Bull. Chem. Soc. Jpn., 55, 2456—2459 (1982)

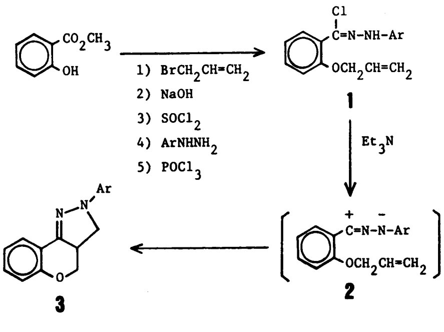
# Intramolecular 1,3-Dipolar Cycloaddition of Nitrilimines Bearing Alkenyl Groups[1]

Tomio Shimizu,* Yoshiyuki Hayashi, Susumu Ishikawa, and Kazuhiro Teramura
*Department of Dyeing, Faculty of Industrial Arts, Kyoto Technical University, Matsugasaki, Sakyo-ku, Kyoto 606*

(Received December 4, 1981)

The reaction of the arylhydrazones of some 2-(alkenyloxy)benzaldehydes(or 1-naphthaldehydes) with $Pb(OAc)_4$ leads, *via* the nitrilimine intermediates, to intramolecular 1,3-dipolar cycloadducts, 3-substituted 2-aryl-2,3,3a,4-tetrahydro[1]benzopyrano(or naphtho[1′,2′:5,6]pyrano)[4,3-*c*]pyrazoles, in 10—80% yields. In the presence of an excess of $Pb(OAc)_4$, these cycloadducts were dehydrogenated to 3-substituted 2-aryl-2,4-dihydro[1]benzopyrano-(or naphtho[1′,2′:5,6]pyrano)[4,3-*c*]pyrazoles. In the presence of a large excess of $Pb(OAc)_4$, some of the pyrazoles were acetoxylated to give the corresponding 4-acetoxypyrazoles. The effect of substituents of the alkenyl group on reactivity of the reaction was interpreted in terms of the frontier molecular orbital (FMO) theory.

1,3-Dipolar cycloaddition reactions are one of the most useful methods for the preparation of five-membered heterocycles.[2] Intermolecular 1,3-dipolar cycloaddition reactions can be rationalized in terms of FMO theory.[3] In this decade, a number of applications for preparation of heterocycles *via* intramolecular cycloadditions have been reported.[4] But the explanation of electronic effects of substituents on the intramolecular cycloaddition in terms of FMO theory is not completely satisfactory, mainly owing to the large entropy term. It is therefore interesting to investigate in detail the substituent effects on the reaction. Besides these mechanistic points of interests, intramolecular 1,3-dipolar cycloaddition reactions are very convenient and useful ones for the preparation of complex polycyclic, annelated, and fused molecules, which are difficult to prepare by other methods. The intramolecular nitrilimine cycloaddition shown below[5] was reported for preparation of benzopyranopyrazoles (**3**), but the method is cumbersome because multi-step reactions are required for the preparation of chlorohydrazone (**1**), a precursor of nitrilimine (**2**). One of the aims of our work was to find a simpler preparative method for **3**.[6] We found that application of the method[7] reported by Gladstone for preparation of the nitrilimine to this system gave the corresponding cycloadducts (**3**) in satisfactory yields.



(1)

## Results and Discussion

Arylhydrazones of 2-(alkenyloxy)benzaldehyde(or 1-naphthaldehydes) (**5**) are prepared in two steps from salicylaldehyde (or 2-hydroxy-1-naphthaldehyde) as shown in the preceding paper.[6c] The reaction of **5** with an equimolar or excess amount of $Pb(OAc)_4$ was carried out in chloroform for 3—6 h at room temperature or below. 2,4-Dihydro[1]benzopyrano[4,3-*c*]pyrazoles (**8**) were isolated from the reaction of **5** in the presence of three equivalents of $Pb(OAc)_4$, while an equimolar mixture of **5** and $Pb(OAc)_4$ gave pyrazolines (**7**). The results of the reaction are shown in Tables 1 and 2, respectively. The structures of **7** and **8** were established on the basis of elemental analyses and spectral data. The assignment of the structures was further supported

Table 1. 2-Aryl-2,3,3a,4-tetrahydro[1]benzopyrano(or naphtho[1′,2′:5,6]pyrano)[4,3-*c*]pyrazoles (**7**)

