(2.0 M in cyclohexane; 4.0 mL, 0.008 mol). The resulting orange solution was allowed to warm to room temperature overnight and then was evaporated in vacuo. The resulting oily residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (2 × 50 mL), dried (Na_2SO_4), and then preadsorbed onto activity III basic Al_2O_3. Column chromatography over activity III basic Al_2O_3 (95:5 EtOAc–Et_3N) gave 0.62 g (56%) of **12** as a pale yellow solid: mp 204–205 °C; ^1H NMR ($CDCl_3$) δ 1.75 (s, 6 H), 2.0 (s, 6 H), 2.05 (s, 6 H), 6.9 (m, 4 H), ~7.6 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 149.2, 148.9, 148.6, 148.3, 129.9, 120.2 (2), 78.2, 75.2, 30.3, 17.4, 12.8; IR (KBr) 2990 (m), 1460 (m), 1380 (m), 1320 (s), 1200 (s), 1155 (s), 1090 (s), 830 (s), 800 (s), 780 (s), 750 (s) cm^{-1}; MS, *m/e* 342.2087 (calcd for $C_{24}H_{26}N_2$: 342.2076.

Anal. Calcd for $C_{24}H_{26}N_2$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.07; H, 7.69, N, 8.17.

1,4,7,10-Tetramethylchrysene (13). To a magnetically stirred solution of **12** (0.13 g, 0.38 mmol) and CH_2Cl_2 (25 mL) at 25 °C was added *m*-CPBA (0.11 g, 0.76 mmol). The resulting yellow solution was stirred for 2 h and then preadsorbed onto activity III neutral Al_2O_3. Chromatography over activity III neutral Al_2O_3 (hexane) gave 0.10 g (93%) of **13** as colorless crystals. Recrystallization from hexane–EtOH gave an analytical sample: mp 165–166 °C; ^1H NMR ($CDCl_3$) δ 2.75 (s, 6 H), 3.05 (s, 6 H), 7.35 (s, 4 H), 8.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 132.7, 131.9, 131.3, 130.9, 129.9, 128.2, 126.8, 126.0, 120.7, 26.0, 19.8; IR (KBr) 2980 (w), 1470 (m), 1460 (m), 1270 (m), 1240 (w), 1100 (w), 1040 (m), 830 (s), 815 (s), 745 (s), cm^{-1}.

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.62; H, 7.34.

17,18-Dimethyl-5,8,13,16-tetrahydrodibenzo[*b*,*k*]chrysene-5,16:8,13-diimine (15). This reaction was carried out as described for **10** by employing the following materials; **6** (2.5 g, 4.0 mmol), 2-methylisoindole[17] (**14**) (2.1 g, 16.0 mmol), THF (250 mL), and phenyllithium (1.70 M in cyclohexane, 4.80 mL, 7.98 mmol). The usual workup and chromatography gave 0.45 g (30%) of **15** as a light brown solid: mp 172–175 °C (dec); ^1H NMR ($CDCl_3$) δ 2.15 (s, 6 H), 5.00 (m, 2 H), 5.30 (m, 2 H), 6.90–7.70 (m, 12 H); IR (KBr) 2960 (m), 1420 (s), 1380 (s), 1185 (s), 1090 (s), 1010 (m), 940 (m), 820 (s), 735 (s), 695 cm^{-1}; UV (EtOH) λ_{max} 326, 302, 290, 253, 235 nm; MS, *m/e* 386.1783 (calcd for $C_{28}H_{22}N_2$: 386.1783).

Dibenzo[*b*,*k*]chrysene (16). To a magnetically stirred solution of **15** (0.10 g, 0.27 mmol) and CH_2Cl_2 (25 mL) at 25 °C was added *m*-CPBA (0.075 g, 0.54 mmol), resulting in an immediate bright yellow precipitate. The suspension was stirred for 1 h and then was filtered to afford 0.075 g (85%) of **16** as a bright yellow solid: mp 402–403 °C (lit.[15] mp 400 °C); IR (KBr) 3060 (m), 1280 (m), 960 (m), 900 (s), 885 (s), 820 (s), 740 (s), 720 (m) cm^{-1}. The UV spectrum was identical with that reported.[15]

17,18-Dimethyl-1,2,3,4,9,10,11,12-octafluoro-5,8,13,16-tetrahydrodibenzo[*b*,*k*]chrysene-5,16:8,13-diimine (18). This reaction was carried out in the same manner as for the preparation of **10** by employing the following materials: **6** (2.0 g, 0.0032 mol), 2-methyl-4,5,6,7-tetrafluoroisoindole[18] (**17**) (3.0 g, 0.015 mol), THF (200 mL), and phenyllithium (1.70 M in cyclohexane, 3.80 mL, 0.0064 mol). the usual workup and chromatography gave 0.73 g (43%) of **18** as a yellow solid: mp 305–306 °C; ^1H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 5.25 (m, 2 H), 5.70 (m, 2 H), 7.60 (s, 4 H); IR (KBr) 2990 (m), 1500 (s), 1490 (s), 1270 (s), 1100 (s), 1040 (s), 925 (m), 800 (s), 755 (s), 730 (s) cm^{-1}; UV (EtOH) λ_{max} 323, 298, 255 nm; MS, *m/e* 530.0987 (calcd for $C_{28}H_{14}N_2F_8$: 530.1029).

1,2,3,4,9,10,11,12-Octafluorodibenzo[*b*,*k*]chrysene (19). To a magnetically stirred solution of **18** (0.18 g, 0.339 mmol) and CH_2Cl_2 (25 mL) at 25 °C was added *m*-CPBA (0.094 g, 0.678 mmol), resulting in an immediate bright yellow precipitate. The suspension was stirred for 1 h and then was filtered to afford 0.12 g (75%) of **19** as a bright yellow solid. Recrystallization from xylene gave the analytical sample, mp >400 °C (evacuated tube sublimed at 400 °C); IR (KBr) 1685 (s), 1600 (s), 1505 (s), 1495 (s), 1425 (s), 1385 (m), 1355 (s), 1325 (m), 1000 (s), 890 (s), 810 (m), 675 (m) cm^{-1}; UV (EtOH) λ_{max} 310, 300, 289, 285 nm.

