Intramolecular 1,3-Dipolar Cycloadditions and Intramolecular Ene Reactions of 2-(Alkenyloxy)benzaldehyde Arylhydrazones[1]

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2-(3-Aryl-2-propenyloxy)benzaldehyde (or 1-naphthaldehyde) arylhydrazones undergo an intramolecular cycloaddition reaction *via* their 1,3-dipolar tautomers, azomethine imines, to the alkenyl group. Initial cycloadducts were converted to dehydrogenated compounds under the reaction conditions. On the other hand, introduction of cyano or ethoxycarbonyl groups instead of the aryl group into 3-position of the ortho propenyloxy group gave 3-cyanomethyl-4-chromanone arylhydrazones or the corresponding ethoxycarbonyl derivatives, respectively. The formation of these hydrazones was interpreted in terms of intramolecular ene reaction. The course of the reactions depends on the nature of the alkenyl substituents.

1,3-Dipolar cycloaddition reactions provide the most versatile synthesis of 5-membered heterocycles.[2] The syntheses of a number of fused ring compounds using intramolecular cycloadditions have been reported.[3]

Hydrazones are ambident nucleophiles and can react with electrophiles at either carbon or nitrogen. Recent investigations show that monosubstituted hydrazones undergo ene reactions (and subsequent cyclization),[4] 1,3-dipolar cycloadditions *via* azomethine imine tautomer,[5] acid-catalyzed [3⁺+2] cycloadditions,[6] and/or Michael additions (and subsequent cyclization)[4] with alkenes (the four reactions may provide a simple route to a variety of unusual pyrazoles). It is interesting to examine substituent effects on the competing processes of arylhydrazones in the presence of intramolecular olefins. As one of a series of benzopyranopyrazoles preparations,[7] we report here thermal transformations of 2-(alkenyloxy)benzaldehyde (or 1-naphthaldehyde) arylhydrazones to [1]benzo (or naphtho[1′,2′:5,6]) pyrano[4,3-*c*]pyrazoles or 3-substituted 4-chromanone arylhydrazones.

Results and Discussion

2-(Alkenyloxy)benzaldehyde (or 1-naphthaldehyde) arylhydrazones (**2**) were prepared from salicylaldehyde (or 2-hydroxy-1-naphthaldehyde) *via* 2-(alkenyloxy)-benzaldehydes (or 1-naphthaldehydes) (**1**) in two steps. Although the preparation of **1** was worked up in the usual manner[8a,b] by etherification with alkenyl bromides in the presence of potassium carbonate, some (**1d—e, 1k—m**) of **1** underwent further base-promoted cyclization, giving furans (**3**) (see Eq. 1). On the other hand, the etherification in the presence of potassium fluoride (fluoride-assisted etherification[8c]) gave **1** in satisfactory yields (Table 1). The reaction of **1** with arylhydrazines gave hydrazones (**2**) in good yields (Table 2). Satisfactory spectral and analytical data for **1** and **2** were obtained. Though some of the hydrazones bearing an ethoxycarbonyl group were not isolated in a crystalline form, it was found from NMR spectra that these hydrazones were formed almost

TABLE 1. YIELDS, MELTING AND BOILING POINTS, AND SPECTRAL DATA OF **1**[a]