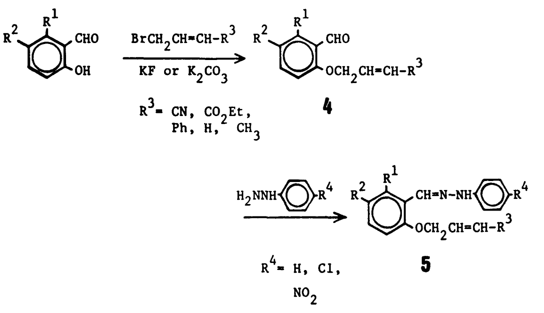
| Compd[a] | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield/% | Mp[b] $\theta_m$/°C | IR $\tilde{\nu}$/cm$^{-1}$ | NMR $\delta$[c] |
|---|---|---|---|---|---|---|---|---|
| **7a** | H | H | $CO_2Et$ | H | 10 | 164—166 | 1740(COO) | 1.3(t, 3H, *J*=7 Hz), 3.6—4.7(m, 6H), 6.6—7.4(m, 9H) |
| **7b** | H | H | CN | H | 24 | d) | 2240(CN) | 3.9—4.9(m, 4H), 6.8—8.0(m, 9H) |
| **7c** | H | H | $CO_2Et$ | Cl | 18 | 121—122 | 1750(COO) | 1.3(t, 3H, *J*=7 Hz), 3.6—4.8(m,6H), 6.7—7.4(m, 7H), 7.75(dt, 1H, *J*=2 and 6 Hz) |
| **7d** | H | H | CN | Cl | 10 | 130—132 | 2240(CN) | 3.8—4.9(m, 4H), 6.8—7.9(m, 8H) |
| **7e** | H | H | $CO_2Et$ | $NO_2$ | 60 | 165—166 | 1750(COO) | 1.3(t, 3H, *J*=7 Hz), 3.75—4.9(m, 6H), 6.8—8.3(m, 8H) |
| **7f** | H | H | CN | $NO_2$ | 53 | 126—128 | 2240(CN) | 4.25—5.5(m, 4H), 6.9—7.4(m, 8H) |
| **7g** | $-(CH)_4-$ | | $CO_2Et$ | $NO_2$ | 80 | 205—207 | 1750(COO) | 1.3(t, 3H, *J*=7 Hz), 4.0—5.0(m, 6H), 6.9—8.3(m, 9H), 9.1(d, 1H, *J*=8 Hz) |
| **7h** | H | H | $C_6H_5$ | $NO_2$ | 10 | 238 | — | 3.5—5.4(m, 4H), 6.7—7.7(m, 13H) |

a) **7a—g** were obtained from the equimolar reaction of **5** with $Pb(OAc)_4$. **7h** was isolated from the reaction mixture of **5** with three equivalents of $Pb(OAc)_4$. b) Recrystallized from ethanol. c) **7f** and **7h** were dissolved in DMSO-$d_6$; the others were dissolved in $CDCl_3$. d) The melting point range of **7b** was very broad because of contamination of a trace amount of **8b**; chromatographic purification failed.

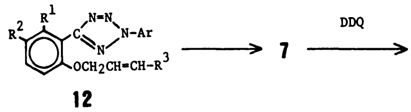
TABLE 2. 2-ARYL-2,4-DIHYDRO[1] BENZOPYRANO(OR NAPHTHO[1′,2′:5,6]PYRANO)[4,3-*c*]PYRAZOLES (**8**)

