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Studies of Acenaphthene Derivatives. XVII.¹⁾ The Reaction of Benzylideneacenaphthenone with Hydrazines*¹

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The reactions of benzylideneacenaphthenones with hydrazines are reported. The reaction of benzylideneacenaphthenone with hydrazine hydrate in methanol at 40°C gave 1-hydroxy-2-hydrazinobenzylacenaphthylene, which was then cyclized to the 1-acetylpyrazoline by treating it with acetic anhydride. The hydrazino compound reacted with phenyl isocyanate to give the 1:2-adduct, which, when then treated with hydrochloric acid, suffered ring closure to the pyrazoline compound. Under severe conditions with hydrazine hydrate, however, the reductive cleavage reaction took place, giving the hydrazones of both acenaphthenone and benzaldehyde. Similar phenomena were also observed in the reaction with *p*-substituted benzylideneacenaphthenones. On the other hand, the reaction with phenylhydrazines in ethanol containing sulfuric acid afforded directly the expected pyrazolines, from which pyrazoles were then prepared by treating them with lead tetraacetate. Furthermore, the corresponding pyridazine was formed in the reaction of phenacylideneacenaphthenone with hydrazine hydrate, while the reaction with 2,4-dinitrophenylhydrazine gave the pyrazoline compound.

Although it is well known that the most general synthetic method for pyrazolines, which are of interest as intermediates in the preparation of cyclopropanes, is the reaction of α,β -unsaturated carbonyl compounds with hydrazines,²⁾ little has

been reported relating to the reaction of benzylideneacenaphthenones (I)¹⁾ with hydrazines.

In the course of preparing the pyrazolines starting with I, we have found that the reaction of I with hydrazine hydrate (II) revealed unusual phenomena, while the reaction with phenylhydrazines (III) in ethanol containing a little sulfuric acid gave the expected pyrazolines in excellent yields; these results will be described in this paper.

This paper will also deal with the reaction of phenacylideneacenaphthenone (IV)¹⁾ with hydrazines.

1) Part XVI: O. Tsuge, M. Tashiro and I. Shinkai, *This Bulletin*, **42**, 181 (1969).

*¹ Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

2) R. C. Elderfield, "Heterocyclic Compounds," Vol. V, John Wiley & Sons, New York, N. Y. (1957), p. 45.

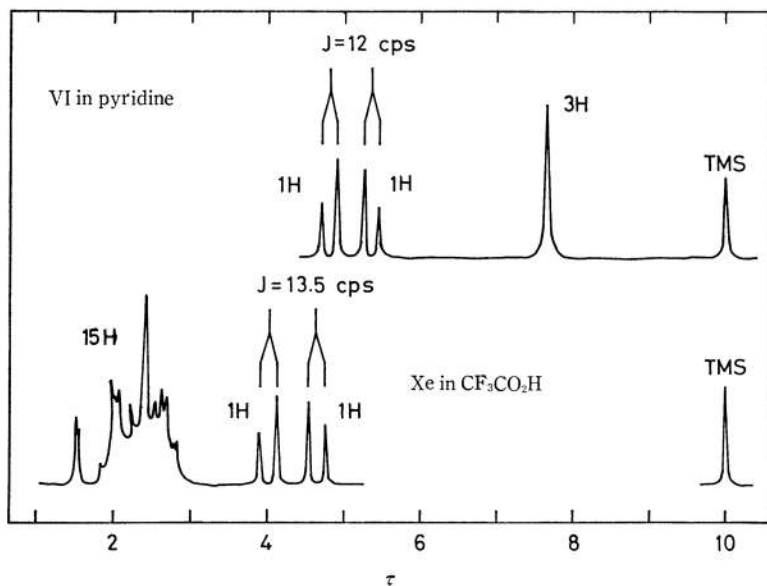
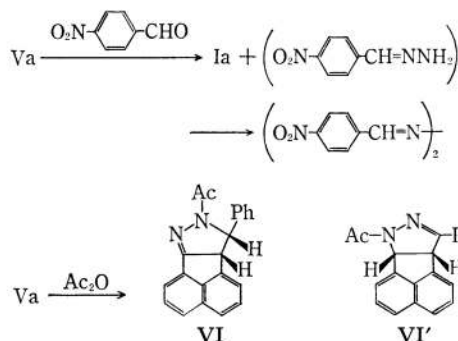
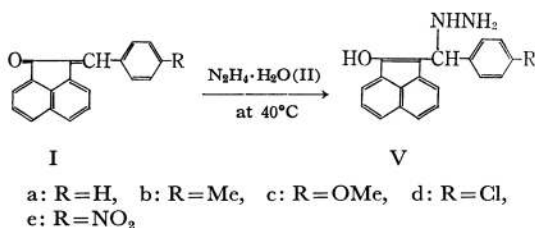


