In general, the observed IP's are within 0.5 eV of the IP's predicted by our method. Agreement is even better for orbitals in which the percent composition remains most constant throughout the series.

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Intermolecular and Intramolecular Cycloaddition Reactions of Azirines by Group 6 Metal Carbonyls and by Titanium Tetrachloride

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Abstract: Reaction of 2-arylazirines with an equimolar amount of a group 6 metal carbonyl [$M(CO)_6$, M = Cr, Mo, W] gives 2,5-diarylpyrazines and isomeric dihydropyrazines in good combined yields. Isoxazoles, pyrazoles, and pyrroles can be synthesized in high yields, and under very mild conditions, by intramolecular cycloaddition of 3-phenyl-2-substituted-2*H*-azirines with molybdenum hexacarbonyl. These reactions occur via carbon–nitrogen bond cleavage of the azirine ring. Pyrazines, pyridazines, α-chloro ketones, and monoketones were formed in low yield by titanium tetrachloride induced cleavage of the azirine ring.

Transition metal carbonyls can effect a number of useful reactions in organic chemistry.[1] Two particularly elegant transformations are the cyclocoupling of α,α′-dibromo ketones with olefins or dienes and diiron enneacarbonyl,[2] and the cleavage of strained ring compounds by di-μ-chloro-tetracarbonyldirhodium(I) [e.g., quadricyclane].[3]

Azirines have been shown to undergo carbon–nitrogen bond cleavage on thermolysis, while photolytic ring opening of these unsaturated heterocycles usually occurs via rupture of the carbon–carbon bond.[4] It is also known that metal carbonyls can effect photolytic-type reactions of organic substrates (e.g., santonin)[5] under nonphotolytic conditions. These findings raise the following questions: will metal carbonyls cleave the azirine ring in a synthetically useful manner; and does such an anticipated reaction take place by carbon–nitrogen or carbon–carbon bond cleavage of the azirine ring? This paper describes the reactions of group 6 metal carbonyls [$M(CO)_6$, M = Cr, Mo, W], principally molybdenum hexacarbonyl, with azirines.[6]

It was of interest to compare the group 6 metal carbonyl results with those obtained for an early transition metal, titanium. Therefore, the cleavage of azirines by titanium tetrachloride is also reported in this paper. This titanium compound is a good Lewis acid[7] and can chlorinate aromatics in the presence of pertrifluoroacetic acid,[8] although chlorination does not occur with $TiCl_4$ alone.

Results and Discussion

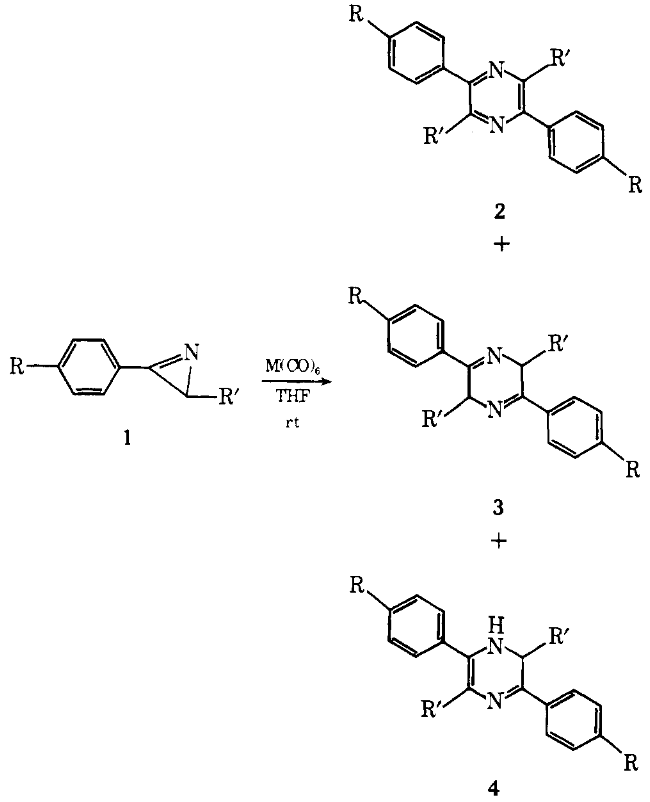
Treatment of 2-arylazirines (**1**, R = H, CH_3, OCH_3; R′ = H) with an equimolar quantity of group 6 metal carbonyls in tetrahydrofuran at room temperature, for 24 h, affords 2,5-diarylpyrazines (**2**) generally as the major product. Also formed in most instances were the isomeric 2,5-diaryl-3,6-dihydro- (**3**) and 2,5-diaryl-1,6-dihydropyrazines (**4**).[9] The combined yields for **2–4** are very good, and are listed in Table I.