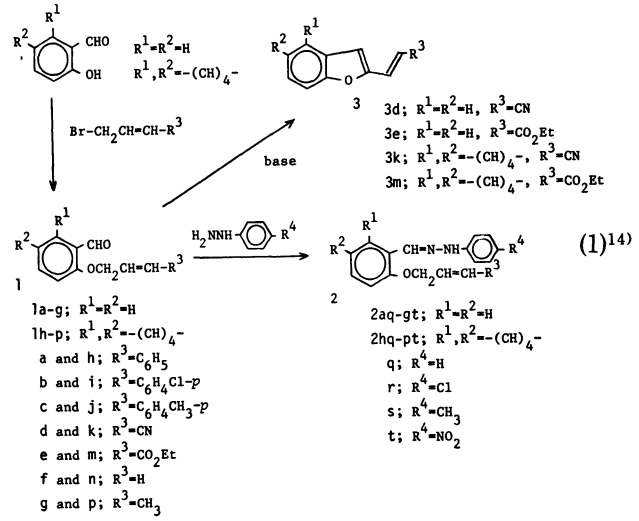
	Yield %	Mp θ_m/°C (Bp θ_b/°C)[b]	IR $\tilde{\nu}$/cm^{-1}	NMR δ $CDCl_3$
1a	86	51	1680(CHO)	4.8(d, 2H, J=5 Hz), 6.1—8.0(m, 1H), 10.6(s, 1H)
1b	83	78—79	1690(CHO)	5.8(d, 2H, J=5 Hz), 6.1—8.0(m, 10H), 10.6(s,1H)
1c	72	90—91	1690(CHO)	2.3(s, 3H), 5.8(d,2H, J=5 Hz), 6.1—8.0(m, 10H), 10.6(s, 1H)
1d	32	95—96	2220(CN)	4.8(dd, 2H, J=2 and 3 Hz), 5.87(dt, 1H, J=16 and 2 Hz),
			1680(CHO)	6.67—8.0(m, 5H), 10.4(s, 1H)
1e	51	66—69	1720(COO)	1.3(t, 3H, J=7 Hz), 4.2(q, 2H, J=7 Hz), 4.7—5.0 (m, 2H)
			1680(CHO)	6.2(d, 1H, J=16 Hz), 6.7—8.0(m, 5H), 10.5(s, 1H)
1f	90	(142 / 17 mmHg)	1680(CHO)	4.5(d, 2H, J=5 Hz), 5.1—5.6(m, 2H), 5.7—6.4(m, 1H), 6.7—7.8(m, 4 H), 10.4(s, 1H)
1g	93	(120 / 4 mmHg)	1680(CHO)	1.73(d, 3H, J=4 Hz), 4.57(d, 2H, J=4 Hz), 5.4—6.3(m, 2H), 6.8—7.2(m, 2H), 7.3—8.0(m, 2H), 10.5(s, 1H)
1h	100	139—140	1670(CHO)	4.9(d, 2H, J=5 Hz), 6.1—8.2(m, 12H), 9.37(d, 1H, J=8 Hz), 11.0(s, 1H)
1i	78	136—137	1670(CHO)	4.8(d, 2H, J=5 Hz), 6.0—6.85(m, 2H), 7.05—8.1(m, 9H), 9.25(d, 1H, J=8 Hz), 10.9(s, 1H)
1j	65	116	1680(CHO)	2.3(s, 1H), 5.8(d, 2H, J=5 Hz), 6.0—8.1(m, 10H), 9.3(d, 1H, J=8 Hz), 10.9(s, 1H)
1k	75	129	2230(CN)	4.9(dd, 2H, J=2 and 3 Hz), 5.85(dt, 1H, J=16 and 2 Hz), 6.6—7.95(m, 5H),
			1670(CHO)	8.1(d, 1H, J=9 Hz), 9.2(d, 1H, J=8 Hz), 10.9(s, 1H)
1m	66	113—115	1720(COO)	1.25(t, 3H, J=7 Hz), 4.2(q, 2H, J=7 Hz), 4.75—4.9(m, 2H),
			1670(CHO)	6.15(dt, 1H, J=16 and 2 Hz), 6.9—8.1(m, 7H), 9.2(d, 1H, J=8 Hz), 10.9(s, 1H)

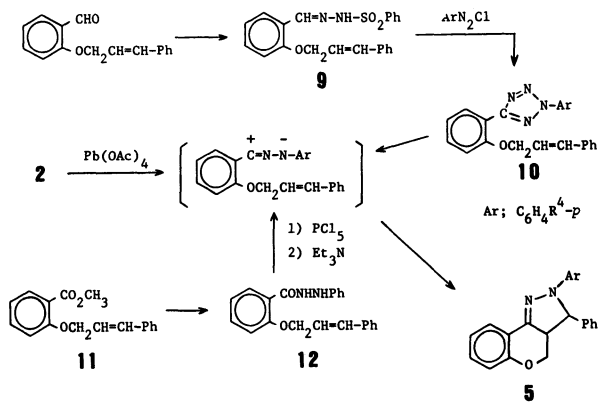
a) Satisfactory analytical data were obtained for these compounds. b) Recrystallized from ethanol.

Table 2. Yields, melting points,[a] and spectral data of 2[b]