Anal. Calcd for $C_{26}H_8F_8$: C, 66.12; H, 1.71. Found: C, 66.08; H, 1.74.

Acknowledgment. This investigation was supported by PHS Grant CA-24422, awarded by the National Cancer Institute, DHEW, and in part by Grant CH-200 from the American Cancer Society and by Merck Sharp & Dohme Research Labs. We thank Dr. Catherine E. Costello (MIT) for the high-resolution mass spectra (National Institutes of Health Research Grant FR00317 from the Division of Research Facilities and Resources).

Registry No. **1**, 218-01-9; **3**, 85337-39-9; **5**, 84-59-3; **6**, 85337-31-1; **7**, 85337-32-2; **8**, 85337-33-3; **9**, 96-54-8; **10**, 85337-34-4; **11**, 930-87-0; **12**, 85337-30-0; **13**, 85337-35-5; **14**, 33804-84-1; **15**, 85337-36-6; **16**, 217-54-9; **17**, 38053-09-7; **18**, 85337-37-7; **19**, 85337-38-8; furan, 110-00-9.

---

(17) Zeeh, B.; Konig, K. H. *Synthesis* **1972**, 45.

(18) Priestley, G. M.; Warrener, R. N. *Tetrahedron Lett.* **1972**, 4295.

Preparation of Benzenetetracarboxylic Acids by the Cobalt-Catalyzed Carbonylation of Schiff Bases from Benzenedicarbaldehydes and Subsequent Oxidation

Tsunesuke Kajimoto* and Jiro Tsuji[1]

Basic Research Laboratories, Toray Industries, Inc., Kamakura, Kanagawa 248, Japan

Received June 1, 1982

Schiff bases (**3a–d** and **4a–c**), synthesized from benzenedicarbaldehydes (terephthalaldehyde and isophthalaldehyde) and primary amines (methylamine, ethylamine, butylamine, and aniline), were carbonylated in the presence of $Co_2(CO)_8$ under an elevated pressure at 200–290 °C to give dicarbonylated products, benzodipyrolediones (**5a–d**, **10a–c**, and **11a–c**), in high yields. 1,2,3,4-Benzenetetracarboxylic acid (prehnitic acid) and 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid) were prepared selectively by the oxidation of the benzodipyrolediones with nitric acid. Structural analysis of the benzodipyrolediones by NMR spectra and the mechanism of the carbonylation reaction are discussed.

Transition-metal carbonyl-catalyzed carbonylation reactions of organic compounds with nitrogen containing multiple bonds such as nitrile,[2] oxime[3], Schiff base,[4] hydrazone,[5] azo compound,[6] and nitro compound[7] have been

Table I. Carbonylation of the Schiff Bases 3 to the Benzodipyrolediones 5 and Phtalimidine 6

expt[a]	R	3[b]	catalyst[c]	solvent[d]	CO,[e] kg/cm²	temp, °C	time, h	yields[f] 5 (%)	6 (%)
1	Ph	**3a**[g]	$Co_2(CO)_8$[h]	C_6H_6	100	230	10	**5a** (67)	**6a** (5.5)
2	Ph	**3a**[g]	$Co_2(CO)_8$[h]	C_6H_6	150	230	10	**5a** (51)	**6a** (3.6)
3	Me	**3b**	$Co_2(CO)_8$	C_6H_6	50	200	1	**5b** (64)	
4	Me	**3b**	$Co_2(CO)_8$	C_6H_6	50	230	1	**5b** (96)	
5	Me	**3b**	$Co_2(CO)_8$	$PhCH_3$[i]	50	290	1	**5b** (96)	
6	Me	**3b**[j]	$Co_2(CO)_6(PPh_3)_2$	C_6H_6	50	230	1	**5b** (90)	
7	Me	**3b**	$Co_2(CO)_8$	C_6H_6	100	230	1	**5b** (78)	
8	Me	**3b**	$Co_2(CO)_8$	C_6H_6	100	230	10	**5b** (52)	
9	Me	**3b**	$Co_2(CO)_8$	C_6H_6	150	230	1	**5b** (89)	
10	Me	**3b**	$Co_2(CO)_8$[k]	C_6H_6	150	230	10	**5b** (37)	
11	Me	**3b**	$Co_2(CO)_8$, Py[l]	C_6H_6[i]	50	230	1	**5b** (0)	
12	Et	**3c**	$Co_2(CO)_8$	C_6H_6	50	230	1	**5c** (96)	
13	Et	**3c**	$Co_2(CO)_8$	C_6H_6	100	230	10	**5c** (65)	
14	*n*-Bu	**3d**	$Co_2(CO)_8$	C_6H_6	50	230	0.75	**5d** (96)	

[a] Experiments were performed in an autoclave (100 mL). [b] 2.0 g. [c] 0.4 g. [d] 30 mL. [e] Initial pressure at room temperature. [f] Yields are based on isolated material. [g] 2.5 g. [h] 1.0 g. [i] 25 mL. [j] 3.0 g. [k] 0.5 g. [l] $Co_2(CO)_8$ of 0.4 g and Py of 5.0 mL.

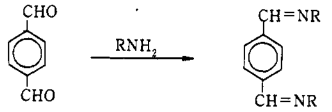
reported. However, only few synthetic applications of these reactions to polyfunctional compounds have been reported except carbonylation of dinitro compounds such as dinitrotoluene.[8] It is often observed that a catalytic reaction carried out with monofunctional compounds cannot be applied satisfactorily to the corresponding polyfunctional compounds. In fact, our attempted carbonylation reaction of bis(alkylazo)benzene did not give any dicarbonylated product expected to be formed from the result with azobenzene. In this paper we report the successful carbonylation reaction of bifunctional aromatic Schiff bases. We examined this reaction as a new preparative method of benzenetetracarboxylic acids, which are useful for the preparation of thermostable polymers and dyes. Benzenetetracarboxylic acids can be prepared by the oxidation of the corresponding polyalkylbenzenes, but the isolation of the latter from their isomers is not so easy.

