= 7.0 Hz), 6.69—8.17 (5.17H, m), 15.01—15.80 (0.83H, b)
10c	1700, 1620	247, 142	6.45—6.90 (2H, m), 7.05—7.66 (7H, m), 7.66—8.29 (3H, m), 15.80—16.57 (1H, b)
10d	1720		0.65—1.05 (3H, m), 1.05—1.98 (4H, m), 2.55 (2H, t, J= 9.0 Hz), 4.00 (2H, s), 7.07—8.10 (5H, m), 9.18(1H, s)
10e	1690	247, 142	4.75 (2H, s), 7.05—7.50 (3H, m), 7.50—8.20 (6H, m), 9.05—9.40 (1H, m)[a]
10f	1720		0.50—1.00 (3H, m), 1.00—1.85 (4H, m), 2.47 (2H, t, J= 7.0 Hz), 4.03 (2H, s), 7.36—8.06 (4H, m), 8.41 (1H, s), 9.13 (1H, s)
10g	1700	247, 142	4.08 (2H, s), 7.10—8.10 (10H, m), 9.22 (1H, b, s)

a) in CF_3COOH

precipitate (KCl) was removed by filtration. Phenyl 3-quinolylmethyl ketone (**2e**) (1.0 g, 0.004 mol) was added to the filtrate and the mixture was refluxed for 21 h, then concentrated to dryness under reduced pressure. Water (20 ml) was added to the residue and the aqueous layer was extracted with chloroform. After removal of the solvent, the residual crystals were recrystallized from MeOH to give the ketone oxime (**5**) as colorless prisms. Yield 0.95 g (85%). mp 178—179°C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685. ^{1}H-NMR (DMSO): 4.73 (2H, s), 7.25—7.85 (6H, m), 7.85—8.60 (4H, m), 8.93 (1H, b, s), 9.15 (1H, d, J=2.0 Hz). *Anal.* Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.84; H, 5.41; N, 10.62.

Phosphorus pentachloride (1.50 g, 0.0073 mol) was slowly added to an ethereal solution (15 ml) of **5** (0.60 g, 0.0023 mol) with stirring at 0—5°C. After the mixture had been stirred at room temperature for 20 h, a small amount of ice was added. The aqueous layer was made alkaline with K_2CO_3 and extracted with chloroform. After removal of the solvent, the residual crystals were recrystallized from MeOH to give N-phenyl-3-quinolylacetamide (**6**) as colorless prisms. Yield 0.33 g (55%). mp 157—158°C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780. *Anal.* Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.75; H, 5.11; N, 10.65.

Acid Hydrolysis of N-Phenyl-3-quinolylacetamide (**6**)——A solution of **6** (0.30 g, 0.001 mol) in 50% H_2SO_4 (30 ml) was heated at 70—80°C for 3 h. The reaction mixture was made alkaline with K_2CO_3 and extracted with ether. The ether extract gave aniline (**7**) (0.077 g, 74%), which was acetylated with acetic anhydride to give acetanilide, mp 114—115°C. The melting point of a mixture of this compound with an authentic sample showed no depression.

The aqueous layer was acidified with conc. HCl and extracted with chloroform. After removal of the solvent, the residual crystals were recrystallized from aqueous MeOH to give 3-quinolylacetic acid (**8**) as pale yellow needles, mp 182—184°C (lit.[11] mp 184—185°C).