	Yield %	Mp θ_m/°C	IR $\tilde{\nu}$/cm^{-1}	NMR δ[c]
2aq	70	105—107	3320(NH)	4.7(d, 2H, J=5 Hz), 6.1—7.6(m, 16H), 7.9—8.2(m, 1H), 8.1(s, 1H), 7.57(s, 1H)
2ar	62	126—128	3330(NH)	4.67(d, 2H, J=5 Hz), 6.1—7-5(m, 15H), 7.85—8.1(m, 1H), 8.07(s, 1H)
2at	100	201—202	3250(NH)	4.75(d, 2H, J=5 Hz), 6.2—8.5(m, 16H), 11.23(s, 1H)
2bq	56	118—120	3330(NH)	4.65(d, 2H, J=5 Hz), 6.0—7.5(m, 14H), 7.8—8.1(m, 1H), 8.1(s, 1H)
2cq	85	126—128	3330(NH)	2.3(s, 3H), 4.7(d, 2H, J=5 Hz), 6.1—7.5(m, 14H), 7.9(d, 1H, J=6 Hz), 8.3(s, 1H), 10.4(s, 1H)
2cr	33	d)	3330(NH)	2.3(s, 1H), 4.6(d, 2H, J=5 Hz), 6.0—7.65(m, 14H), 7.8—8.1(m, 1H), 8.05(s, 1H)
2dq	83	145—146	3280(NH) 2230(CN)	4.77(dd, 2H, J=2 and 4 Hz), 6.03(dt, 1H, J=2 and 17 Hz), 6.5—7.5(m, 9H), 7.9(dd, 1H, J=2 and 8 Hz), 8.3(s, 1H), 10.3(s, 1H)
2dr	81	170—171	3270(NH) 2230(CN)	4.79(dd, 2H, J=2 and 4 Hz), 5.98(dt, 1H, J=2 and 17 Hz), 6.8—7.45 (m, 8H), 7.9(dd, 1H, J=2 and 8 Hz), 8.25(s, 1H), 10.4(s, 1H)
2dt	100	248—250	3260(NH) 2240(CN)	4.75—4.95(m, 2H), 6.05(d, 1H, J=18 Hz), 6.95—7.4(m, 6H), 7.8—8.2(m, 3H), 8.35(s, 1H), 11.25(s, 1H)
2et	93	142—143	3240(NH) 1720(COO)	1.3(t, 3H, J=7 Hz), 4.2(q, 2H, J=7 Hz), 4.7(dd, 2H, J=2 and 4 Hz), 6.15(dt, 1H, J=2 and 16 Hz), 6.7—7.45(m, 6H), 7.85—8.3(m, 4H), 8.6(s, 1H)
2fq	100	63	3260(NH)	4.4—4.6(m, 2H), 5.1—5.6(m, 2H), 5.7—6.4(m, 1H), 6.6—7.3(m, 9H), 7.8—8.1(m, 1H), 8.0(s, 1H)
2ft	95	213—215	3270(NH)	4.6(d, 2H, J=5 Hz), 5.1—5.7(m, 2H), 5.75—6.4(m, 1H), 6.8—7.6 (m, 5H), 7.8—8.27(m, 3H), 8.4(s,1H), 11.23(s, 1H)
2gt	95	188—190	3360(NH)	1.7(d, 3H, J=5 Hz), 4.5(d, 2H, J=5 Hz), 5.7—5.9(m, 2H), 6.8—8.4(m, 9H), 11.3(s, 1H)
2gq	91	51—55	3300(NH)	1.7(d, 3H, J=5 Hz), 4.4(d, 2H, J=5 Hz), 5.4—6.1(m, 2H), 6.6—7.5(m, 8H), 7.8—8.1(m, 1H), 8.0(s, 1H)
2hq	86	122—123	3300(NH)	4.8(d, 2H, J=5 Hz), 6.1—8.0(m, 18H), 8.5(s, 1H), 9.33(d, 1H, J=8 Hz)
2hr	80	124—127	3300(NH)	4.8(d, 2H, J=5 Hz), 6.1—7.9(m, 17H), 8.4(s, 1H), 9.2(d, 1H, J=8 Hz)
2jq	90	139—141	3300(NH)	2.3(s, 3H), 4.8(d, 2H, J=5 Hz), 6.1—7.9(m, 17H), 8.46(s, 1H), 9.2(d, 1H, J=8 Hz)
2kq	78	168—169	3300(NH) 2240(CN)	4.85—5.1(m, 2H), 6.1(dt, 1H, J=2 and 16 Hz), 6.65—8.0(m, 11H), 8.7(s, 1H), 9.36(d, 1H, J=8 Hz)10.4(s, 1H)
2kr	95	139—140	3280(NH) 2230(CN)	4.9—5.1(m, 2H), 6.15(dt, 1H, J=2 and 8 Hz), 6.95—8.05(m, 10H), 8.64(s, 1H), 9.25(d, 1H, J=8 Hz), 10.45(s, 1H)
2kt	84	210—212	3300(NH) 2220(CN)	4.9—5.1(m, 2H), 6.2(d, 1H, J=7Hz), 6.85—8.4(m, 10H), 8.9(s, 1H), 9.35(d, 1H, J=7 Hz), 11.43(s, 1H)
2mt	90	144—145	3300(NH) 1730(COO)	1.25(t, 3H, J=7 Hz), 4.15(q, 2H, J=7 Hz), 4.8—5.1(m, 2H), 6.2(d, 1H, J=16 Hz), 6.9—8.3(m, 10H), 8.8(s, 1H), 9.25(d, 1H, J=8 Hz), 11.4(s, 1H)

a) Recrystallized from ethanol. b) Satisfactory analytical data were obtained for these compounds. c) **2at**, **cq**, **dq**, **dr**, **kq**, **kr**, **kt**, **dt**, and **2mt** were dissolved in DMSO-d_6, the others were dissolved in $CDCl_3$. d) This material is so hygroscopic that we could not determine the melting point.





