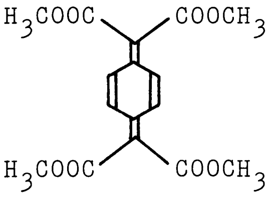
CHEMISTRY LETTERS, pp. 517-520, 1982.

SYNTHESES AND HOMOPOLYMERIZATION OF 7,8-DIALKOXYCARBONYL-7,8-DICYANOQUINODIMETHANES

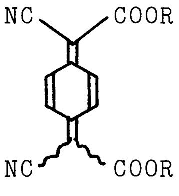
Shouji IWATSUKI,* Takahito ITOH, Katsumi NISHIHARA,
and Hidehiko FURUHASHI
Department of Chemical Research for Resources, Faculty of Engineering,
Mie University, Kamihama-cho, Tsu 514

7,8-Dimethoxycarbonyl-7,8-dicyanoquinodimethane and 7,8-diethoxycarbonyl-7,8-dicyanoquinodimethane were prepared successfully as novel compounds. These two compounds homopolymerized readily under thermal, radical, and anionic conditions except for cationic one. Moreover, weak bases such as triethylamine, pyridine, and pyrrolidine were found to induce the homopolymerization.

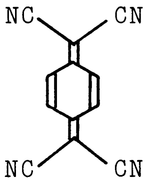
In the previous studies on the polymerization behaviors of a series of quinodimethane and quinone derivatives$^{1-5)}$ with strong electron accepting character, it was found that 7,7,8,8-tetramethoxycarbonylquinodimethane$^{3)}$ (1) reacts in an amphoteric fashion. 7,8-Dimethoxycarbonyl-7,8-dicyanoquinodimethane (2a) and 7,8-diethoxycarbonyl-7,8-dicyanoquinodimethane (2b) were expected to manifest an intermediate property between 1 and 7,7,8,8-tetracyanoquinodimethane (3). They had not been synthesized so far. In this letter, we describe the syntheses and polymerization of 2a and 2b.



1

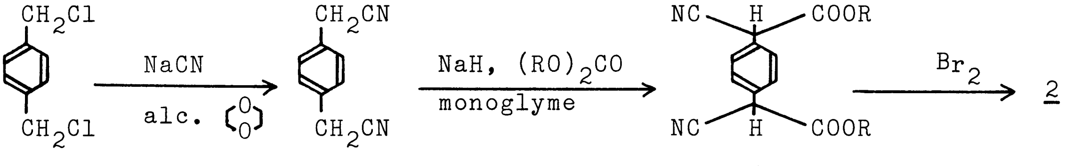


2 a: R=Me
b: R=Et



3

2a and 2b were prepared successfully in the following procedure:



4 5 6 a: R=Me
b: R=Et

p-Xylylene dicyanide (5), melting at 97-98 °C (lit,6) 98 °C), was prepared in 75 % yield by treating the *p*-xylylene dichloride (4) with sodium cyanide in aqueous ethanol-dioxane according to the procedure of Sandman and Garito.7) 6a, melting at 131-133 °C (lit,8) 133.5-135.6 °C; yield 65 %), was obtained in 60 % yield by treating 5 with dimethyl carbonate in monoglyme according to the method of Dejongh et al..8) 6b, melting at 77-80 °C, was obtained in 54.0 % yield after recrystallization from methanol by treating diethyl carbonate instead of dimethyl carbonate, bp 205 °C/0.3 mmHg; IR(KBr) 2250 and 1740 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$): δ1.30 (6H, t, J=7Hz), 4.32 (4H, q, J=7Hz), 4.85 (2H, s), and 7.62 (4H, s). 2a was obtained as follows: Finely powdered 6a (2g, 7.45 mmol) was suspended in 600 ml of water, and water containing 1.19 g (7.45 mmol) of bromine in 100 ml of water was added dropwise. The mixture turned yellow gradually. After stirring for 15 hr, the yellow product was separated from the solution by filtration, washed well with water and dried (under vacuum). The product was recrystallized from ethyl acetate, yield: 53.3 %; mp 252 °C dec; IR(KBr) 2220, 1750, 1720, and 1550 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$): δ4.00 (3H, s), 7.58 (2H, d, J=10Hz), and 8.62 (2H, d, J=10Hz); UV (CH_2Cl_2): 397 nm (ε29000); Found: C, 62.20; H, 3.50; N, 10.30 %. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.20; H, 3.73; N, 10.37 %. 2b was prepared in a similar procedure as above and recrystallized from isopropyl ether, yield: 20 %;mp 222 °C; IR(KBr) 2200, 1750, 1705, and 1550 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$): δ1.40 (6H, t, J=7Hz), 4.43 (4H, q, J=7Hz), 7.55 (2H, d, J=10Hz), and 8.58 (2H, d, J=10Hz); UV (C_6H_6): 403 nm (ε49000); Found: C, 64.32; H, 4.82; N, 9.43 %. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.74; N, 9,39 %. Both 2a and 2b can exhibit geometrical isomerism such as *cis* and *trans* (or *syn* and *anti*) forms. Since two kinds of ester-cabonyl group were observed in IR spectra of 2a (1750 and 1720 cm^{-1}) and 2b (1750 and 1705 cm^{-1}), 2a and 2b might be the mixture of both isomers. At the moment, it was impossible to distinguish their isomers on the basis of their IR and ^{1}H NMR spectra.