Taking the fact that carbonyl group can be introduced cleanly at the ortho position by the carbonylation of aromatic Schiff bases into consideration, we examined the selective formation of 1,2,3,4-benzenetetracarboxylic acid (prehnitic acid) (**12**) and 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid) (**9**) from terephthalaldehyde (**1**) and isophthalaldehyde (**2**) by carbonylation of their corresponding Schiff bases and the subsequent oxidation of the dicarbonylated products.

Structural analysis of the products of the carbonylation reaction from NMR and IR spectra and probable mechanisms of the reaction are discussed.

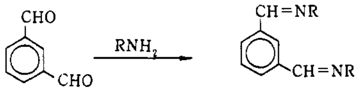
Results and Discussion

The Schiff bases (**3a–d** and **4a–c**) were prepared in nearly quantitative yields by the condensation reactions of benzenedicarbaldehydes (**1** and **2**) with aniline, methylamine, ethylamine, and butylamine in benzene or diethyl ester.



1

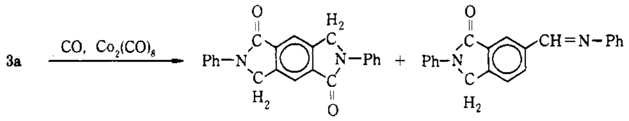
3a, R=Ph
b, R=Me
c, R=Et
d, R=*n*-Bu



2

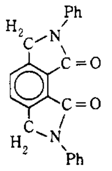
4a, R=Me
b, R=Et
c, R=*n*-Bu

In a stainless steel autoclave, *N,N'*-(*p*-phenylenedimethylidyne)dianiline (**3a**) was carbonylated in benzene by using $Co_2(CO)_8$ as a catalyst at 230 °C under pressure (170–260 kg/cm²) for 10 h to give 2,3,6,7-tetrahydro-2,6-diphenylbenzo[1,2-*c*:4,5-*c*']dipyrrole-1,5-dione (**5a**) and 2-phenyl-6-((phenylimino)methyl)phthalimidine (**6a**) in the yields as shown in Table I.



5a (67%) 6a (5.5%)

The isomeric benzodipyrroledione 7 was expected to be formed, but not obtained. The phthalimidine **6a** was



7

separated from **5a** by extraction with hot xylene. In common organic solvents such as acetone, ethanol, or chloroform, **5a** is scarcely soluble. In order to prepare more soluble derivatives, the Schiff bases from aliphatic amines were selected as a reactant in place of **3a**. The benzodi-

---

(1) Department of Chemical Engineering, Faculty of Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan.

(2) A. Rosenthal and J. Gervay, *Chem. Ind.* (*London*), 1623 (1963).

(3) A. Rosenthal, R. F. Astbury, and A. Hubschner, *J. Org. Chem.*, **23**, 1037 (1958).

(4) W. W. Prichard (Du Pont), U.S. Patent 2841591 (1958); *Chem. Abstr.*, **52**, 20197 (1958); S. Murahashi and S. Horiie, *J. Am. Chem. Soc.* **77**, 6403 (1955); **78**, 4816 (1956); S. Murahashi, S. Horiie, and T. Jo, *Bull. Chem. Soc. Jpn.*, **33**, 7881 (1960).

(5) A. Rosenthal and M. R. S. Weir, *J. Org. Chem.*, **28**, 3025 (1963).

(6) S. Murahashi and S. Horiie, *J. Am. Chem. Soc.*, **87**, 4816 (1965); *Bull. Chem. Soc. Jpn.*, **33**, 80 (1960).

(7) T. Kajimoto and J. Tsuji, *Bull. Chem. Soc. Jpn.*, **42**, 827 (1969); J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965).

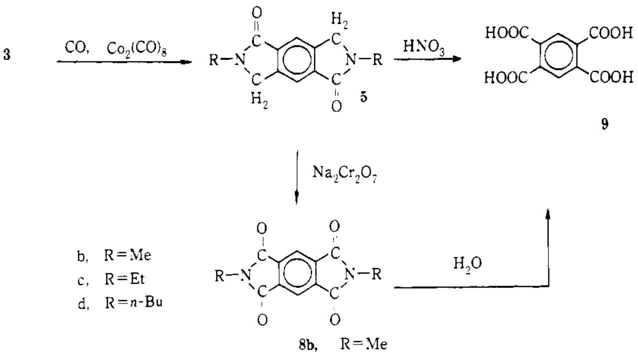
(8) V. I. Monov-Yuvenskii, *Chem. Abstr.*, **93**, 46094g (1980).

Table II. Oxidation of the Benzodipyrrolediones 5, 10, and 11 with Nitric Acid to the Benzenetetracarboxylic Acids 9 and 12

compd[a]	R	HNO_3, %	temp, °C	time, h	prodt	yield,[b] %
5b	Me	60	115	20	**9**	81
5b	Me	60	130	17	**9**	99
5b	Me	30	145	4	**9**	56
5b	*n*-Bu	30	130	4	**9**	99
10b	Et	30	140	4	**12**	92
11b	Et	30	140	4	**9**	95
10a + **11a**	Me	30	130	7	**9** + **12**	87
10b + **11b**	Et	30	130	5	**9** + **12**	85
10c + **11c**	*n*-Bu	30	130	5	**9** + **12**	92

[a] All experiments were performed in a sealed glass tube with **5** (0.5 g). [b] Yields are based on isolated material.

pyrrolediones **5b–d** were obtained by carbonylation of **3b–d** in high yields as shown in Table I.