Scheme 1.

TABLE 3. YIELDS, MELTING POINTS[a], AND SPECTRAL DATA OF 5[b]

	Reaction[c] condition	Yield %	Mp θ_m/°C	NMR δ[d]
5aq	A	36	146—147	3.3—4.8(m, 4H), 6.6—7.5(m, 13H), 7.73—7.97(m, 1H)
5ar	A	12	180—183	3.3—4.8(m, 4H), 6.73—7.5(m, 12H), 7.73—7.95(m, 1H)
5as	C	10	148—150	2.2(s, 3H), 2.23—4.77(m, 4H), 6.7—7.5(m, 12H), 7.75—7.95(m, 1H)
5bs	C	52	191—193	2.2(s, 3H), 3.17—4.75(m, 4H), 6.4—7.5(m, 11H), 7.65—7.9(m, 1H)
5cq	A	50	145—146	2.3(s, 3H), 3.2—4.8(m, 4H), 6.5—7.5(m, 12H), 7.7—7.95(m, 1H)
5cr	A	13	190—192	2.25(s, 3H), 3.3—5.2(m, 4H), 6.8—7.5(m, 11H), 7.6—7.9(m, 1H)
5cs	C	34	187—188	2.15(s, 3H), 2.3(s, 3H), 3.2—5.2(m, 4H), 7.0—7.75(m, 11H), 7.8—8.1(m, 1H)
5hq	A	31	194—195	3.35—4.85(m, 4H), 6.55—7.8(m, 15H), 9.33(d, 1H, J=8 Hz)
5hr	A	50	206—208	3.35—4.87(m, 4H), 6.8—7.85(m, 14H), 9.3(d, 1H, J=8 Hz)
5hs	C	24	208—210	2.2(s, 3H), 3.3—4.8(m, 4H), 6.8—7.95(m, 14H), 9.4(d, 1H, J=8 Hz)
5iq	B	79	182—184	3.3—5.1(m, 4H), 6.5—8.0(m, 14H), 8.57(d, 1H, J=8 Hz)
5ir	B	64	239—240	3.3—5.0(m, 4H), 6.8—8.0(m, 13H), 9.45(d, 1H, J=8 Hz)
5is	C	35	230—231	2.2(s, 3H), 3.2—4.9(m, 4H), 6.7—7.9(m, 13H), 9.35(d, 1H, J=8 Hz)
5jq	A	26	188—191	2.35(s, 3H), 3.3—4.87(m, 4H), 6.5—7.9(m, 14H), 9.4(d, 1H, J=8 Hz)
5jr	B	62	217—218	2.33(s, 3H), 3.3—4.9(m, 4H), 6.8—7.9(m, 13H), 9.3(d, 1H, J=8 Hz)
5js	C	23	202—203	2.2(s, 3H), 2.4(s, 3H), 3.25—4.8(m, 4H), 6.7—7.8(m, 13H), 9.4(d, 1H, J=8 Hz)
5mq	D	55	134—136	1.27(t, 3H, J=7 Hz), 3.5—4.9(m, 6H), 6.5—7.8(m, 10H), 9.2(d, 1H, J= 8 Hz)
5mr	D	70	162—165	1.3(t, 3H, J=7 Hz), 3.9—5.0(m, 6H), 6.4—7.9(m, 9H), 9.2(d, 1H, J=8 Hz)
5ms	D	70	148—151	1.3(t, 3H, J=7 Hz), 2.2(s, 3H), 3.8—4.95(m, 6H), 6.87—7.9(m, 9H), 9.3(d, 1H, J=8 Hz)

a) Recrystallized from ethanol. b) Satisfactory analytical data were obtained for these compounds. c) A: Refluxing the solution of **2** in xylene for 24 h; B: Refluxing the ethanol solution of **1** and arylhydrazine for 24 h : C: Refluxing the pyridine solution of **1** and *p*-tolylhydrazine hydrochloride for 24 h; D: Refluxing the solution of **1** and arylhydrazine in ethanol containing acetic acid for 24 h. d) **5cr** and **5cs** were dissolved in DMSO-d_6, the others were dissolved in $CDCl_3$.