All of the pyrazines, and several of the dihydropyrazines, are known compounds and were identified by comparison of

Table I. Products Obtained from Reaction of Azirines with $M(CO)_6$

Azirine	$M(CO)_6$, M =	Reaction time, h	Product[a]	Yield, %	Mp [bp], °C	Lit. mp [bp], °C
1, R = R′ = H	Mo	10	**2**	44[b]	196-198	196-198[c]
			3	16	164-165	164[d]
			4	18	170-172	169[d]
1, R = R′ = H	Cr	24	**2**	17		
			4	17		
1, R = R′ = H	W	168	**2**	29		
			4	13		
1, R = OCH_3, R′ = H	Mo	12	**2**	40[b]	275-276	274-276[e]
			3	28	238-240	
			4	21	246-247	
1, R = CH_3, R′ = H	Mo	18	**2**	27[b]	200-201	201[f]
			3	21	195-197	198-200[g]
			4	40	186-187	
1, R = H, R′ = CHO	Mo	5	**5**	81		[40 (0.01)][h]
1, R = H, R′ = [$CH{=}NC_6H_5$]	Mo	24	**6**, R″ = H	73	83-84.5	84-85[h]
1, R = H, R′ = [$CH{=}NC_6H_4Cl$-*p*]	Mo	24	**6**, R″ = Cl	67	130.5-131.5	
1, R = H, R′ = [$CH{=}NC_6H_4CH_3$-*p*]	Mo	24	**6**, R″ = CH_3	75	112-113	
1, R = H, R′ = [$CH{=}NC_6H_4OCH_3$-*p*]	Mo	24	**6**, R″ = OCH_3	96	106-107	
1, R = H, R′ = [$CH{=}CHCOOCH_3$]	Mo	48	**7**	91	143-144	142-143.5[h]

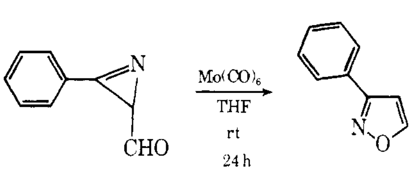
[a] Except for the following new compounds, the products were identified by comparison of melting points or boiling points and spectral data (IR, NMR, UV, MS) with those for authentic samples. **3** (R = OCH_3, R′ = H); NMR (CCl_4) δ 3.76 (6 H, s), 4.38 (4 H, s), 6.70-7.70 (8 H, m); MS (*m/e*) 294 (M^+). **4** (R = OCH_3, R′ = H); NMR (CCl_4-$CDCl_3$) δ 3.72 (3 H, s), 3.77 (3 H, s), 4.20 (2 H, d), 6.60-7.58 (10 H, m); MS (*m/e*) 294 (M^+); UV (C_2H_5OH) λ_{max} 419 nm. **4** (R = CH_3, R′ = H); NMR ($CDCl_3$) δ 2.22 (3 H, s), 2.29 (3 H, s), 4.12 (2 H, d), 6.74-7.80 (10 H, m); MS (*m/e*) 262 (M^+); UV (C_2H_5OH) λ_{max} 414 nm. **6** (R″ = Cl); IR ($CHCl_3$) 1595, 1510 cm^{-1}; NMR ($CDCl_3$) δ 6.75 (1 H, d, *J* = 2 Hz), 7.20-8.10 (10 H, m); MS (*m/e*) 255 (M^+). **6** (R″ = CH_3); IR ($CHCl_3$) 1595, 1515 cm^{-1}; NMR ($CDCl_3$) δ 2.26 (3 H, s), 6.78 (1 H, d, *J* = 2 Hz), 7.00-7.90 (10 H, m); MS (*m/e*) 234 (M^+). **6** (R″ = OCH_3); IR ($CHCl_3$) 1598 cm^{-1}; NMR ($CDCl_3$) δ 3.72 (3 H, s), 6.68 (1 H, d, *J* = 2 Hz), 6.73-7.80 (10 H, m); MS (*m/e*) 250 (M^+). [b] Improved product yields have been obtained when compared with the yields reported in the communication (ref 6). [c] L. Wolff, *Ber.*, **20**, 432 (1887). [d] J. Armand, K. Chekir, and J. Pinson, *Can. J. Chem.*, **52**, 3971 (1974). [e] E. Zbiral and J. Stroh, *Justus Liebigs Ann. Chem.*, **727**, 231 (1969). [f] D. Demus, K. H. Kolz, and H. Sackmann, *Z. Phys. Chem. (Leipzig)*, **249**, 217 (1972). [g] B. Reichert and H. Baege, *Pharmazie*, **2**, 451 (1947). [h] Reference 4.