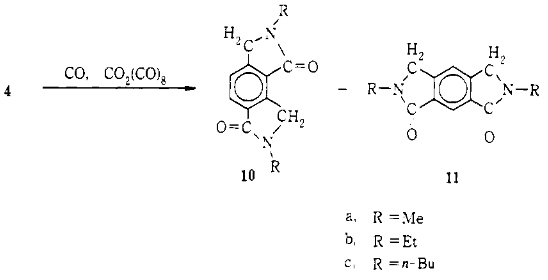
8b, R=Me

The carbonylation reaction of these Schiff bases from aliphatic amines to give **5** was almost completed in 1 h. When the reaction was continued for 10 h, the yield of **5** was decreased and resinous substance was formed as a byproduct. The carbonylation reaction proceeded smoothly at temperatures between 200 and 290 °C under initial pressure of carbon monoxide higher than 30 kg/cm^2. The initial pressure means the pressure applied to the autoclave at room temperature. When the reaction was carried out under an initial pressure between 100 and 150 kg/cm^2, no decomposition of the catalyst was observed, while in the reaction under the initial pressure of 50 kg/cm^2 the catalyst decomposed to form black powder. As the catalyst, $Co_2(CO)_6(PPh_3)_2$ was also as effective as $Co_2(CO)_8$, but $Fe_2(CO)_4(C_5H_5)_2$ was not effective.

Oxidation of **5** with 30% or 60% nitric acid at 115–145 °C in a sealed glass tube gave **9** in high yields as shown in Table II. Concentration of the reaction solution after the oxidation gave dihydrate of **9**, which was dehydrated to give **9** under reduced pressure.

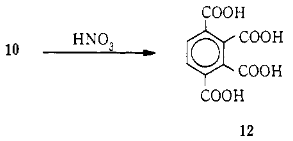
Oxidation with other oxidizing agents was tried. *N*,*N′*-Dimethylpyromellitic acid diimide (**8b**) was obtained by the reaction of **5b** with $Na_2Cr_2O_7$ in glacial acetic acid at 90 °C for 15 h in 96% yield. Hydrolysis of **8b** with hydrochloric acid in a sealed glass tube at 160 °C gave the dihydrate of **9** in 79% yield, and hydrolysis of **8b** with 30% KOH gave **9** in 59%. $KMnO_4$ was not an effective oxidizing agent of **5b**.

The Schiff bases **4a–c** were also reacted with carbon monoxide, and the benzodipyrrolediones **10a–c** and **11a–c** were obtained in high yields as shown in Table III. The main product was **10**, and the ratio of **10** to **11** became larger as the R group became larger: 2.5/1.0 for Me, 3.4–3.6/1.0 for Et, and 6.0–6.1/1.0 for *n*-Bu.



Separation of **10** from **11** was performed by extraction with proper solvents because there is a considerable difference in their solubilities in certain solvents. Chloroform was used for the extraction of **4a** from **10a**. For the extraction of **10b** from **11b**, ethanol was used successfully. Benzene was used for the separation of **10c** from **11c**.

Oxidation of **10** and **11** with 30% nitric acid in a sealed glass tube gave **12** and **9**, respectively, as shown in Table II.



The benzodipyrrolediones **5**, **10**, and **11** were identified by ^1H NMR and IR spectral data as shown in Table IV. The deshielding effect of the carbonyl group was taken into consideration in the assignment of chemical shift of the protons on the benzene ring and the methylene protons in the pyrrole ring. The configuration of carbonyl group is fixed by the benzopyrrole ring so that the effect of carbonyl group can be clearly analyzed as shown in Tables IV and V. The chemical shift of H_b of **10** is shifted 0.41–0.45 ppm downfield compared with that of H_a by the effect of one carbonyl group. The chemical shift of H_c of **11** is shifted 0.56–0.71 ppm downfield by the effect of two carbonyl groups. As for the chemical shift of the methylene proton, H_e of **10** is shifted 0.22–0.25 ppm downfield compared with that of H_d. The IR spectum of **10** shows two kinds of absorption at 1680–1690 cm^{-1} attributed to the two carbonyl groups.

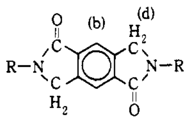
The probable mechanism of the carbonylation reaction of **3** is shown in Scheme I. At first, the ortho hydrogen

Table III. Carbonylation of the Schiff Bases 4 to the Benzodipyrrolediones 10 and 11

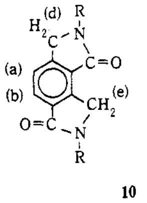
expt[a]	R	**4**[b]	catalyst[c]	solvent[d]	CO,[e] kg/cm^2	temp, °C	time, h	product[f]		total yield, %
								10 (%)	**11** (%)	
15	Me	**4a**	$Co_2(CO)_8$	C_6H_6[i]	50	230	1	**10a** (61)	**11a** (25)	86
16	Me	**4a**[g]	$Co_2(CO)_8$	C_6H_6	150	230	1	**10a**	**11a**	74
17	Me	**4a**	$Co_2(CO)_6(PPh_3)_2$	C_6H_6	100	230	1	**10a**	**11a**	60
18	Et	**4b**	$Co_2(CO)_8$	C_6H_6[i]	50	230	1	**10b** (61)	**11b** (18)	79
19	Et	**4b**[j]	$Co_2(CO)_8$[k]	C_6H_6	65	230	1	**10b** (70)	**11b** (20)	90
20	*n*-Bu	**4c**[l]	$Co_2(CO)_8$	C_6H_6	50	230	1	**10c** (82)	**11c** (13)	95

[a] Experiments were performed in an autoclave (100 mL). [b] 2.0 g. [c] 0.4 g. [d] 30 mL. [e] Initial pressure at room temp temperature. [f] Yields are based on isolated material. [g] 3.0 g. [h] 0.5 g. [i] 25 mL. [j] 5.0 g. [k] 0.8 g. [l] 2.5 g.