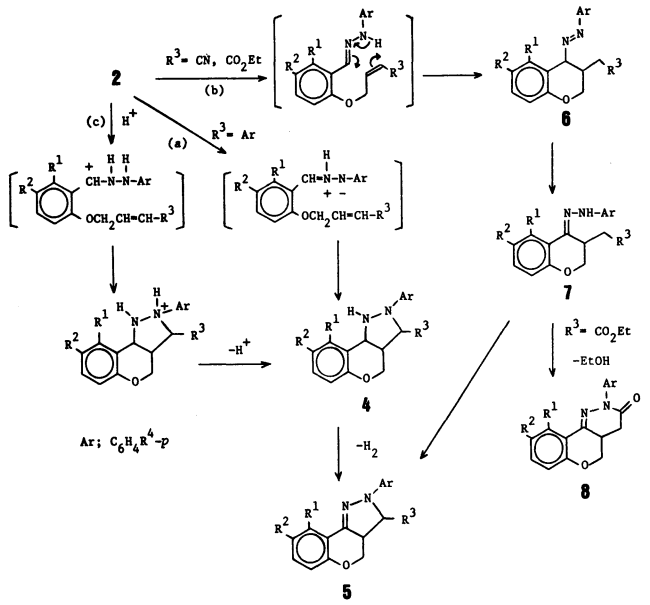
TABLE 4. YIELDS, MELTING POINTS[a], AND SPECTRALDATA OF 7 AND 8[b]

	Reaction[c] condition	Yield %	Mp θ_m/°C	IR $\tilde{\nu}$/cm^{-1}	NMR δ[d]
7dq	A	60	173—175	3310(NH) 2250(CN)	2.7(d, 2H, J=8 Hz), 3.4(t, 1H, J=8 Hz), 4.17(d, 1H, J=12 Hz), 4.58(d, 1H, J=12 Hz), 6.8—7.5(m, 8H), 7.9(s, 1H), 7.95—8.3(m, 1H)
7dr	A	38	216—218	3330(NH) 2250(CN)	2.73(d, 2H, J=8 Hz), 3.2—3.9(m, 2H), 4.12(d, 1H, J=12 Hz), 4.43(d, 1H, J=12 Hz), 6.7—7.35(m, 7H), 7.8—8.03(m, 1H)
7ds	C	42	181—185	3300(NH) 2250(CN)	2.2(s, 3H), 2.7(d, 2H, J=8 Hz), 3.3(s, 1H), 3.67(t, 1H, J=8 Hz), 4.1(d, 1H, J=12 Hz), 4.3(d, 1H, J=12 Hz), 6.7—7.3(m, 7H) 7.8—8.1(m, 1H)
7eq	B	45	129—130	3250(NH) 1700(COO)	1.27(t, 3H, J=7 Hz), 2.83—3.3(br, 1H), 4.27(q, 2H, J=7 Hz), 4.05—4.8(m, 5H), 6.5—7.3(m, 8H), 7.43—7.67(m, 1H)
7kq	A	58	209—212	3270(NH) 2240(CN)	4.05—4.8(m, 3H), 5.15(d, 1H, J=8 Hz), 5.9(d, 1H, J=12 Hz), 6.7—8.15(m, 10H), 8.37(d, 1H, J=8 Hz), 9.2(d, 1H, J=8 Hz)
7kr	A	31	240—241	3280(NH) 2240(CN)	4.3—5.2(m, 4H), 5.95(d, 1H, J=8 Hz), 7.1—8.15(m, 10H), 9.23(d, 1H, J=8 Hz)
8eq	C	49	159—162	1680(CON)	2.2—4.53(m, 5H), 6.67—7.7(m, 8H), 7.8—8.03(m, 1H)
8er	C	26	209—211	1670(CON)	2.5—4.7(m, 5H), 6.8—7.7(m, 7H), 7.9—8.15(m, 1H)
8es	C	43	165—166	1670(CON)	2.33(s, 3H), 2.5—4.6(m, 5H), 6.77—7.63(m, 7H), 7.83—8.1(m, 1H)

a) Recrystallized from ethanol. b) Satisfactory analytical data were obtained for these compounds. c) A: Refluxing the solution of **2** in xylene for 24 h; B: Refluxing the ethanol solution of **1** and aryl hydrazine for 24 h; C: Refluxing the pyridine solution of **1** and *p*-tolylhydrazine hydrochloride for 24 h. d) **7dr**, **ds**, **kq**, and **7kr** were dissolved in DMSO-d_6, the others were dissolved in $CDCl_3$.

quantitatively. The oily hydrazones were used for the thermal reaction without further purification.