physical properties (mp; infrared, nuclear magnetic resonance, and mass spectra) with those reported in the literature. Of the three metal hexacarbonyls, molybdenum hexacarbonyl was the most reactive and further studies were carried out using this metal carbonyl.

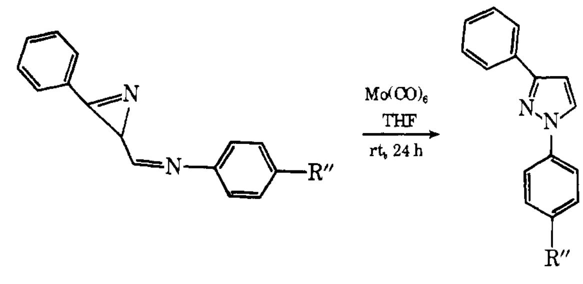
A study of the reactions of 3-phenyl-2-substituted-2*H*-azirines with molybdenum hexacarbonyl was also undertaken, the substituents used being capable of participating in intramolecular cycloaddition reactions. Such cycloaddition reactions, effected under gentle conditions, might lead to synthetically useful heterocycles. Furthermore, the nature of the products formed in these reactions would provide definitive evidence regarding the site of cleavage of the azirine ring (carbon-nitrogen vs. carbon-carbon).

Treatment of 2-formyl-3-phenyl-2*H*-azirine (**1**, R = H, R′ = CHO) with $Mo(CO)_6$ in tetrahydrofuran at room temperature for 5 h gave 3-phenylisoxazole (**5**) in 81% yield. The latter was previously obtained in 80% yield by thermolysis of the azirine in toluene at 200 °C (sealed tube) for 3 days.[4]



A series of *N*-arylimines [**1**, R = H; R′ = ($CH{=}NC_6H_4R''$-*p*), R″ = H, Cl, CH_3, OCH_3] of 2-formyl-3-phenyl-2*H*-azirine (readily prepared by reaction of **1** (R = H, R′ = CHO) with the appropriate aniline in the presence of *p*-toluenesulfonic acid[4] or molecular sieves[10]) were cleanly converted to 1-aryl-3-phenylpyrazoles (**6**) in 67-96% yield by exposure to $Mo(CO)_6$. Similarly, treatment of (*E*)-3-phenyl 2*H*-azirine-2-acrylate [**1**, R = H, R′ = ($CH{=}CHCOOCH_3$)] with $Mo(CO)_6$ afforded 2-phenyl-5-carbomethoxypyrrole (**7**) in 91% yield.