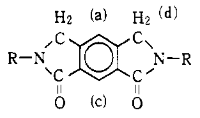
Table IV. ^{1}H NMR and IR Spectra of the Benzodipyrolediones 5, 10, and 11



5



10



11

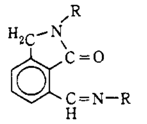
compd	R	H_a	H_b	H_c	H_d	H_e	R	IR (KBr), cm^{-1} C=O
		NMR (CDCl$_3$), ppm, multiplicity, area						
5b	Me		7.73 s, 2 H		4.39 s, 4 H		3.20, s, 6 H	1680
5c	Et		7.68, s, 2 H		4.35, s, 4 H		3.66, q, 4 H; 1.26, t, 6 H	1680
5d	*n*-Bu		7.90, s, 2 H		4.48, s, 4 H		3.68, t, 4 H; 2.0-1.0, m, 8 H; 0.98, t, 6 H	1680
10a	Me	7.33, d, 1 H	7.78, d, 1 H		4.39, s, 2 H	4.62, s, 2 H	3.11, s, 3 H; 3.14, s, 3 H	1690, 1670
10b	Et	7.53, d, 1 H	7.94, d, 1 H		4.51, s, 2 H	4.73, s, 2 H	3.71, q, 2 H; 3.70, q, 2 H; 1.29, t, 6 H	1690, 1670
10c	*n*-Bu	7.34, d, 1 H	7.77, d, 1 H		4.38, s, 2 H	4.63, s, 2 H	3.56, t, 2 H; 3.58, t, 2 H; 2.0-1.0, m, 8 H; 0.94, t, 6 H	1690, 1670
11a	Me	7.28, s, 1 H		7.98, s, 1 H	4.34, s, 4 H		3.14, s, 1 H	1680
11b	Et	7.59, s, 1 H		8.14, s, 1 H	4.50, s, 4 H		3.71, q, 4 H; 1.31, t, 6 H	1680
11c	*n*-Bu	7.34, s, 1 H		8.02, s, 1 H	4.34, s, 4 H		3.55, t, 4 H; 2.0-1.0, m, 8 H; 0.94, t, 6 H	1680

Table V. Shielding Effects of Carbonyl Group on the Chemical Shifts of Nearby Protons in the Benzodipyrolediones 10 and 11

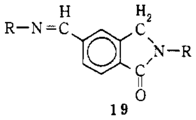
R	observed differences of chemical shift, ppm $H_b - H_a$ in 10	$H_c - H_a$ in 11	$H_e - H_d$ in 10
Me	0.45	0.70	0.23
Et	0.41	0.56	0.22
n-Bu	0.44	0.71	0.25

on benzene is substituted by cobalt to give a Co–phenyl complex 13 and HCo(CO)$_4$. Related ortho-substitution reactions have been reported for other metal complexes.[9] Insertion of carbon monoxide into the Co–phenyl bond gives the acyl complex 14, which is further converted to the monocarbonylated product, 6 and Co$_2$(CO)$_8$ by the reaction with HCo(CO)$_4$. Successive abstraction of protons from the ortho position with respect to another CH=NR group and insertion of carbon monoxide gives the acyl complex 17. Further reaction of 17 with HCo(CO)$_4$ gives the dicarbonylated product 5 and Co$_2$(CO)$_8$. The fact that 7 was not obtained indicates that the formation of another complex 15 from 6 seems to be inhibited by steric hindrance.

In the carbonylation reaction of 4, formation of two kinds of monocarbonylated products, 18 and 19, are expected. One of the dicarbonylated products, 10, is produced from both 18 and 19 as a main product, and another dicarbonylated product, 11, is only produced from 19 as a byproduct. The fact that the ratio of 10 to 11 became larger as the R group became larger is interesting, but the

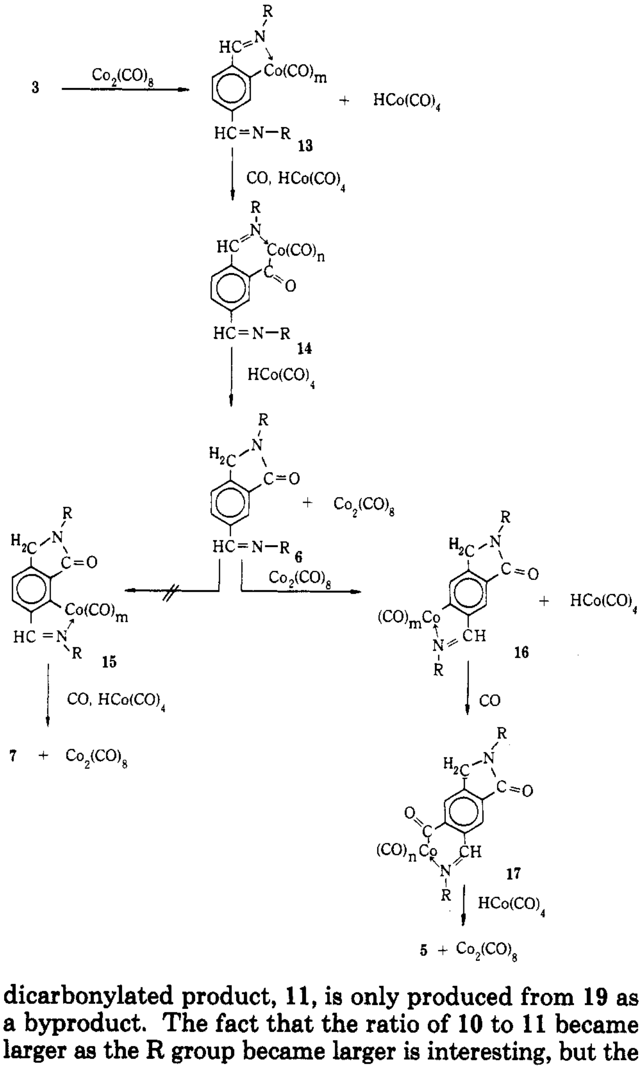


18



19

Scheme I



---

[9] P. E. Baikie and O. S. Mills, *Chem. Commun.*, 707 (1966); A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, **87**, 3273 (1965); J. M. Thompson and R. F. Heck, *J. Org. Chem.*, **40**, 2667 (1975).

reason is not clear at present.

In conclusion, the present results present a new preparative method of benzenepolycarboxylic acids from benzenedicarbaldehydes by means of the carbonylation reaction of aromatic Schiff bases to introduce a new substituent group on benzene ring.

Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra were taken on a Shimazu IR-27 spectrometer and a Hitachi EPI-S infrared spectrometer and ^{1}H NMR spectra on a Varian A-60 spectrometer.