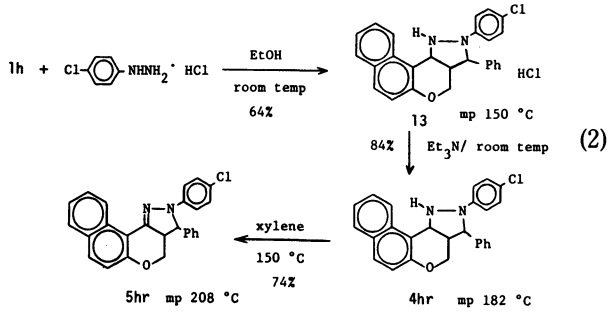
The treatment of the arylhydrazones (**2**) in xylene at 150 °C for 20 h gave 2-aryl-2,3,3a,4-tetrahydro[1]-benzo (or naphtho[1′,2′:5,6])pyrano[4,3-*c*]pyrazoles (**5**). The structure of **5** was assigned on the basis of a comparison of its physical properties (Table 3) with those of specimens prepared by authentic methods[9] (see Scheme 1). On the other hand, 3-cyanomethyl-4-chromanone arylhydrazones (**7**) were the only isolable products from the reaction mixtures of hydrazones (**2**) bearing a 3-cyano-2-propenyloxy group at *o*-position and none of the corresponding cycloadducts (**5**) could be detected. The structure of **7** was determined on the basis of its spectral and analytical data (see Table 4). Reaction of the hydrazones (**2**) bearing an ethoxycarbonyl group as R^3 might occur by different mechanisms: for example, a) The reaction of **1e** with phenylhydrazine



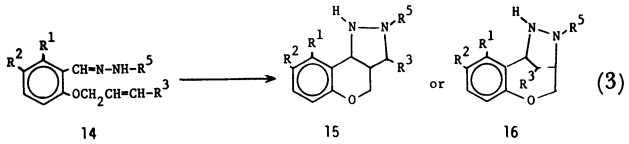
Scheme 2.

in neutral solvents such as ethanol or xylene at refluxing temperatures over 20 h resulted in the formation of ene type product **7eq** in 45% yield. The same reaction in a basic solvent such as pyridine gave **8eq** along with **7eq**. b) The reaction in ethanol containing a small amount of an acid such as acetic acid or sulfuric acid gave the cycloadduct **5mq** in 55% yield without contamination of the ene product.

One of the most plausible mechanisms of the formation of **5** is as follows: arylhydrazones (**2**) undergo intramolecular 1,3-dipolar cycloaddition reaction *via* their azomethine imine tautomer[5] to give pyrazolidines (**4**). which were dehydrogenated to pyrazolines (**5**) under the reaction conditions [route (a) in Scheme 2]. Several possible pathways for the reaction of aldehyde or ketone hydrazones with alkenes are shown in Scheme 2. The route (c) in Scheme 2 is an alternative mechanism, an acid-catalyzed concerted [3+2] cycloaddition reaction,[6] for the formation of **4**. Presence or absence of a base ($NaHCO_3$, Et_3N, or DABCO) has no effect on the reaction of **2jq** in refluxing xylene giving only **5jq**, but an addition of an acid in the reaction of some hydrazones even at room temperature induced a marked increase in yields of the cycloadducts (**5**). The temperatures (150 °C) used in our reactions are apparently high enough to permit substantial presence of the azomethine imine tautomer. If the cyclization reaction of **2** was carried out in solvents containing trace amounts of acid,



(2)



(3)

the [3+2] cycloaddition proceeds much faster than the azomethine imine cycloaddition. Therefore the treatment of **2** in the presence of acid is more convenient for the preparation of **5** (see Eq. 2) and we confirmed that the reaction was facilitated in order of $CO_2Et \approx CN > Ph > alkyl$ group at R^3. Another alternative pathway for the formation of **5** suggested by Snider *et al.*,[4a] intramolecular *N*-alkylation (**7**→**5**) of initial ene type product (**6**→**7**), would be excluded because **7** was stable under the reaction conditions. The intramolecular ene reaction [route (b) in Scheme 1] of the substrate bearing cyano or ethoxycarbonyl group as R^3 may proceed faster than the intramolecular 1,3-dipolar cycloaddition reaction, although we could not find a reasonable explanation of the competitive reactivity in the ene and 1,3-dipolar reaction studied here in terms of FMO theory.[10] Azo compound (**6**), apparent ene reaction products, would easily isomerize to hydrazone structure (**7**), which is a thermodynamically more stable structure under the reaction conditions.

In the case of the reaction with the substrate bearing electron-rich alkenyl group (**2fq** and **2gq**), neither cycloadducts nor ene reaction products was obtained from the reaction mixture, and starting materials were recovered unchanged. It is known[10] that these electron-rich olefins are more reluctant than electron-poor or conjugated olefines to either nucleophilic addition or 1,3-dipolar cycloaddition. Electron-withdrawing substituents on the hydrazone would lower its reactivity, because of the lowered HOMO energy. Thus, we examined the reactivity of phenyl-, *p*-tolyl-, and *p*-chlorophenylhydrazones in the reaction. The more electron-deficient mono- and dinitrophenylhydrazones should be less reactive toward electrophilic species[11] and we, in fact, could not obtain any **5**, **7**, or **8** from the thermal treatment of **2at**—**qt**. Intramolecular Michael type cyclization (Eq. 3) bearing electron deficient olefins would give a product (**16**) containing a seven-membered ring and we could isolate no such products. On the other hand, alkylhydrazones (R^5= alkyl at **14**) have higher reactivity at nitrogen than at carbon atom[12] and only a small amount of Michael adducts (the structure is not yet confirmed) were isolated from the reaction.