Since the products obtained in these reactions correspond to those formed by thermolysis rather than photolysis of azirines,[4] $Mo(CO)_6$ effects carbon-nitrogen, rather than car-



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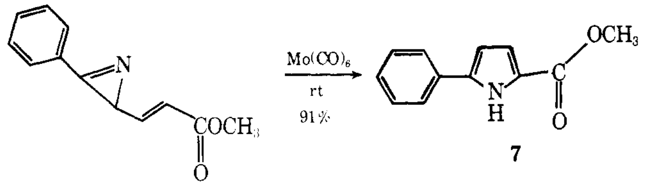

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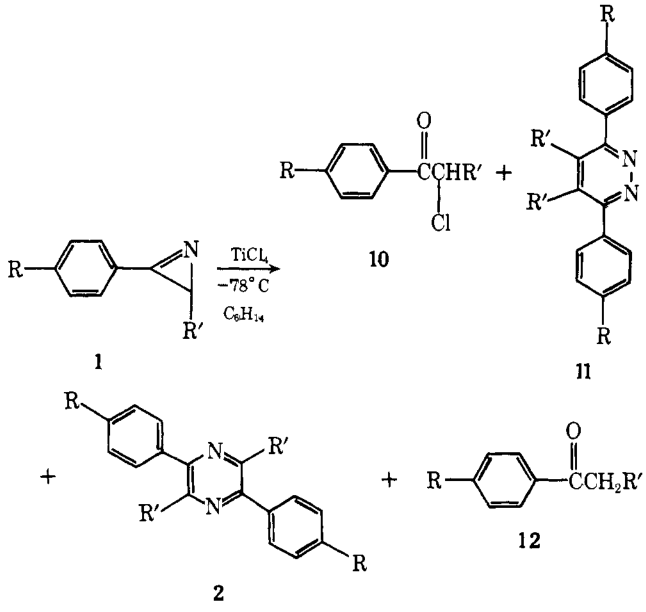
bon-carbon, bond cleavage of the azirine ring via complex **8** (Scheme I). The yields and rates of formation of **6** (qualitatively **1** (R = H, R′ = [CH=NC$_6$H$_4$OCH$_3$-*p*]) reacts much faster than **1** (R = H, R′ = [CH=NC$_6$H$_4$Cl-*p*])) are consistent with a complexed dienyl nitrene intermediate **9.** The charge-separated structure **9b** is a significant contributor to the resonance hybrid of **9** (other charge-separated resonance structures are possible), and is stabilized by electron-donating groups attached to X (e.g., Y = *p*-CH$_3$OC$_6$H$_4$). Ring closure of **9** would afford the heterocycle. It is likely that this proposed mechanism is applicable to the intermolecular process as well, but C-C and/or C=N bond cleavage of the azirine ring cannot be ruled out in reactions leading to the dimer, **2.**



Treatment of a 2-arylazirine (**1**) with twice the molar amount of TiCl$_4$ in hexane at −78 °C gave the *α*-chloro ketone, **10,** and the pyridazine, **11,** in modest yields (except for **1** (R = H, R′ = CH$_3$) where no pyridazine was detected). Also formed in several instances were small amounts of the 2,5-diarylpyrazine (**2**) and the monoketone, **12.** These reactions are exothermic, even at −78 °C, and afford significant amounts of intractable material. The product yields are given in Table II.

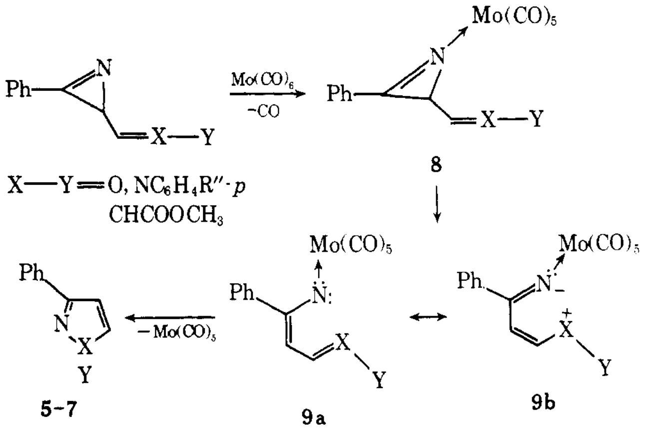
It is noteworthy that the *α*-chloro ketone is the principal product in all cases except for **1** (R = R′ = H), where the pyridazine was the major product. In addition, no heterocycle was detected when a methyl group was at the 3-position of the azirine ring.