Materials. Commercially available carbon monoxide of 99.78% purity was used. $Co_2(CO)_8$ was prepared from cobalt hydroxide.[10] $Co_2(CO)_6(PPh_3)_2$ was prepared from $Co_2(CO)_8$.[11] Benzene, toluene, and xylene were dried with sodium metal and distilled before use. Terephthalaldehyde and isophthalaldehyde were prepared by the known procedures.[12] Methylamine and ethylamine were prepared from their hydrochlorides and stored in glass tubes. Butylamine and aniline were commercial grade and purified by distillation before use. Nitric acid and $Na_2Cr_2O_7$ were commercial grade.

***N*,*N'*-(*p*-Phenylenedimethylidyne)dianiline (3a).** To a solution of 1 (5.4 g, 40 mmol) in ethyl ether (150 mL) was added aniline (7.5 g, 81 mmol) dropwise. The reaction mixture was stirred for 1 h and then cooled in ice. The precipitate was collected by filtration, washed with ethyl ether, and dried in vacuo to give **3a** (10.3 g, 36 mmol, 90%): mp 162–163 °C; IR (KBr pellet) 1620, 1585, 1490, 840, 780, 705 cm^{-1}. Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.69; N, 9.85. Found: C, 84.35; H, 5.73; N, 9.76.

***N*,*N'*-(*p*-Phenylenedimethylidyne)bis(methylamine) (3b).** The solution of 1 (10 g, 74.5 mmol) in 100 mL of benzene was cooled in ice to 5 °C, and excess methylamine was bubbled into the solution. The solution was allowed to stand for 2 h at room temperature, and water was removed from the solution by azeotropic distillation with benzene. Further evaporation of benzene from the solution gave **3b** (11 g, 68.8 mmol, 92.1%): mp 92 °C; IR (KBr pellet) 3000, 2800, 1640, 995, 930, 805 cm^{-1}; NMR ($CDCl_3$) δ 3.51 (d, 6, $|J_{H,CH_3}| = 1.5$ Hz), 7.68 (s, 4 H), 8.25 (m, 2 H). Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55, N, 17.49. Found: C, 74.89; H, 7.57; N, 17.20.

***N*,*N'*-(*p*-Phenylenedimethylidyne)bis(ethylamine) (3c).** Gaseous ethylamine was made to react with 1 (10 g, 74.5 mmol) by the same method as in the preparation of **3b** to give **3c** (13 g, 69.1 mmol, 92.8%): mp 51 °C; IR (KBr pellet) 2820, 1630, 980, 910, 860 cm^{-1}; NMR ($CDCl_3$) δ 1.31 (t, 6 H, $|J_{CH_2,CH_3}| = 7.0$ Hz), 3.67 (d of q, 4 H, $|J_{H,CH_2}| = 1.5$ Hz), 7.62 (s, 4 H), 8.5 (t, 2 H). Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 75.81; H, 8.56; N, 14.51.

***N*,*N'*-(*p*-Phenylenedimethylidyne)bis(*n*-butylamine) (3d).** To a solution of 1 in benzene was added butylamine dropwise, and water was removed by azeotropic distillation. Further distillation under reduced pressure afforded **3d** in nearly quantitative yield: bp 143 °C (0.03 mm); IR (neat) 2950, 2840, 1640, 995, 840 cm^{-1}. Anal. Calcd for $C_{16}H_{24}N_2$: C, 78.63; H, 9.90; N, 11.46. Found: C, 78.34; H, 9.93; N, 11.75.

Carbonylation of 3a. In a stainless steel 100-mL autoclave **3a** (2.5 g, 8.79 mmol), $Co_2(CO)_8$ (1.0 g, 2.92 mmol), and benzene (30 mL) were added. After the atmosphere was replaced with N_2, CO was introduced up to the pressure of 100 kg/cm^2 and the autoclave was heated to 230 °C and kept at that temperature for 10 h. The autoclave was cooled to room temperature, and the gas was purged to give precipitates in benzene. The precipitates were collected by filtration, and the solid mixture was extracted with hot xylene to give **2-phenyl-6-((phenylimino)methyl)phthalimidine (6a)** (0.15 g, 0.48 mmol, 5.5%) from xylene: mp 218–219 °C; IR (KBr pellet) 1690, 1620, 1605, 1595, 1500, 1395, 1190, 780, 755, 705, 700 cm^{-1}. Calcd for $C_{21}H_{16}N_2O$: C, 80.95; H, 5.16; N, 8.97. Found: C, 80.97; H, 5.21; N, 8.97. The remainder of the extraction with xylene was washed with concentrated hydrochloric acid (ca. 20 mL) and then with water (20 mL) and dried to give white **2,3,6,7-tetrahydro-2,6-diphenylbenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,5-dione (5a)** (2.0 g, 5.88 mmol, 66.8%): mp >250 °C; IR (KBr pellet) 1690, 1605, 1495, 1400, 890, 770, 720, 700 cm^{-1}. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63, H, 4.74; N, 8.23. Found: C, 77.51; H, 4.82; N, 8.32.

2,3,6,7-Tetrahydro-2,6-dimethylbenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,5-dione (5b). In a 500-mL autoclave **3b** (2 g, 12.5 mmol), $Co_2(CO)_8$ (0.4 g, 1.20 mmol), and benzene (30 mL) were added, and CO was introduced to a pressure of 50 kg/cm^2. The autoclave was heated at 230 °C for 1 h and cooled to room temperature. The gas was purged and the precipitates were collected by filtration to give a benzene solution and grayish solid. The benzene solution was concentrated to give **5b** (0.31 g, 1.43 mmol, 12%). The grayish solid was extracted with hot ethanol to give black powder of cobalt (0.17 g) and **5b** (2.27 g, 10.5 mmol, 84%) from ethanol. Total yield of **5b** was 96%; mp 233–234 °C; NMR see Table IV; IR (KBr pellet) 1680, 1490, 1270, 1210, 1120, 1160, 760, 705 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.71; H, 5.56; N, 13.22.