Our results show that the thermal intramolecular 1,3-dipolar and ene reactions of **2** proceed in a manner similar to the intermolecular 1,3-dipolar[5] and ene reactions,[4] giving good yields of complex heterocycles. We could obtain **5** in two or three steps from salicylaldehyde (or 2-hydroxy-1-naphthaldehyde) and our procedure is simpler than a reported one.[9b] Our procedure is also suitable for the preparation of 3-substituted 4-chromanone derivatives (**7** or **8**), which are generally difficult to prepare by other methods.

Experimental

Measurements. All the melting and boiling points are

uncorrected. The IR spectra were determined on a Hitachi 215 Infrared Spectrophotometer. The ^1H NMR spectra were measured on a Varian T-60A instrument with TMS as an internal standard.

Materials. 3-Bromo-1-*p*-tolyl-1-propene[13a] and 3-bromo-1-(*p*-chlorophenyl)-1-propene[13b] were prepared according to the method described in the literature.

Preparation of the 2-(Alkenyloxy)benzaldehydes (or 1-naphthaldehydes) (1). *General Procedure*: A mixture of salicylaldehyde (or 2-hydroxy-1-naphthaldehyde) (0.2 mol), 1-substituted 3-bromo-1-propenes (0.25 mol), and potassium fluoride (0.8 mol) in acetone (300 ml) was refluxed for 72 h. After filtration of inorganic salts, evaporation of the filtrate gave a viscous oil which solidified upon scratching with a glass rod. Recrystallization from ethanol gave colorless needles (**1a**—**m**) in the yields shown in Table 1. In the cases of **1d**—**e** and **1k**—**m**, 0.4 mol of KF was used.

Preparation of Hydrazones (2). *General Procedure*: Into a stirred ethanol solution (300 ml) of **1** (0.1 mol) was added first an ethanol solution (50 ml) of phenylhydrazine (or *p*-chlorophenylhydrazine) (0.1 mol) and then 3 ml of acetic acid at room temperature. After stirring the mixture for 6 h at room temperature, evaporation of the ethanol and acetic acid *in vacuo* gave hydrazones (**2**), which was recrystallized from ethanol. Yields and spectral data are shown in Table 2. *p*-Tolylhydrazones are apt to undergo subsequent cycloaddition under the conditions described above, and several attempts to isolate the *p*-tolylhydrazones failed because of subsequent thermal transformation of the hydrazones.

Thermal Reactions of Hydrazones (2) *General Procedure*: Hydrazones (5 mmol) shown in Table 2 and hydrazones bearing an ethoxycarbonyl group as R^3 were refluxed in xylene (50 ml) with a small amount of hydroquinone for 24 h. After distillation of the solvent, the residue was mixed with a small amount of ethanol and was allowed to stand for several days. The crystals which separated were recrystallized from ethanol to give colorless needles (**7**) or yellow crystals (**5**). A chloroform solution of **5** has a brilliant greenish fluorescence.

Specific Procedure. *A)*: A mixture of **1** (10 mmol) and *p*-tolylhydrazine hydrochloride (10 mmol) in pyridine (50 ml) was heated to reflux for 24 h. Then the reaction mixture was poured into water and extracted with ether several times. The ethereal layer was washed with a dilute hydrochloric acid solution, dried over anhydrous sodium sulfate, and evaporated to give **5** from **1a**—**c**, **1h**, and **1j** or **8** along with **7** from **1d** or **1e**, respectively. The results are shown in Tables 3 and 4.

B): A mixture of **1e** (or **1m**) (10 mmol) and arylhydrazines (10 mmol) was refluxed in ethanol (150 ml) for 24 h. The evaporation of the solvent gave a viscous oil without contamination of **5**. Crystallization from ethanol gave **7**.

C): An ethanol solution (150 ml) of **1m** (10 mmol), arylhydrazine (or arylhydrazine hydrochloride) (10 mmol), and acetic acid (3 ml) was allowed to stand for 10 h at 20—80 °C. Concentration of the reaction gave yellowish crystals, which were recrystallized from ethanol to give **5mq**—**ms** in 40—70% yields.

Intramolecular Condensation Reaction of 7 to 8. A solution of **7eq** (1 mmol) in acetic acid (10 ml) was heated to reflux for 6 h, then poured into water (50 ml), and extracted with ether several times. The combined ether layer was washed with a dilute sodium carbonate aqueous solution and dried over anhydrous sodium sulfate. Evaporation of the solvent gave **8eq** in 85% yield. Treatment of **7eq** in pyridine also gave **8eq** in 82% yield.