| Compd[a)] | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield % | Mp[b)] $\theta_m$/°C | IR $\tilde{\nu}$/cm$^{-1}$ | NMR $\delta$[c)] |
|---|---|---|---|---|---|---|---|---|
| **8a** | H | H | $CO_2Et$ | H | 26 | 129—130 | 1730(COO) | 1.2(t, 3H, $J$=7 Hz), 4.2(q, 2H, $J$=7 Hz), 5.45(s, 2H), 6.75—7.75(m, 9H) |
| **8b** | H | H | CN | H | 39 | 159—160 | 2230(CN) | 5.35(s, 2H), 6.85—7.9(m, 9H) |
| **8c** | H | H | $CO_2Et$ | Cl | 32 | 159—161 | 1740(COO) | 1.25(t, 3H, $J$=7 Hz), 4.3(q, 2H, $J$=7 Hz), 5.45(s, 2H) 6.8—7.85(m, 8H) |
| **8d** | H | H | CN | Cl | 41 | 183—185 | 2240(CN) | 5.35(s, 2H), 6.8—7.9(m, 8H) |
| **8e** | H | H | $CO_2Et$ | $NO_2$ | 38 | 204—205 | 1720(COO) | 1.3(t, 3H, $J$=7 Hz), 4.3(q, 2H, $J$=7 Hz), 5.45(s, 2H), 6.8—8.4(m, 8H) |
| **8f** | H | H | CN | $NO_2$ | 38 | 184—185 | 2240(CN) | 5.5(s, 2H), 6.95—8.6(m, 8H) |
| **8g** | -(CH)$_4$- | | $CO_2Et$ | $NO_2$ | 78 | 178—188 | 1740(COO) | 1.3(t, 3H, $J$=7 Hz), 4.3(q, 2H, $J$=7 Hz), 5.5(s, 2H), 6.9—8.4(m, 9H), 9.1(d, 1H, $J$=8 Hz) |
| **8h** | H | H | $C_6H_5$ | $NO_2$ | 21 | 174 | —— | 5.3(s, 2H), 3.8—8.3(m, 13H) |

a) **8a**—**f** and **8h** were obtained from the reaction of **5** with three equivalents of $Pb(OAc)_4$. **8g** was obtained from the oxidation of **7g** with DDQ. b) Recrystallized from ethanol. c) **8f** was dissolved in DMSO-$d_6$; the others were dissolved in $CDCl_3$.

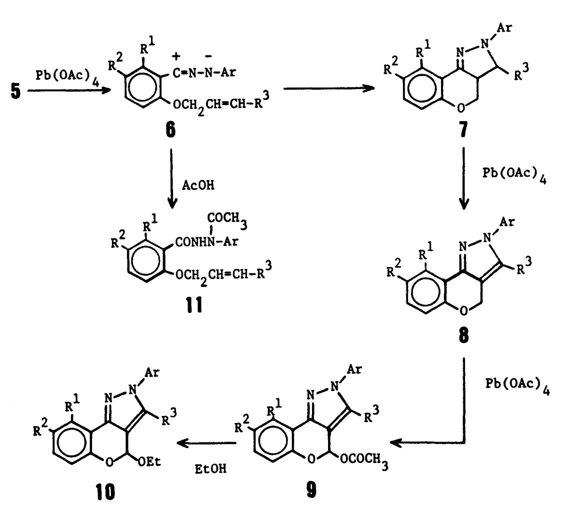


(2)



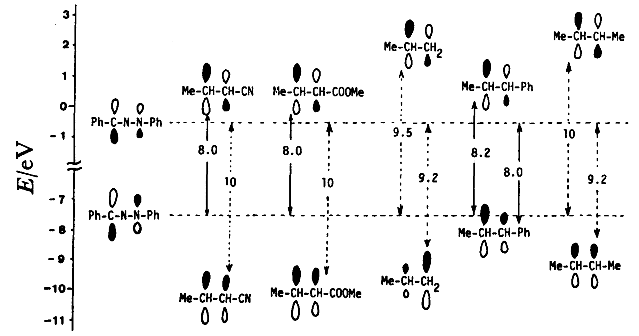
(3)

**12**



Scheme 1.