Fig. 1. The NMR spectra of VI and Xe.



When benzylideneacenaphthene (Ia) was treated with II in a 1 : 3 molar ratio in methanol at 40°C for 20 min, white needles (Va), C₁₉H₁₆ON₂, were obtained in a 96% yield, instead of the expected hydrazone, azine or pyrazoline compound. The infrared spectrum of Va exhibited characteristic bands due to the hydroxyl group at 3400 cm⁻¹ and to the NH group at 3280 and 3220 cm⁻¹, but it did not reveal any bands for the carbonyl group. The NMR spectrum in DMSO-d₆ exhibited peaks at τ 7.5 (1H, methine-proton, singlet), 5.2–6.2 (4H, hydroxyl- and NH-protons, broad peak), and 2.2 (11H, aromatic protons, multiplet).

The above observations can be explained on the assumption that Va is 1-hydroxy-2-(hydrazinobenzyl)acenaphthylene. This structure was also confirmed by the following results.

The treatment of Va with *p*-nitrobenzaldehyde in ether at room temperature afforded Ia and *p*-nitrobenzaldazine; the latter was formed by the condensation of the hydrazone and aldehyde.

When Va was allowed to react with acetic anhydride at room temperature for 2 hr, the *N*-acetylpyrazoline compound (VI) was obtained in a 53% yield. Its structure was confirmed by the results of elemental analysis and by the infrared and NMR spectra. The infrared spectrum of VI showed absorptions at 1670 and 1620 cm⁻¹, while the NMR spectrum in pyridine exhibited peaks at τ 7.6 (3H, acetyl-protons, singlet), 5.3 (1H, methine-proton, doublet), and 4.8 (1H, methine-proton, doublet) ($J=12$ cps), as is shown in Fig. 1.

It has been reported by Hassner and Michelson³ that *cis*-pyrazolines exhibit higher coupling constants (10–14 cps) than those (3–10 cps) of the corresponding *trans* isomers. On the other hand, in our study of the NMR spectra of acenaphtho[1,2-*d*]oxazolines, in which 1- and 2-hydrogen are located in the *cis*-manner, the protons appeared as doublets at τ 4.0 and 4.3 ($J=6$ cps) respectively.⁴

Although two pyrazoline structures for VI are possible, the above observations support the structure of 4,5-*cis*-1-acetyl-5-phenylpyrazoline com-

3) A. Hassner and M. J. Michelson, *J. Org. Chem.*, **27**, 3974 (1962).