Table II. Yields (%) of Products Obtained from Reaction of **1** with TiCl$_4$[a]

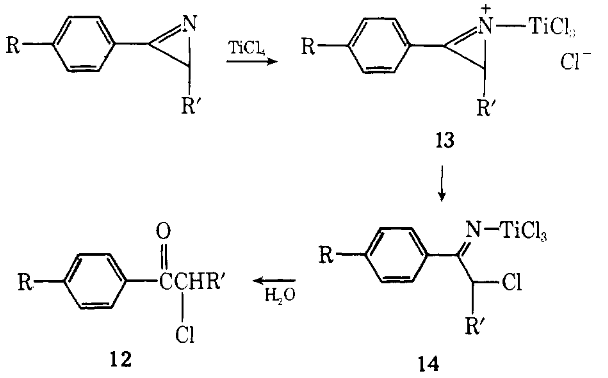
1, R =, R′ =	**10**	**11**	**2**	**12**
H, H	4	22	5	1
CH$_3$, H	13	5	Trace	
Br, H	23	8	Trace	6
H, CH$_3$	20			5

[a] The products were identified by comparison of melting points and spectral data (IR, NMR, MS) with those for authentic samples.

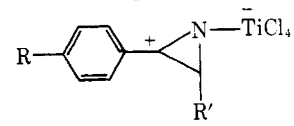
Scheme I



Scheme II



The *α*-chloro ketone may result by initial formation of a nitrogen-titanium bonded compound **13** (Scheme II), which can undergo carbon-nitrogen bond cleavage by chloride ion to give **14.** Hydrolysis of the latter would afford the *α*-chloro ketone (**12**). The heterocycles **2** and **11** may arise either from **14** or from the zwitterionic species **15.**



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In summary, these results clearly demonstrate that molybdenum hexacarbonyl is a very useful reagent for synthesizing pyrazines, pyrazoles, isoxazoles, and pyrroles from appropriately substituted azirines. Furthermore, the preparation of these important heterocycles, using Mo(CO)$_6$, can be achieved in high yields and under exceedingly mild conditions. Ring cleavage of azirines by titanium tetrachloride affords a series of interesting products, but in modest yields.

Experimental Section

General. Melting points were determined using a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectral determinations were made using a Beckman 1R-20A spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian T-60 or HA-100 spectrometer. Mass spectra were run on a Varian MS902 spectrometer. A Perkin-Elmer 202 spectrometer was used for ultraviolet spectra. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., The Butterworth Microanalytical Consultancy Ltd., Teddington, Great Britain, and by Drs. F. and E. Pascher, Bonn, West Germany.

Solvents were purified and dried by standard methods. All reactions were effected under a dry nitrogen atmosphere.

Azirines. The 2-arylazirines [**1**, R = H, CH_3, OCH_3, Br; R′ = H] were synthesized from the appropriate styrenes, using the procedure of Hortmann and co-workers.[11] Azirines **1** (R = H; R′ = CHO, $CH{=}NC_6H_5$, $CH{=}CHCOOCH_3$) were prepared according to literature methods.[4] Azirines **1** (R = H; R′ = [$CH{=}NC_6H_4Cl$-*p*] (95% yield), [$CH{=}NC_6H_4CH_3$-*p*] (80%), and [$CH{=}NC_6H_4OCH_3$-*p*] (92%)) were prepared by reaction of **1** (R = H, R′ = CHO) with *p*-chloroaniline, *p*-toluidine, and *p*-anisidine, respectively, over molecular sieves. The following general procedure was used: An equimolar mixture (4-60 mmol) of **1** (R = H, R′ = CHO) and the appropriate aniline in dry tetrahydrofuran was stirred at room temperature for 2 days over 4Å molecular sieves. The solution was filtered, and the filtrate was evaporated in vacuo. The residue was treated with carbon tetrachloride (50-100 mL) and filtered, and concentration of the filtrate afforded the pure imine.

1 (R = H, R′ = [$CH{=}NC_6H_4Cl$-*p*]; IR ($CHCl_3$) 1761, 1640, 1605 cm^{-1}; NMR ($CDCl_3$) δ 3.18 (1 H, d, J = 7 Hz), 6.90-8.50 (10 H, m); MS (*m/e*) 255 (M^+).