by comparison of the physical properties of **7d** and **8d** with those of the authentic samples prepared according to the published procedures:[8,9)] **12**→**7d**→**8d**. The most plausible reaction mechanism for the reaction is shown in Scheme 1; formation of nitrilimines (**6**) was followed by intramolecular cycloaddition to give pyrazolines (**7**), which were further oxidised to **8**. The rates of the oxidation of hydrazones (**5**) to nitrilimines (**6**), the following intramolecular cycloaddition, and the oxidation of **7** to **8** were quite fast. It was found that **5** disappeared within ten minutes in the presence of three equivalents of $Pb(OAc)_4$ and the product was shown to be **8f** along with a trace amount of **7f**. Thus, it was rather difficult to isolate some of **7** in high yields from the equimolar reaction of **5** with $Pb(OAc)_4$. Phenylhydrazones bearing an alkenyl group may exhibit other intramolecular reactions besides the reaction mentioned here: a) thermal 1,3-dipolar cycloaddition *via* azomethine imine,[6c,10)] b) ene reaction,[6c,11)] and c) acid-catalyzed $[3^+ + 2]$ cycloaddition.[6c,12)] It was confirmed that none of the three intramolecular reactions occurred under our reaction conditions. Thus the starting materials (**5**) in chloroform were definitely stable at room temperature, even in the presence of acetic acid. The most remarkable substituent effects on the reaction products were observed in the case of the substituents of $R^3$ on **5**, as expected from the results of intermolecular nitrilimine cycloaddition, while relatively small substituent effects were observed in spite of the wide variation in $R^1$, $R^2$, and $R^4$. The reactivity in the cycloaddition has been rationalized in terms of FMO theory,[3)] although some of the intramolecular cycloaddi-



Scheme 2. Interaction scheme of diphenylnitrilinime with several 1-substituted 1-propenes (see Refs. 3a, 13, and 14).

TABLE 3. 2-ARYL-4-ETHOXY-2,4-DIHYDRO[1]BENZOPYRANO(OR NAPHTHO[1′,2′:5,6]PYRANO[4,3-*c*]PYRAZOLES (**10**)

| Compd[a)] | $R^1$ $R^1$ | $R^3$ | $R^4$ | Yield / % | Mp[b)] $\theta_m$/°C | IR $\tilde{\nu}$/cm$^{-1}$ | NMR $\delta$[c)] |
|---|---|---|---|---|---|---|---|
| **10a** | H H | CN | $NO_2$ | 82 | 176—180 | 2240(CN) | 1.2(t, 3H, $J$=7 Hz), 3.7—4.25(m, 2H), 6.6(s, 1H), 7.0—8.6(m, 8H) |
| **10b** | $-(CH)_4-$ | $CO_2Et$ | H | 63 | 165—167 | 1740(COO) | 1.08(t, 3H, $J$=7 Hz), 1.17(t, 3H, $J$=7 Hz), 3.5—4.6(m, 2H), 4.32(q, 2H, $J$=7 Hz), 6.7(s, 1H), 7.2—8.0(m, 10H), 9.2(d, 1H, $J$=8 Hz) |
| **10c** | $-(CH)_4-$ | CN | H | 61 | 167—168 | 2240(CN) | 1.27(t, 3H, $J$=7 Hz), 4.0(d, quintet, 2H, $J$=3 and 7 Hz), 6.57(s, 1H), 7.15—8.15(m, 10H), 9.5(d, 1H, $J$=8 Hz) |
| **10d** | $-(CH)_4-$ | $CO_2Et$ | Cl | 49 | 197—198 | 1750(COO) | 1.23(t, 3H, $J$=7 Hz), 1.3(t, 3H, $J$=7Hz), 4.3(q, 2H, $J$=7 Hz), 3.66—4.47(m, 2H), 6.6(s, 1H), 7.0—8.0(m, 9H), 9.3(d, 1H, $J$=8 Hz) |
| **10e** | $-(CH)_4-$ | CN | Cl | 35 | 180—181 | 2250(CN) | 1.23(t, 3H, $J$=7 Hz), 3.95(d, quintet, 2H, $J$=3 and 7 Hz), 6.4(s, 1H), 7.0—7.95(m, 9H), 9.25(d, 1H, $J$=8 Hz) |
| **10f** | $-(CH)_4-$ | $CO_2Et$ | $NO_2$ | 60 | 174—176 | 1750(COO) | 1.23(t, 3H, $J$=7 Hz), 3.66—4.5(m, 2H), 1.33(t, 3H, $J$=7 Hz), 4.33(q, 2H, $J$=7 Hz), 6.53(s, 1H), 7.0—7.9 (m, 7H), 8.3(d, 2H, $J$=9 Hz), 9.23(d, 2H, $J$=8 Hz) |
| **10g** | $-(CH)_4-$ | CN | $NO_2$ | 46 | 196—197 | 2240(CN) | 1.23(t, 3H, $J$=7Hz), 4.0(q, 2H, $J$=7Hz), 6.7(s, 1H), 7.0—8.3(m, 9H), 9.2(d, 1H, $J$=8 Hz) |

a) **10a** was obtained from the reaction of **8f** with a large excess of $Pb(OAc)_4$. The others were obtained from the reaction of **5** with three equivalents of $Pb(OAc)_4$. b) Recrystallized from ethanol. c) **10b** and **10g** were dissolved in DMSO-$d_6$; the others were dissolved in $CDCl_3$.