4) O. Tsuge, M. Tashiro and K. Oe, The 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

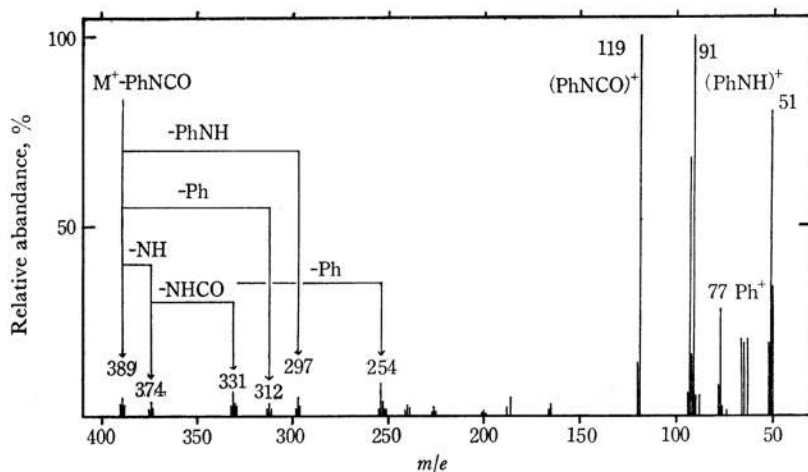
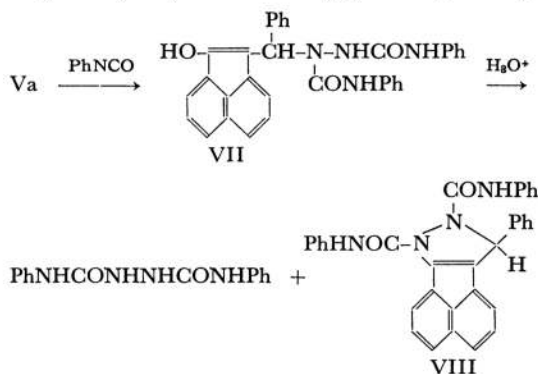


Fig. 2. The mass spectrum of VIII.

compound (VI) rather than the isomeric 4,5-*cis*-1-acetyl-3-phenylpyrazoline (VI').

Furthermore, the treatment of Va with two equivalents of phenyl isocyanate afforded the 1:2-adduct (VII) (C₃₃H₂₆O₃N₃) in a 96% yield. Its infrared spectrum showed bands to be ascribed to the NH group at 3300 cm⁻¹ and to the carbonyl groups at 1700, 1690, and 1670 cm⁻¹. Also, VII hydrolyzed with 15% hydrochloric acid, giving *N,N'*-bisphenylcarbamoylhydrazine and orange yellow grains (VIII) in 34 and 44% yields respectively.



Compound VIII was assumed, on the basis of elemental analysis and a study of its infrared and mass spectra, to be 1,2-bisphenylcarbamoyl-3-phenylacenaphtho[1,2-*c*]pyrazoline. Its infrared spectrum exhibited characteristic bands due to carbonyl groups at 1720, 1680, and 1650 cm⁻¹, but it did not reveal any bands for the hydroxyl and NH groups.

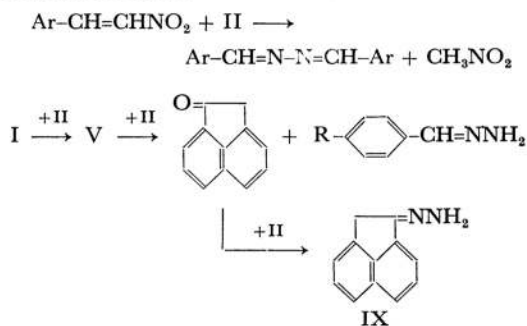
The fragmentation on electron impact supported the proposed structure for VIII. As is shown in Fig. 2, the mass spectrum shows the *m/e* 389 peak, which is derived from the molecular ion upon the loss of a phenyl isocyanate moiety.

Similar reactions of *p*-methoxy- (Ic) and *p*-chlorobenzylideneacenaphthenone (Id) with II

afforded the corresponding 1-hydroxy-2-hydrazino-benzyl compounds, Vc and Vd, in quantitative yields.

When an ethanol solution of Ia and II was refluxed for 10 min, the hydrazones of both acenaphthenone (IX) and benzaldehyde were obtained in excellent yields. In the reaction of Ib (R=Me), Id, and Ie (R=NO₂) under similar conditions, IX and the respective benzaldehyde hydrazone were obtained.