2,3,6,7-Tetrahydro-2,6-di-*n*-butylbenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,5-dione (5d). **3d** (2.0 g 7.81 mmol), $Co_2(CO)_8$ (0.5 g, 1.46 mmol) in benzene (25 mL), and CO (50 kg/cm^2) were allowed to react at 230 °C for 45 min. Concentration of the benzene solution obtained and extraction of the residue with ethanol gave **5d** (2.25 g, 7.49 mmol, 96%); mp 210–211 °C; NMR see Table IV; IR (KBr pellet) 1680, 1480, 1305, 1225, 760 cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 71.90% H, 8.17; N, 9.35.

Carbonylation of 4a. **4a** (2.0 g, 12.5 mmol), $Co_2(CO)_8$ (0.4 g, 1.20 mmol) in benzene (25 mL), and CO (50 kg/cm^2) were allowed to react at 230 °C for 1 h to give precipitates that were extracted with hot ethanol. Concentration of the ethanolic solution gave pale yellow crystals (2.33 g), which were extracted with $CHCl_3$ to give **2,3,7,8-tetrahydro-2,7-dimethylbenzo[1,2-*c*:3,4-*c'*]dipyrrole-1,6-dione (10a)** (1.66 g, 7.68 mmol, 61%) from $CHCl_3$: mp 199–201 °C; NMR see Table IV; IR (KBr pellet) 1690, 1670, 1495, 780, 760, 680, cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.74; H, 5.51; N, 13.23.

The residue of the extraction with $CHCl_3$ was **2,3,5,6-tetrahydro-2,6-dimethylbenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,7-dione (11a)** (0.67 g, 3.10 mmol, 25%): mp 269–271 °C; NMR see Table IV; IR (KBr pellet) 1690, 1480, 1430, 1250, 1140, 1040, 760, 705, 680 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59: N, 12.96. Found: C, 66.72% H, 5.54; N, 13.18.

Carbonylation of 4b. **4b** (2.0 g, 7.81 mmol), $Co_2(CO)_8$ (0.4 g, 1.20 mmol) in benzene (25 mL), and CO (50 kg/cm^2) were allowed to react at 230 °C for 1 h. The precipitated product was collected by filtration, washed with benzene (ca. 5 mL), and dissolved in hot ethanol. Cobalt metal powder was filtered off from the ethanolic solution. The ethanolic solution was concentrated to give white precipitates of **2,3,5,6-tetrahydro-2,6-diethylbenzo[1,2*c*:4,5-*c'*]dipyrrole-1,7-dione (11b)** (0.47 g, 1.92 mmol, 18.1%): mp 199–200 °C; NMR see Table IV; IR (KBr pellet) 1680, 1440, 1280, 1250, 900, 800, 760, 720, 680 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.79; H, 6.72; N, 11.59.

The benzene filtrate obtained above was concentrated to give precipitates of **2,3,7,8-tetrahydro-2,7-diethylbenzo[1,2-*c*:3,4-*c'*]dipyrrole-1,6-dione (10b)** (1.58 g, 6.47 mmol, 60.9%); mp 159–161 °C. NMR see Table V; IR (KBr pellet) 1690, 1670, 1470, 1420, 1310, 1240, 1070, 840, 805, 770, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 1147. Found: C, 68.53; H, 6.71; N, 11.59.

Carbonylation of 4c. **4c** (2.5 g, 9.80 mmol) was carbonylated by the same method as applied to **4b** to give **2,3,5,6-tetrahydro-2,6-di-*n*-butylbenzo[1,2-*c*:4,5-*c'*]dipyrrole-1,7-dione (11c)** (0.39 g, 1.30 mmol, 13%) and **2,3,7,8-tetrahydro-2,7-di-*n*-butylbenzo[1,2-*c*:3,4-*c'*]dipyrrole-1,6-dione (10c)** (2.58 g, 7.92 mmol, 81.2%).

11c: mp 231–232 °C; NMR see Table V; IR (KBr pellet) 1680, 1480, 1410, 1260, 1090, 780, 710, 680 cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 71.75; H, 7.97; N, 9.39.

---

[10] G. Kato, S. Wakamatsu, and H. Ishihara (Ajinomoto Co.), Japanese Patent Tokkosho 35-4315 (1960).

[11] W. Hieber and W. Freyer, *Chem. Ber.* 91, 1230 (1958).

[12] "Organic Syntheses", Wiley, New York, 1956, Collect. Vol. 3, p 788.

10c: mp 61.5 °C (from petroleum ether); NMR see Table IV; IR (KBr pellet) 1690, 1670, 1440, 840, 780, 760, 680 cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 72.02; H, 8.05; N, 9.32.

Oxidation of 5, 10, and 11 with Nitric Acid. Oxidation was carried out by heating **5**, **10**, or **11** together with excess 30–60% nitric acid in a sealed unit such as the glass tube or the autoclave at 115–145 °C for several hours. The sealed unit was cooled to room temperature and opened, and then the reaction mixture was freed from nitric acid by distillation under reduced pressure to give **12** or dihydrate of **9** as residue.

Preparation of 9 from 5b. **5b** (0.5 g, 2.31 mmol) was sealed in a glass tube together with 30% nitric acid (10 mL), and the tube was heated at 115 °C for 20 h. The reaction mixture was concentrated under reduced pressure to give the dihydrate of **9** (0.55 g, 1.88 mmol, 81%) as white crystals; mp >250 °C (lit.[13] mp 273 °C). The IR spectrum was identical with that of an authentic sample. Anal. Calcd for $C_{10}H_{10}O_{10}$: C, 41.39; H, 3.47. Found: C, 41.39; H, 3.48.

Preparation of 9 from 5d. **5d** (0.5 g, 1.7 mmol) was treated with 30% nitric acid (10 mL) at 130 °C for 4 h to give the dihydrate of **9** (0.481 g, 1.7 mmol, 99%).