In order to estimate an electron accepting power (electron affinity) of 2a and 2b, the absorption spectrum of charge-transfer transition between hexamethylbenzene (HMB) and 2a or 2b was measured in benzene at room temperature and the absorption maximum, λmax, was 506 or 495 nm, respectively. The charge-transfer transition between HMB and 3 appears at 580 nm. The charge-transfer absorption band of the complex between HMB and 1 appears not as a definite peak, but as shoulder (an increase in intensity) at the longer wavelength side of the absorption band of 1. In the comparison of these peak positions, it can be seen that electron accepting characters of 2a and 2b are intermediate between 1 and 3. Electron affinities of 2a and 2b could be calculated numerically to be of 2.39 and 2.17 eV, respectively, by using the following equation9): $h\nu_{CT}=Ip-Ea+C$ and 2.48 eV10) for *p*-chloranil.

Tables 1 and 2 summarize the results of homopolymerization of 2a and 2b, respectively. The products were obtained as white powder. The homopolymer of 2a is insoluble in benzene, acetone, and methanol, swollen in chloroform, N,N-dimethylformamide, and dimethylsulfoxide, and soluble only in sulfuric acid. That of 2b is insoluble in isopropyl ether, methanol, and *n*-hexane and soluble in chloroform, acetone, and tetrahydrofuran.

Table 1. Homopolymerization of 7,8-Dimethoxycarbonyl-7,8-dicyanoquinodimethane (2a) in Dichloromethane[a)]

Run no	2a mg	Catalyst		Time, hr	Temp, °C	Conv, %	η_{sp}/C[b)] $dl \cdot g^{-1}$
1	100.1	—	—	3.0	60	38.8	0.46
2	149.9	AIBN[c)]	0.006 mmol	0.5	60	90.0	0.26
3	99.6	$BF_3 \cdot OEt_2$	0.1 ml	21.8	0	0	—
4	96.3	*n*-BuLi[d)]	one drop	0.5	0	82.5	0.10
5	80.2	Pyridine	0.011 mmol	0.5	0	54.0	0.21
6	100.0	Et_3N	0.006 mmol	0.5	0	100	0.37
7	99.9	Pyrrolidine	0.016 mmol	0.5	0	100	0.34

a) Solvent: 20 ml. Precipitant: methanol. Under nitrogen.

b) Solvent: concentrated H_2SO_4. At 40 °C.

c) AIBN: 2,2'-azobisisobutyronitrile.

d) *n*-Butyllithium solution in benzene.

Table 2. Homopolymerization of 7,8-Diethoxycarbonyl-7,8-dicyanoquinodimethane (2b) in Tetrahydrofuran[a)]

Run no.	2b mg	Catalyst		Time, hr	Temp, °C	Conv, %	$\overline{Mn}$[b)]
1	99.6	—	—	2.0	60	78.2	5000
2	99.5	AIBN	0.007 mmol	2.0	60	55.7	3800
3	100.0	$BF_3 \cdot OEt_2$	0.1 ml	0.5	0	0	—
4	100.0	*n*-BuLi	one drop	0.5	0	84.5	4300
5	49.5	Pyridine	0.005 mmol	0.5	0	88.5	4200
6	49.6	Et_3N	0.005 mmol	0.5	0	46.4	3000
7	49.4	Pyrrolidine	0.004 mmol	0.5	0	100	3700

a) Solvent: 10 ml for run no. 1-4 and 5 ml for run no. 5-7. Precipitant: isopropyl ether. Under nitrogen.

b) Measured by vapor pressure osmometer. Solvent: chloroform.

Table 3. Homopolymerization of 7,7,8,8-Tetramethoxycarbonylquinodimethane (1) in Tetrahydrofuran[a)]

Run no.	1 mg	Catalyst		Time, hr	Temp, °C	Conv, %
1	51.9	Pyridine	0.005 mmol	0.5	0	0[b)]
2	56.4	Et_3N	0.005 mmol	0.5	0	0[b)]
3	41.0	Pyrrolidine	0.005 mmol	0.5	0	0[b)]

a) Solvent: 5 ml. Under nitrogen.
b) 1 was recovered quantitatively.

Both 2a and 2b were found to homopolymerize readily under thermal, radical, and anionic conditions except for cationic one. These polymerization behaviors are similar to that of 1 as reported by Hall and Bentley.[11)] Homopolymerization of 3 has not been known yet under any conditions such as thermal, radical, anionic, and cationic ones. While 2a and 2b are intermediate in electron accepting character between 1 and 3, 2a and 2b are much more similar in polymerization behavior to 1. However, it was found that weak bases such as triethylamine, pyridine, and pyrrolidine induces the homopolymerization of 2a and 2b, whereas they could not initiate the homopolymerization of 1 (see Table 3), indicating that 2a and 2b are different from 1 and react as more acidic monomers. Detailed studies on their polymerization behaviors as acceptor monomer are now in progress.

References

1) S. Iwatsuki, T. Itoh, and K. Horiuchi, Macromolecules, 11, 497 (1978).
2) S. Iwatsuki and T. Itoh, Macromolecules, 12, 208 (1979).
3) S. Iwatsuki and T. Itoh, Macromolecules, 13, 983 (1980).
4) S. Iwatsuki, T. Itoh, and S. Sadaike, Macromolecules, 14, 1608 (1981).
5) S. Iwatsuki and T. Itoh, J. Polym. Sci., Polym. Chem. Ed., 18, 2971 (1980).
6) A. F. Titley, J. Chem. Soc., 1926, 508.
7) D. J. Sandman and A. F. Garito, J. Org. Chem., 39, 1165 (1974).
8) H. A. P. Dejongh, C. R. H. I. Dejonge, H. J. M. Sinnige, E. P. Magré, and W. J. Mijs, J. Polym. Sci., Polym. Chem. Ed., 11, 345 (1973).
9) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, 1969, p 33.
10) E. C. M. Chen and W. E. Wentworth, J. Chem. Phys., 63, 3183 (1975).
11) H. K. Hall, Jr. and J. H. Bentley, Polymer Bulletin, 3, 203 (1980).

(Received January 28, 1982)