Similar phenomena were observed by Musante⁵: *o*-nitrostyrene was cleft with II to give the azine and nitromethane.



It may be inferred that both the hydrazones are formed by the reductive cleavage of the carbon-carbon bond in V with II.

Raiford and Manley⁶ have reported that phenyl hydrazones, which rearrange to isomeric pyrazolines on refluxing, can be isolated in the reaction of chalcones with phenylhydrazine (IIIa) in acetic acid at room temperature, and that pyrazolines forms directly when methanol containing a little acetic acid is used as the reaction medium.

When I was allowed to react with III in acetic

5) C. Musante, *Gazz. Chim. Ital.*, **67**, 579 (1937).

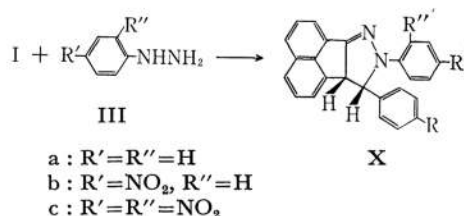
6) L. C. Raiford and R. H. Manley, *J. Org. Chem.*, **5**, 590 (1940).

acid at room temperature, the expected phenylhydrazones were not obtained; instead, a resinous material was exclusively formed.

In a methanol solution containing a little acetic acid, Id and Ie reacted with IIIa and IIIb ($R' = \text{NO}_2$, $R'' = \text{H}$) to give the corresponding pyrazolines in moderate yields (60—75%). In the reactions of Ia, Ib, and Ic, however, a resinous material was formed exclusively. When Id and Ie were treated with IIIc ($R' = R'' = \text{NO}_2$) under similar conditions, the expected pyrazoline was not obtained, but predominantly a resinous material was formed.

On the other hand, it has been found that I reacted smoothly with III in ethanol containing a little sulfuric acid, giving the corresponding pyrazolines (X) in quantitative yields.

The structures for X were confirmed on the basis



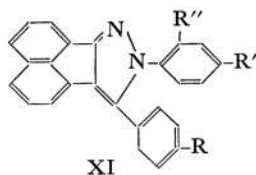
of elemental analyses, and on the basis of a study of the infrared and NMR spectra. The infrared spectra of all X structures exhibited the band ascribed to the C=N bond at about 1600 cm^{-1} , but there were no bands for the carbonyl, hydroxyl, and NH groups.

As is shown in Fig. 1, the NMR spectrum of Xc ($R = \text{Cl}$, $R' = R'' = \text{H}$) in trifluoroacetic acid reveals peaks at τ 4.64, 4.04 (each 1H, methine-proton,

TABLE 1. 4,5-*cis*-1,5-DIARYLACENAPHTHO[1,2-*c*]PYRAZOLINES (X)

X	R			Mp, °C (From solvent)	IR (C=N) cm^{-1}	Appearance	Microanalyses, %					
	R	R'	R''				Found			Calcd		
							C	H	N	C	H	N
a	H	NO_2	H	231 (pyridine)	1600	red needles	76.69	3.94	10.67	76.07	4.34	10.73
b	H	NO_2	NO_2	266 (dioxane)	1610	brown needles	68.99	3.17	12.26	68.70	3.66	12.83
c	CH_3	NO_2	H	233 (dioxane-MeOH)	1600	brown needles	77.11	4.26	9.94	77.10	4.69	10.35
d	CH_3	NO_2	NO_2	261 (dioxane)	1610	brown needles	69.01	3.81	11.97	69.30	4.00	12.42
e	Cl	H	H	172 (benzene-EtOH)	1600	reddish yellow needles	79.29	4.10	7.41	79.00	4.47	7.36
f	Cl	NO_2	H	238 (benzene-EtOH)	1595	reddish yellow needles	71.16	3.27	9.70	70.70	3.76	9.89
g	Cl	NO_2	NO_2	278 (pyridine)	1610	brown needles	63.94	2.97	11.88	63.80	3.19	11.90
h	NO_2	H	H	192 (pyridine)	1600	brown needles	76.68	3.93	10.41	76.70	4.35	10.75
i	NO_2	NO_2	H	281 (pyridine-dioxane)	1595	red needles	69.02	3.24	12.43	68.80	3.67	12.83
j	NO_2	NO_2	NO_2	291 (pyridine)	1610	yellow needles	62.63	2.93	13.99	62.40	3.12	14.55