TABLE VII. ^{1}H-NMR Spectral Data for **11b—e** and **12b—e**

Compd. No.	^{1}H-NMR δ ($CDCl_3$)
11b	0.50—1.02 (3H, m), 1.02—2.10 (8H, m), 2.92 (2H, t, J=7.5 Hz), 7.06—8.20 (6H, m),
11c	3.20 (4H, s), 7.20 (5H, s), 7.01—8.20 (6H, m)
11d	0.52—1.03 (3H, m), 1.03—1.98 (8H, m), 2.71 (2H, t, J=7.8 Hz), 7.21—8.20 (5H, m), 8.76 (1H, d, J=2.0 Hz)
11e	2.95 (4H, s), 7.15 (5H, s), 7.30—8.20 (5H, m), 8.71 (1H, d, J=2.0 Hz)
12b	0.58—1.10 (3H, m), 1.10—1.83 (4H, m), 2.00—3.12 (2H, m), 6.00 (1H, d, t, J=11.0 Hz, J=7.0 Hz), 6.66 (1H, d, J=11.0 Hz), 6.95—8.27 (6H, m)
12c	6.90—7.90 (11H, m), 7.90—8.26 (2H, m)
12d	0.60—1.08 (3H, m), 1.08—1.73 (4H, m), 2.07—2.93 (2H, m), 5.78 (1H, d, t, J=12.0 Hz, J=8.0 Hz), 6.48 (1H, d, J=12.0 Hz), 7.18—8.68 (5H, m), 8.76 (1H, d, J=2.0 Hz)
12e	6.64 (1H, d, J=12.0 Hz), 6.76 (1H, d, J=12.0 Hz), 7.21 (5H, s), 7.37—8.63 (5H, m), 8.76 (1H, d, J=2.0 Hz)

TABLE VIII. ^{1}H-NMR Spectral Data for **13b,c,f,g** and **14b,c,f,g**

Compd. No.	^{1}H-NMR δ ($CDCl_3$)
13b	0.60—1.08 (3H, m), 1.08—2.21 (8H, m), 3.26 (2H, t, J=7.0 Hz), 7.17—7.93 (4H, m), 7.93—8.30 (1H, m), 8.41(1H, d, J=6.0 Hz)
13c	2.91—3.80 (4H, m), 7.27 (5H, s), 7.38—8.25 (5H, m), 8.45 (1H, d, J=6.0 Hz)
13f	0.50—1.07 (3H, m), 1.07—2.05 (8H, m), 2.94 (2H, t, J=9.0 Hz), 7.32—8.10 (4H, m), 8.37 (1H, s), 9.09 (1H, s)
13g	2.72—3.50 (4H, m), 7.12 (5H, s), 7.98—8.15 (4H, m), 8.83 (1H, s), 9.12 (1H, s)
14b	0.53—1.33 (3H, m), 1.33—2.00 (4H, m), 2.00—2.83 (2H, m), 6.37 (1H, d, t, J=12.0 Hz, J=7.0 Hz), 7.03 (1H, d, J=12.0 Hz), 7.20—8.01 (4H, m), 8.01—8.43 (1H, m), 8.43—9.10 (1H, m)
14c	7.20—7.92 (9H, m), 7.97 (2H, s), 8.16—8.48 (1H, m), 8.55 (1H, d, J=8.0 Hz)
14f	0.57—1.06 (3H, m), 1.06—1.74 (4H, m), 1.85—2.52 (2H, m), 6.01 (1H, d, t, J= 11.0Hz, J=7.0 Hz), 6.73 (1H, d, J=11.0 Hz), 7.18—8.13 (4H, m), 8.43 (1H, s), 9.16 (1H, s)
14g	6.90 (2H, s), 7.06 (5H, s), 7.46—8.09 (4H, m), 8.41 (1H, s), 7.15 (1H, s)

General Procedure for the Catalytic Reduction of Alkynylquinoline and Alkynylisoquinoline——The catalyst, 10% Pd-charcoal (1.0 g), was added to a solution of an alkynylquinoline (0.005 mol) in MeOH (30 ml) and the mixture was shaken under an H_2 stream (1 atm) at room temperature. After H_2 absorption had ceased, the catalyst was removed by filtration. The filtrate was concentrated to dryness and the residual oil was purified by vacuum distillation.

General Procedure for the Catalytic Reduction of Alkynylquinoline and Alkynylisoquinoline with 5% Pd-$CaCO_3$ and Quinoline——An alkynylquinoline (0.005 mol) was dissolved in MeOH (30 ml), then 5% Pd-$CaCO_3$ (0.1 g) and quinoline (0.1 g) was added to this solution and the mixture was shaken under an H_2 stream (1 atm) at room temperature. After H_2 absorption had ceased, the catalyst was removed by filtration. The filtrate was concentrated to dryness and the residue was passed through a short SiO_2 column (benzene). After removal of the solvent, the crude product was purified by vacuum distillation or (and) recrystallization.

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