tions take place easier than the intermolecular one because of an activation in entropy terms.[4)] The interaction scheme of frontier orbitals of diphenylnitrilimine[3a,13)] and several 1-substituted 1-propenes[3a,14)] are shown in Scheme 2. Examination of the scheme led us to expect following general tendencies:

i) Dipole-HOMO controlled cycloaddition is the most probable route for the substrates bearing cyano or methoxycarbonyl group as $R^3$.

ii) Both dipole-HOMO and dipole-LUMO controlled cycloaddition may be allowed for the substrates bearing a phenyl group as $R^3$ but the rate of the reaction would be slower than that described in i).

iii) The substrates bearing H or $CH_3$ as $R^3$ would be less reactive, due to the relatively lowered HOMO energy of the dipolarophile by the substituents.

The qualitative reactivity of **5** was in accordance with the tendencies mentioned above. When $R^3$=Ph on **5**, the reaction gave pyrazoline (**7f**), pyrazole (**8h**), and *N*-acetyl hydrazide (**11a**), roughly in the ratio of 1 : 2 : 2. On the other hand, none of cycloadducts could be isolated when $R^3$=H or $CH_3$, and *N*-acetyl hydrazide (**11b**) was only isolable product. The reaction of aldehyde hydrazones with $Pb(OAc)_4$ generally gave *N*-acetyl hydrazides in the absence of suitable dipolarophiles.[15)]

2-(Alkenyloxy)-1-naphthaldehyde arylhydrazones (**5**) gave better yields of cycloadducts (**8**), partly because of the ease of isolation from the reaction mixture. Whereas the cycloadducts, **8a**—**f** and **8h**, from 2-(alkenyloxy)benzaldehyde arylhydrazones are stable in the presence of an excess amount of $Pb(OAc)_4$, **8** from 2-(alkenyloxy)-1-naphthaldehyde aryhydrazones gave acetoxylated products (**9**) at position 4 under the same reaction conditions. Radical acetoxylation has been achieved wiht $Pb(OAc)_4$.[15b)] Thus, when **8f** was treated with an excess of $Pb(OAc)_4$ in refluxing chloroform for 3 h, the susceptible position in **8**, the $\alpha$-position of the ethers, was acetoxylated to give product (**9**). The acetoxyl group was easily displaced by the ethoxyl group, giving **10**, when **9** was recrystallized from ethanol.

## Experimental

*Measurements.* All the melting and boiling points are uncorrected. The IR spectra were recorded on a Hitachi 215 Infrared Spectrophotometer. The NMR spectra were measured on a Varian T-60A instrument using suitable solvents and TMS as an internal standard.

*Materials.* Lead tetraacetate (90.6%) was commerically available (Nakarai Chem. Co.,) and was used without further purification. The arylhydrazones of 2-(alkenyloxy)benzaldehydes (or 1-naphthaldehydes) (**5**) were prepared according to the method described in the preceding paper.[6c)]

*Reaction of Arylhydrazones (5) with Three Equivalents of Pb(OAc)$_4$. General Procedure*: A mixture of **5** (5.4 mmol) and $Pb(OAc)_4$ (7.97 g, 16.2 mmol) was stirred in chloroform (300 ml) for 6 h at room temperature. The insoluble material thus precipitated was filtered off using a Celite bed. The filtrate was mixed with water, and the mixture was filtered using the Celite bed. The organic layer was washed with water several times and dried over magnesium sulfate. Evaporation of the organic layer yielded a viscous oil, which solidified upon being scratched with a glass rod. Recrystallization from ethanol gave colorless needles of the cycloadducts (**8**). Concentration of the filtrate and subsequent chromatography on silica gel with chloroform gave an additional amount of needles (**8**). The yields and some physical data are given in Table 2.