TABLE 2. 1,5-DIARYLACENAPHTHO[1,2-*c*]PYRAZOLES (XI)



XI	R			Yield %	Mp, °C (From solvent)	IR (C=N) cm^{-1}	Appearance	Microanalyses, %					
	R	R'	R''					Found			Calcd		
								C	H	N	C	H	N
a	CH_3	NO_2	NO_2	53	242 (benzene-EtOH)	1610	brown needles	69.57	3.43	12.27	69.50	3.56	12.49
b	Cl	NO_2	H	48	142 (EtOH)	1610	brown needles	71.04	3.41	9.86	71.10	3.32	9.95
c	Cl	NO_2	NO_2	60	270 (EtOH)	1615	yellow needles	63.87	2.53	11.74	63.96	2.77	11.92

doublet, $J=13.5$ cps), and 2.4 (15H, aromatic protons, multiplet). For reasons pointed out in the discussion of VI, the above observations indicate that Xe is the 4,5-*cis*-1-phenyl-5-*p*-chlorophenylpyrazoline compound.

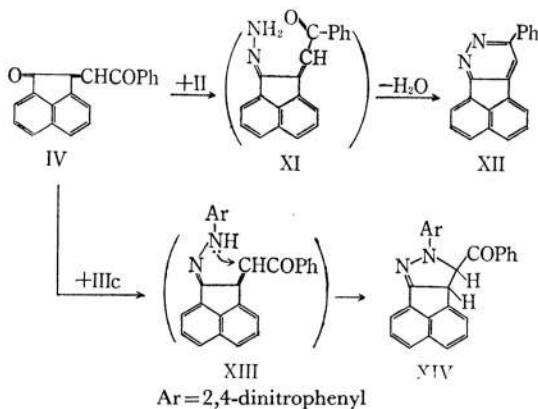
The physical properties and elemental analyses are summarized in Table 1.

It has been reported by Gladstone and Norman⁷⁾ that lead tetraacetate is an effective reagent for oxidizing pyrazolines to pyrazoles.

When X was oxidized with lead tetraacetate in dichloromethane, the corresponding pyrazole (XI), whose infrared spectrum was very similar to that of the pyrazoline, was obtained in a fairly good yield.

The yields, physical properties, and results of the elemental analyses of XI are listed in Table 2.

On the other hand, an ethanol solution of phenacylideneacenaphthenone (IV) and II was refluxed for 30 min, giving yellow needles (XII), mp 147°C, in a 33% yield. The molecular formula of XII agreed with $C_{20}H_{12}N_2$, and its infrared spectrum exhibited the band ascribed to the C=N bond at 1610 cm^{-1} , but it did not reveal any bands for the carbonyl group. On the basis of the above observations, the compound XII was assumed to be the pyridazine compound which was formed through the hydrazone intermediate (XI).



While II exclusively attacked the carbon atom of benzylidene moiety in I, the reaction with IV proceeded through the formation of hydrazone.

When IV was treated with IIIc in ethanol containing a little sulfuric acid, reddish brown needles (XIV), mp 253°C, were obtained in a 75% yield. The compound XIV agreed with the formula, $C_{26}H_{16}O_5N_4$, and its infrared spectrum exhibited characteristic bands due to the carbonyl and C=N groups at 1650 and 1610 cm^{-1} respectively.

Considering the above observations, it may be

deduced that the compound XIV is the pyrazoline compound formed through the hydrazone (XIII).

