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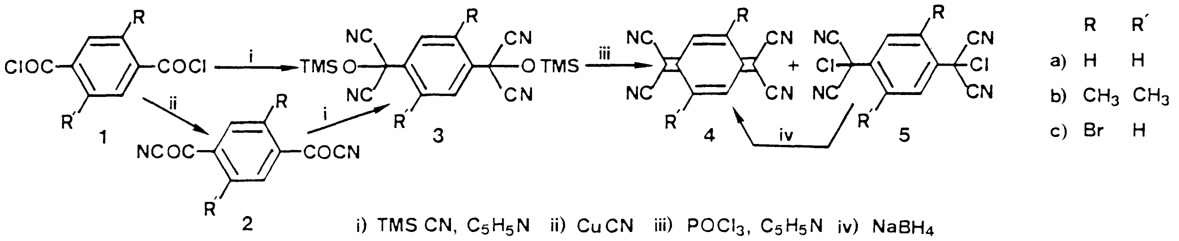
PREPARATION OF 7,7,8,8-TETRACYANOQUINODIMETHANE AND ITS DERIVATIVES

Shunro YAMAGUCHI* and Terukiyo HANAFUSA
The Institute of Scientific and Industrial Research,
Osaka University, Mihogaoka, Ibaraki, Osaka 567

The reaction of terephthaloyl chloride with cyanotrimethylsilane in the presence of pyridine gave 1,4-bis(dicyanotrimethylsiloxymethyl)benzene, which was treated with $POCl_3$-pyridine to afford tetracyanoquinodimethane (TCNQ) along with its dichloride. Similarly, 2,5-dimethyl-TCNQ and 2-bromo-TCNQ were prepared from the corresponding terephthaloyl chlorides.

Tetracyanoquinodimethane (TCNQ) is an excellent π-acceptor and charge transfer complexes of TCNQ with π-donors such as tetrathiafulvalene (TTF) possess high electrical conductivities.[1] In previous preparations of TCNQ,[2,3] malononitrile or highly toxic cyanogen chloride has been employed for the introduction of dicyanomethylene group of TCNQ.



Scheme 1.

We report here a new approach to TCNQ from terephthaloyl chloride with the use of cyanotrimethylsilane.[4] Terephthaloyl chloride (1a) was treated with excess cyanotrimethylsilane in the presence of pyridine at 110 °C to give 1,4-bis(dicyanotrimethylsiloxymethyl)benzene (3a), mp 57-59 °C, in 70% yield. This compound 3a could be also prepared in 62% yield by the reaction of the same reagents, cyanotrimethylsilane and pyridine, with terephthaloyl cyanide (2a) which was obtained from 1a and cupper(I) cyanide in good yield.[5] Compound 3a was reacted with $POCl_3$-pyridine at room temperature for 15 min to afford TCNQ (4a) and dichloride (5a)[2] in 71% and 15% yields, respectively. In this reaction, as shown in Table 1, the dichloride 5a was obtained as the major product when the amount of pyridine was reduced. But treatment of dichloride 5a with $NaBH_4$ in 2-propanol at room temperature afforded TCNQ in 90% yield.

Table 1. The formation of TCNQ 4a and dichloride 5a[a]

	Substrate	Reagent		Yield/%	
No.	3a (mmol)	$POCl_3$ (mmol)	Pyridine (mmol)	TCNQ 4a	Dichloride 5a
1	0.30	10.8	15.5	71	15
2	0.30	10.8	12.4	69	16
3	0.30	10.8	9.3	34	48
4	2.60	75.6	12.4	5	70

a) The products were isolated by silica gel column chromatography.

In a similar manner, 2,5-dimethyl-TCNQ (4b)[3] and 2-bromo-TCNQ (4c)[3] were prepared from the corresponding terephthaloyl chlorides. Thus, (3b), mp 132-133 °C, and (3c), mp 102-103 °C, were produced in 79% and 71% yields, respectively. Under the conditions of No.1 in the Table, 3b was converted into 4b, mp 278-280 °C,[3] and (5b), mp 158-159 °C, in 43% and 53% yields, respectively. Treatment of 3c under the conditions of No.3 in the Table gave 4c, mp 204-206 °C,[3] in 38% yield, but (5c) could not be isolated.

The present method may provide the most facile laboratory preparation of TCNQ and its derivatives and be widely applicable to other related systems.

References

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