*Reaction of 2-(3-Phenyl-2-propenyloxy)benzaldehyde* p-*Nitrophenylhydrazone with Pb(OAc)$_4$.* The reaction was carried out by the General Procedure. The reaction mixture was chromatographed (silica gel) with chloroform to give cycloadducts (**7h** and **8h**) and *N*-acetylated compound (**11a**) in 10, 21, and 17% yield, respectively. The spectral data for **7h** and **8h** are shown in Tables 1 and 2, respectively. The spectral data for **11a** (mp 114 °C from ethanol) was as follows: IR (Nujol): 3250 (NH), 1710 (CONH), and 1670 cm$^{-1}$ (CON). NMR ($CDCl_3$): $\delta$ 2.25 (s, 3H), 4.9 (d, 2H, $J$=6 Hz), 6.5—8.3 (m, 13H), and 10.2 (s, 1H).

*Reaction of 2-(3-Butenyloxy)benzaldehyde* p-*Nitrophenylhydrazone with* $Pb(OAc)_4$. The reaction was carried out by the General Procedure. An *N*-acetylated compound (**11b**) was obtained from the reaction mixture in 41% yield; mp 159 °C (from ethanol). IR (Nujol): 3200 (NH), 1700 (CONH), and 1670 cm$^{-1}$ (CON). NMR ($CDCl_3$): $\delta$ 2.7 (d, 3H, $J$=5 Hz), 3.3 (s, 3H), 5.5—5.8 (m, 2H), 6.7—7.0 (m, 2H), 8.0—9.3 (m, 8H), and 11.2 (s, 1H).

*An Equimolar Reaction of Arylhydrazones with* $Pb(OAc)_4$. A mixture of **5** (5.4 mmol) and $Pb(OAc)_4$ (2.66 g, 5.4 mmol) was stirred in chloroform for 6 h at room temperature. The reaction mixture was washed with water several times. The organic layer was dried over magnesium sulfate. Evaporation of the solvent yielded cycloadducts (**7**) in the yields shown in Table 1.

*Oxidation of 7f to 8f with* $Pb(OAc)_4$. A mixture of **7f** (1.0 g, 3.1 mmol) and $Pb(OAc)_4$ (1.37 g, 3.1 mmol) was stirred in chloroform for 6 h at room temperature. The reaction mixture was treated in a manner similar to the procedure described above to give **8f** in 76% yield.

*Oxidation of 7g to 8g with DDQ (2,3-Dichloro-5,6-dicyano-*p-*benzoquinone).* A mixture of **7g** (0.5 g, 1.3 mmol) and DDQ (0.29 g, 1.3 mmol) was heated to reflux in benzene (50 ml) for 12 h. The reaction mixture was washed with water and evaporation of the organic layer gave **8g**, 0.39 g (78%) (recrystallized from ethanol).

*Reaction of 8f with* $Pb(OAc)_4$. A mixture of **8f** (0.2 g, 0.65 mmol) and $Pb(OAc)_4$ (2.0 g, 4.1 mmol) was heated to reflux in chloroform (50 ml) for 3 h. The reaction mixture was treated in a manner similar to the General Procedure. Crystals obtained were shown to be 4-acetoxylated product (**9**) in 92% yield; IR (Nujol): 2230 (CN) and 1760 cm$^{-1}$ (COO). NMR (DMSO-$d_6$): $\delta$ 2.1 (s, 3H) and 7.0—8.6 (m, 9H). Found: C, 60.03; H, 3.25; N, 14.62%. Calcd for $C_{19}H_{12}N_4O_5$: C, 60.64; H, 3.21; N, 14.89%. Recrystallization of this compound from ethanol gave the corresponding 4-ethoxy derivative quantitatively; Found: C, 62.88; H, 3.94; N, 15.26%. Calcd for $C_{19}H_{14}N_4O_4$: C, 62.98; H, 3.89; N, 15.46%.

*Preparation of an Authentic Sample of 7d.* 2-(*p*-Chlorophenyl)-5-[2-(3-cyano-2-propenyloxy)phenyl]-2*H*-tetrazole (**12**) was prepared from the reaction of 2-(3-cyano-2-propenyloxy)benzaldehyde *p*-tolylsulfonylhydrazone[6a] with *p*-chlorobenzenediazonium chloride according to a method analogous to that of Ito *et al.*,[8] in 73% yield; mp 192—193 °C (decomp). IR (Nujol): 2230 cm$^{-1}$ (CN). Found: C, 60.43; H, 3.45; N, 20.69%. Calcd for $C_{17}H_{12}N_5OCl$: C, 60.45; H, 3.58; N, 20.73%. Pyrolysis of **12** at 200 °C for 3 h gave **7d** in 30% yield.