Anal. Calcd for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00. Found: C, 70.70; H, 4.38; N, 10.72.

1 (R = H, R′ = [$CH{=}NC_6H_4CH_3$-*p*]: IR ($CHCl_3$) 1760, 1642, 1603 cm^{-1}; NMR ($CDCl_3$) δ 2.30 (3 H, s), 3.28 (1 H, d, J = 8 Hz), 6.90-8.35 (10 H, m); MS (*m/e*) 234 (M^+).

Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.66; H, 6.03; N, 11.99.

1 (R = H, R′ = [$CH{=}NC_6H_4OCH_3$-*p*]: IR ($CHCl_3$) 1764, 1638, 1605 cm^{-1}; NMR ($CDCl_3$) δ 3.30 (1 H, d, J = 8 Hz), 3.75 (3 H, s), 6.65-8.30 (10 H, m); MS (*m/e*) 250 (M^+).

Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.39; H, 5.58; N, 11.47.

General Procedure for Reactions of Azirines with $M(CO)_6$ [M = Cr, Mo, W]. An equimolar mixture of the azirine (**1**) and the metal hexacarbonyl (5-30 mmol) in dry tetrahydrofuran was stirred at room temperature. The reaction times are indicated in Table I. The solution was filtered, and the filtrate was evaporated in vacuo to remove solvent and any unreacted metal carbonyl. Workup was effected as follows in the individual cases.

(**a**) **1 (R = H, CH_3, OCH_3; R′ = H).** Crystallization of the residue (using benzene) obtained from evaporation gave the pyrazine, **2.** The dihydropyrazines, **3** and **4,** were separated by column chromatography on neutral alumina [activity grade III] using benzene-chloroform as eluent.

3 (R = OCH_3, R′ = H). Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.77; H, 6.09; N, 9.48.

3 (R = CH_3, R′ = H). Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.67. Found: C, 82.45; H, 7.16; N, 10.41.

4 (R = OCH_3, R′ = H). Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.61; H, 6.29; N, 9.23.

(**b**) **1 (R = H, R′ = CHO).** Distillation of the residual oil gave pure 3-phenylisoxazole (**5**).

(**c**) **1 (R = H; R′ = [$CH{=}NC_6H_5$], [$CH{=}NC_6H_4Cl$-*p*], [$CH{=}NC_6H_4CH_3$-*p*], [$CH{=}NC_6H_4OCH_3$-*p*].** Recrystallization from aqueous ethanol (80-95%) afforded the pure pyrazole (**6**).

6 (R″ = Cl). Anal. Calcd for $C_{15}H_{11}ClN_2$: C, 70.73; H, 4.35; N, 11.00. Found: C, 71.03; H, 4.41; N, 11.34.

6 (R″ = CH_3). Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.89; H, 5.88; N, 11.60.

6 (R = OCH_3). Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 77.16; H, 5.74; N, 11.06.

(**d**) **1 (R = H, R′ = ($CH{=}CHCOOCH_3$).** Recrystallization from aqueous ethanol gave 2-phenyl-5-carbomethoxypyrrole (**7**).

General Procedure for Reactions of 2-Arylazirines with $TiCl_4$. A hexane (150 mL) solution of the azirine (10 mmol) was cooled to −78 °C (dry ice-acetone). Titanium tetrachloride (20 mmol) was dissolved in hexane (50 mL) and then added dropwise over a 30-min period to the azirine solution. After addition was complete, the mixture was stirred at −78 °C for 1 h. The dry ice-acetone bath was removed and the solution was allowed to warm, with stirring, to room temperature. The mixture was poured into 400 mL of water and then extracted with methylene chloride. The methylene chloride extract was dried ($MgSO_4$) and evaporated in vacuo. The residue was dissolved in benzene or toluene and chromatographed on Florisil. Elution with benzene or toluene gave the pyrazine (**2**) and the pyridazine (**11**). The ketone (**12**) and the α-chloro ketone (**10**) were eluted off the column with toluene or 3:1 ether-benzene.

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