Experimental

All melting points are uncorrected. The infrared spectra were measured in KBr disks, and the NMR spectra were determined at 60 Mc with a Japan Electron Optics JNM-3H-60 NMR spectrometer, using TMS as the internal reference. The mass spectrum was obtained on a Hitachi RMU-6D instrument using a heated inlet, an ionization energy of 70 eV, an inlet temperature of 250°C, and a source temperature of 250°C. The elemental analyses were done by Mr. Eiji Shiozaki in our laboratory.

Benzylidene- (I) and phenacylideneacenaphthenone (IV) were prepared by a previously-reported method.¹⁾

General Method for the Reaction of the Benzylideneacenaphthenone (I) with Hydrazine Hydrate (II).

i) After a solution of I (1.5 mmol) and II (4.5 mmol) in methanol (20 ml) had been heated at 40°C for 20 min, the reaction mixture was evaporated *in vacuo* to give white crystals. Recrystallization from methanol gave the corresponding 1-hydroxy-2-(hydrazinobenzyl)acenaphthylene (V).

Va (R=H), yield, 96%. Mp 74–75°C (decomp.), white needles. Found: C, 78.95; H, 5.59; N, 9.27%. Calcd for $C_{18}H_{16}ON_2$: C, 79.10; H, 5.56; N, 9.71%.

Vc (R=OCH₃), quantitative yield. Mp 96°C (decomp), white needles. Found: C, 75.13; H, 5.45; N, 9.25%. Calcd for $C_{20}H_{18}O_2N_2$: C, 75.45; H, 5.70; N, 8.80%.

Vd (R=Cl), quantitative yield. Mp 62°C (decomp.), white needles. Found: C, 70.04; H, 4.20; N, 8.55%. Calcd for $C_{18}H_{15}ON_2Cl$: C, 70.60; H, 4.64; N, 8.67%.

ii) After a solution of I (3 mmol) and II (9 mmol) in ethanol (20 ml) had been refluxed for 10 min, ethanol was distilled off *in vacuo* to leave an oily material. A solution of the oily material in petroleum benzene (bp 45–60°C) was then allowed to stand overnight, giving white crystals. Filtration afforded acenaphthenone hydrazone (IX), mp 107°C (decomp.), as white needles, in an excellent yield.

This compound was identical with the authentic sample prepared from acenaphthenone and II.

Found: C, 79.32; H, 5.27; N, 15.30%. Calcd for $C_{12}H_{10}N_2$: C, 79.12; H, 5.49; N, 15.39%.

A petroleum benzene solution was concentrated, leaving the benzaldehyde hydrazone as a colorless liquid. The corresponding benzaldazine was obtained by the treatment of the hydrazone with acetic acid.

The Reaction of Va with *p*-Nitrobenzaldehyde.

A solution of Va (280 mg) and *p*-nitrobenzaldehyde (150 mg) in ether (10 ml) was stirred at room temperature for 2 hr; during this time yellow crystals appeared. Filtration gave *p*-nitrobenzaldazine (mp 293–295°C (decomp.)) in a quantitative yield. The ether filtrate was concentrated to give Ia.

The Reaction of Va with Acetic Anhydride.

After acetic anhydride (430 mg) had been added to a solution of Va (1.2 g) in ether (30 ml), the reaction mixture was stirred at room temperature for 2 hr; during this time white crystals appeared. The crystals were collected by filtration, washed with ether, and dried. Yield, 645 mg (53%). Recrystallization from

7) W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc., (C)*, **1966**, 1536.

benzene afforded white needles, *cis*-1-acetyl-5-phenylpyrazoline compound (VI), mp 168°C.

Found: C, 80.49; H, 4.69; N, 9.00%. Calcd for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.97%.

The Reaction of Va with Phenyl Isocyanate.