*Oxidation of 7d to 8d with DDQ.* A mixture of **7d** (1.0 g, 3.3 mmol) and DDQ (0.67 g, 3.3 mmol) was heated to reflux in benzene (50 ml) for 12 h. The reaction mixture was washed with water and evaporation of the organic layer gave **8d**, 0.58 g (58%) (recrystallized from ethanol).

## References

1) Presented in part at 44th National Meeting of the Chemical Society of Japan, Okayama, October 1981, Abstr. Vol. II, p. 495.

2) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).

3) a) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, **95**, 7301 (1973); K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *ibid.*, **95**, 7287 (1973); b) K. N. Houk, "Pericyclic Reacitions. II," ed by R. E. Lehr and A. P. Marchand, Academic Press, New York (1977); c) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," John Wiley and Sons, New York (1976),

4) a) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, **16**, 10 (1977); b) A. Padwa, *ibid.*, **15**, 123 (1976).

5) G. Schmidt and B. Laude, *Tetrahedron Lett.*, **1978**, 3727.

6) a) T. Shimizu, Y. Hayashi, Y. Nagano, and K. Teramura, *Bull. Chem. Soc. Jpn.*, **53**, 429 (1980); b) T. Shimizu, Y. Hayashi, K. Yamada, T. Nishio, and K. Teramura, *ibid.*, **54**, 217 (1981); c) T. Shimizu, Y. Hayashi, Y. Kitora, and K. Teramura, *ibid.*, **55**, 2450 (1982).

7) W. A. F. Gladstone, *J. Chem. Soc., Chem. Commun.*, **1969**. 179; W. A. F. Gladstone, J. B. Aylward, and R. O. C. Norman, *J. Chem. Soc., C*, **1969**, 2587.

8) S. Ito, Y. Tanaka, A. Kakehi, and K. Kondo, *Bull. Chem. Soc., Jpn.*, **49**, 1920 (1976).

9) R. Huisgen, M. Siedel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).

10) R. Grigg, J. Kemp, and N. Tompson, *Tetrahedron Lett.*, **1978**, 2827; R. Grigg and J. Kemp, *J. Chem. Soc., Chem. Commun.*, **1978**, 109; G. Le Fevre and J. Hamelin, *Tetrahedron Lett.*, **1978**, 4503; *Tetrahedron*, **36**, 887 (1980).

11) a) B. B. Snider, R. S. E. Conn, and S. Sealfon, *J. Org. Chem.*, **44**, 218 (1979); b) B. T. Gillis and F. A. Daniher, *ibid.*, **27**, 4001 (1962); c) E. Fahr and H. D. Rupp, *Angew. Chem., Int. Ed. Engl.*, **3**, 693 (1964).

12) G. Le Fevre, S. Sinbandhit, and J. Hamelin, *Tetrahedron*, **35**, 1821 (1979); G. Le Fevre and J. Hamelin, *Tetrahedron Lett.*, **1979**, 1757.

13) M. Bonadeo, C. De Micheli, and R. Gandolfi, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 939; G. Bianchi, R. Gandolfi, and C. De Micheli, *J. Chem. Res. (S)*, **1981**, 6; *J. Chem. Res. (M)*, **1981**, 0135.

14) J. Bastide, N. El Chandour, and O. Henri-Rousseau, and L. Aspart-Pascot, *Tetrahedron*, **30**, 3355 (1974); K. N. Houk, *J. Org. Chem.*, **43**, 3006 (1978); M. Joucla, F. Tonnard, D. Gree, and J. Hamelin, *J. Chem. Res. (M)*, **1978**, 2901; K. B. Lipkowitz, S. Scarpone, B. P. Mundy, and W. G. Bornmann, *J. Org. Chem.*, **44**, 486 (1979).

15) a) F. L. Scott and R. N. Butler. *J. Chem. Soc., C*, **1966**, 1202; b) R. N. Butler, F. L. Scott, and T. A. F. O'Mahony, *Chem. Rev.*, **73**, 93 (1973).