Independent Synthesis of 5aq and 5as. *A)*: 2-Phenyl-5-[2-(3-phenyl-2-propenyloxy)phenyl]-2*H*-tetrazole (**10a**) was prepared from 2-(3-phenyl-2-propenyloxy)benzaldehyde phenylsulfonylhydrazone (**9**)[7a] and benzenediazonium chloride according to a method analogous to that of Ito *et al.*[9a] in 34% yield; mp 104—105 °C (from ethanol). NMR ($CDCl_3$): δ 4.82 (d, 2H, J=4 Hz), 6.15—7.6 (m, 13H), and 8.0—8.3 (m, 3H). Found: C, 74.68; H, 5.13; N, 15.77%. Calcd for $C_{21}H_{18}N_4O$: C, 74.55; H, 5.12; N, 15.81%. 2-(*p*-Tolyl)-5-[2-(3-phenyl-2-propenyloxy)phenyl]-2*H*-tetrazole (**10b**) was prepared in the same manner as described above in 53% yield; mp 106—108 °C (from ethanol). NMR ($CDCl_3$): δ 2.37 (s, 3H), 4.80 (d, 2H, J=4 Hz), 6.12—7.8 (m, 10H), and 7.9—8.2 (m, 3H). Found: C, 74.97; H, 5.31; N, 15.38%. Calcd for $C_{22}H_{20}N_4O$: C, 74.98; H, 5.47; N, 15.21%. Pyrolysis of **10a** (or **10b**) at 140—160 °C for 5 h gave **5aq** (or **5as**) in 100 (or 83) % yields.

B): A mixture of methyl salicylate (0.1 mol), 3-bromo-1-propenyl-2-propene (0.11 mol) and potassium carbonate (0.1 mol) in acetone (400 ml) was set to reflux for 25 h. Filtration of inorganic salts and evaporation of the solvent gave a solid, which was recrystallized from ethanol to give methyl 2-(3-phenyl-2-propenyloxy)benzoate (**11**) in 71% yield; mp 67—68 °C. IR (Nujol): 1725 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$): δ 3.9 (s, 3H), 4.95 (d, 2H, J=6 Hz), and 6.2—7.7 (m, 11H). A mixture of **11** (10 mmol) and phenylhydrazine (17 mmol) was heated at 80 °C for 10 h and subsequently allowed to stand at room tempetature for several days, giving crystals of 1-phenyl-2-[2-(3-phenyl-2-propenyloxy)benzoyl]hydrazine(**12**) as precipitate in 30% yield; mp 161—163 °C (from ethanol). IR (Nujol): 3360 and 3230 cm^{-1} (NH), 1635 cm^{-1} (CONH); NMR ($CDCl_3$): δ 4.95 (d, 2H, J=6 Hz), 6.23—7.70 (m, 16H), 8.17—8.40 (m, 1H) and 9.6 (s, 1H). Found: C, 76.69; H, 5.75; N, 8.00%. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13%. Chlorination of **12** with PCl_5 was carried out in ether at 35 °C for 6 h. The reaction mixture was poured into ice–water and extracted with ether several times. The combined ether layer was washed with water several times and dried over anhydrous sodium sulfate. Subsequent evaporation of the ether yielded a viscous oil (chlorohydrazone). To a stirred benzene solution of the oil was added dropwise an excess mole of triethylamine at 5 °C. The mixture was stirred at the same temperature for 1 h and then at room temperature for 5 h. The reaction mixture was washed with water and dried over sodium sulfate. Evaporation of the solvent gave a viscous oil, which was chromatographed (silica gel) with chloroform to give **5aq** in 5% yield.

The Reaction of 1h with p-*Chlorophenylhydrazine Hydrochloride at Room Temperature.* 0.7 g (3.91 mmol) of *p*-chlorophenylhydrazine hydrochloride was dissolved in hot ethanol (200 ml). The solution was allowed to cool to room temperature. We added an ethanol solution (20 ml) of **1h** (1 g, 3.48 mmol) into the ethanol solution of the hydrazine at room temperature and stirred for 2 h. Precipitated crystals (**13**) was filtered, 64% yield (1.0 g); mp 149—150 °C. After treatment of a chloroform solution (50 ml) of **13** (1.0 g, 2.23 mmol) with triethylamine (3 ml) at room temperature for 2 h, the mixture was washed with water several times. Subsequent evaporation of the solvent gave pyrazolidine (**4hr**) in 84% yield (0.77 g); mp 180—182 °C (from ethanol). Thermal treatment of **14** (0.5 g, 1.22 mmol) in xylene (50 ml) at 150 °C for 4 h yielded pyrazoline (**5hr**) in 74% yield (0.37 g).

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14) The notation of the suffix of **2** is as follows: the first alphabetical suffix (**a**—**p**) is same as for **1** and the second one (**q**—**t**) is for R^4. The notation of the suffixes for compounds used here is the same as for **2**.