To a solution of Va (500 mg) in ether (15 ml), a solution of phenyl isocyanate (410 mg) in ether (10 ml) was added, drop by drop, at room temperature. The reaction mixture was then stirred at room temperature for 30 min; during this time white crystals appeared. After the crystals had been collected by filtration, recrystallization from a dioxane-benzene mixture to give the 1:2 adduct (VII) as white grains, mp 225–226°C. Yield, 870 mg (96%).

Found: C, 74.98; H, 4.67; N, 10.53%. Calcd for $C_{33}H_{26}O_3N_4$: C, 75.20; H, 4.94; N, 10.64%.

The Hydrolysis of VII. After a suspension of VII (200 mg) in 15% hydrochloric acid (10 ml) had been heated at 100°C for 3 min, crystals were collected by filtration. These crude crystals were extracted with dioxane, leaving 35 mg (34%) of *N,N'*-bis(phenylcarbamoyl)hydrazine as white needles, mp 270°C; this compound was identical with the authentic sample prepared from the reaction of phenyl isocyanate with hydrazine.

The dioxane extract was concentrated *in vacuo* to afford the 1,2-bis(phenylcarbamoyl)-3-phenylpyrazoline compound (VIII) as orange yellow grains, mp 227–229°C. Yield, 85 mg (44%).

Found: C, 77.61; H, 4.63; N, 10.92%. Calcd for $C_{33}H_{24}O_2N_4$: C, 77.93; H, 4.76; N, 11.02%.

General Method for the Preparation of Pyrazoline Compounds (X). A solution of equimolar amounts of I and phenylhydrazines III (each 1.5 mmol) in 20 ml of ethanol containing a few drops of concentrated sulfuric acid was heated on a water-bath for 10 min. The crystals were then collected and purified by recrystallization. The yields of X were quantitative in all cases.

The physical properties and results of the elemental analyses of X are summarized in Table 1.

The Oxidation of the Pyrazoline (X) to the Pyrazole (XI). To a suspension of 240 mg of Xg (R=Cl, R'=R''=NO₂) in 6 ml of dichloromethane, a solution of 250 mg of lead tetraacetate in 3 ml of dichloromethane was added at room temperature. After the mixture had been stirred at room temperature for 24 hr, it was decomposed with acetic acid and hydrazine hydrate to give a tarry material. The benzene solution of the product was chromatographed on alumina, affording yellow crystals. Recrystallization from ethanol gave 140 mg (60%) of pyrazole (XIc), mp 270°C.

Similar oxidations of Xd and Xf gave the corresponding pyrazoles, XIa and XIb. The yields, physical properties, and elemental analyses of XI are listed in Table 2.

The Reaction of Phenacylideneacenaphthenone (IV) with II. A solution of 200 mg of IV and 1.5 equimolar amounts of II in 10 ml of ethanol was refluxed for 30 min. After the mixture had been concentrated *in vacuo*, it was allowed to stand overnight, thus giving crystals. Recrystallization from ethanol gave 65 mg (33%) of 3-phenylacenaphtho[1,2-*c*]pyridazine (XII) as yellow needles, mp 147°C.

Found: C, 85.85; H, 3.99; N, 10.03%. Calcd for $C_{20}H_{12}N_2$: C, 85.69; H, 4.32; N, 9.90%.

The Reaction of IV with 2,4-Dinitrophenylhydrazine (IIIc). A solution of 280 mg of IV and 200 mg of IIIc in 10 ml of ethanol containing two drops of concentrated sulfuric acid was refluxed for 15 min. After the reaction mixture had then been cooled, crystals were collected by filtration. Recrystallization from dioxane gave 350 mg (75%) of 1-(2,4-dinitrophenyl)-5-benzoylacenaphtho[1,2-*c*]pyrazoline (XIV) as reddish-brown needles, mp 235°C.

Found: C, 67.31; H, 3.52; N, 11.83%. Calcd for $C_{26}H_{16}O_5N_4$: C, 67.23; H, 3.47; N, 12.06%.