Preparation of 12 from 10b. **10b** (0.75 g, 3.1 mmol) was sealed in a glass tube together with 30% nitric acid (10 mL) and heated at 140 °C for 4 h. **12** (0.72 g, 2.8 mmol, 92%) was obtained as white crystals; mp 236–237 °C (lit.[14] mp 236 °C). The IR spectrum was identical with that of an authentic sample. Anal. Calcd. for $C_{10}H_6O_8$: C, 47.26; H, 2.38. Found: C, 47.08; H, 2.57.

Preparation of 9 from 11b. **11b** (0.5 g, 2.0 mmol) was oxidized with nitric acid to give dihydrate of **9** (0.54 g, 1.86 mmol, 92%).

Oxidation of 5b to 8b by $Na_2Cr_2O_7$ and Acid and Alkaline Hydrolysis of 8b to 9. A mixture of **5b** (2.0 g, 2.31 mmol) and glacial acetic acid (30 mL) was heated at 90 °C, and $Na_2Cr_2O_7$ (5.0 g) was added in a small portion with stirring in 1 h. Heating at 90 °C was continued for 14 h, and then the mixture was cooled to room temperature to precipitate white needles (1.72 g) of **8b**. Concentration of the filtrate and dilution with water gave 0.3 g of **8b**. Total amount of **8b** was 2.02 g (8.85 mmol, 95.7%); mp >250 °C. The IR spectrum was identical with that of an authentic sample. Anal. Calcd for $C_{12}H_8N_2O_4$: C, 59.02; H, 3.30; N, 11.47. Found: C, 58.83; H, 3.41; N, 11.46.

A mixture of **8b** (0.7 g, 3.07 mmol) and 36% hydrochloric acid (10 mL) was heated in a sealed glass tube at 160 °C for 10 h to give 0.7 g (2.41 mmol, 78.5%) of the dihydrate of **9** by concentration of the reaction solution. The IR spectrum was identical with that of an authentic sample.

A mixture of **8b** (2.0 g, 8.76 mmol) and 30% KOH solution (30 mL) was heated under reflux and then neutralized with concentrated hydrochloric acid. The solution was concentrated, and the residue was extracted twice with hot EtOH, which was further concentrated to give the dihydrate of **9** (1.5 g, 5.17 mmol, 59%).

Registry No. 1, 623-27-8; **2**, 626-19-7; **3a**, 14326-69-3; **3b**, 41464-83-9; **3c**, 72891-08-8; **3d**, 30862-11-4; **4a**, 85067-98-7; **4b**, 85067-99-8; **4c**, 85068-02-6; **5a**, 19048-38-5; **5b**, 85067-95-4; **5c**, 85067-97-6; **5d**, 85067-96-5; **6a**, 85067-94-3; **8b**, 26011-79-0; **9**, 89-05-4; **10a**, 23966-19-0; **10b**, 85068-01-5; **10c**, 85068-04-8; **11a**, 23966-18-9; **11b**, 85068-00-4; **11c**, 85068-03-7; **12**, 476-73-3; $Co_2(CO)_8$, 10210-68-1; aniline, 62-53-3; methylamine, 74-89-5; ethylamine, 75-04-7; butylamine, 109-73-9.

---

[13] H. Meyer and K. Steiner, *Monatsh. Chem.*, **35**, 391 (1913).

[14] H. Bamford and J. L. Simonsen, *J. Chem. Soc.*, **97**, 1909 (1910).

A Novel Reaction Type Promoted by Aqueous Titanium Trichloride. Synthesis of Allylic Pinacols

Angelo Clerici* and Ombretta Porta*

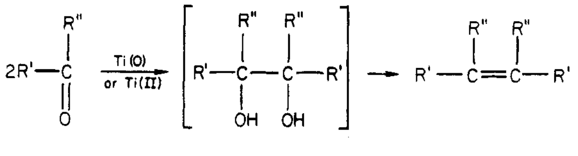
Dipartimento di Chimica del Politecnico, 20133 Milano, Italy

Received August 26, 1982

Electron-withdrawing substituted carbonyl compounds which are allowed to react with 2 equiv of aqueous titanium trichloride selectively add to the carbonyl carbon atom of α,β-unsaturated aldehydes. Highly functionalized allylic pinacols are obtained in good yields under very simple experimental conditions. The fundamental role played by the titanium(III) ion is discussed.

Low-valent titanium species such as Ti(0) or Ti(II), prepared by reduction of anhydrous titanium trichloride with either lithium aluminum hydride[1] or reactive metals,[2–4] efficiently induce reductive coupling of carbonyl compounds to olefins, diols being the reaction intermediates (Scheme I).

Scheme I



For some time, now, we have been carrying out investigations regarding the reducing properties of titanium trichloride in aqueous acidic[5,6] or basic[7] solution. The Ti(III) species, certainly a milder reducing agent, has no effect in aqueous acidic medium ($E° = -0.1$ V) on aliphatic and aromatic ketones and aldehydes but easily[5,6] couples carbonyl compounds **1**, activated toward reduction by an electron-withdrawing group, to the corresponding symmetrical diols **3** (Scheme II, eq 1).

Next[6] we have observed that an interesting mixed pinacol reaction takes place between **1** and simple aldehydes (Scheme II, eq 2) or ketones (Scheme II, eq 3), affording the mixed diols **4** and **5** in very good yields.

All the reactions in eq 1–3 can be schematically shown to involve a common radical intermediate, **2**. Radicals of this type[9] enjoy a particular stabilization, being simulta-

---

[1] McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708.

[2] Tyrlik, S.; Wolochowicz, I. *Bull. Soc. Chim. Fr.* **1973**, 2147.

[3] Nakuiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041.

[4] McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255.

[5] Clerici, A.; Porta, O. *Tetrahedron* **1982**, *38*, 1293.

[6] Clerici, A.; Porta, O. *J. Org. Chem.* **1982**, *47*, 2852.

[7] Clerici, A.; Porta, O. *Tetrahedron Lett.* **1982**, *23*, 3517.

[8] Clerici, A.; Porta, O., unpublished results.

[9] Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.

0022-3263/83/1948-1690$01.50/0 © 1983 American Chemical Society