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A NEW SYNTHESIS OF TETRACYANOTETRATHIOFULVALENE

Zen-ichi Yoshida*, Tokuzō Kawase and Shigeo Yoneda
Department of Synthetic Chemistry, Kyoto University,
Yoshida, Kyoto, 606, Japan

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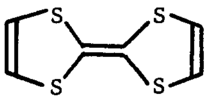
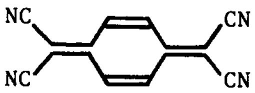
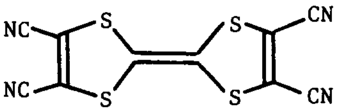
Since the recent papers on a new highly conducting donor-acceptor complex tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) have been reported by Cowan et al.[1] and Coleman et al.,[2] TTF-type compounds as electron donors have attracted much attention.[3,4] Of those, we have been interested in tetracyano-TTF (I), because semiempirical SCF MO calculations suggested the possibility of both intramolecular and intermolecular charge-transfer (CT) in this molecule.



TTF



TCNQ

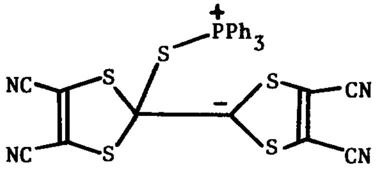


I

We wish to report a new synthesis of I by desulfurization of 4,5-dicyano-1,3-dithiole-2-thione (II)[5] with triphenyl phosphite[6] and together with the related reactions of II.

Reaction of II with triphenylphosphine in benzene at reflux temperature, which is the same condition as preparation[3] of tetratrifluoromethyl-TTF from 4,5-di-trifluoromethyl-1,3-dithiole-2-thione, didn't afford the expected product (I) but quantitatively an orange solid (III), m.p. 169-172°C (dec). The analytical and mass spectral data indicate this solid to be one to one adduct of I with triphenylphosphine thioxide. Mass: m/e 304(TTF), 294(S = PPh_3). Anal. Calcd. for $C_{28}H_{15}N_4PS_5$: C, 56.17; H, 2.53; N, 9.36; P, 5.17.

Found: C, 56.65; H, 2.78; N, 9.37; P, 4.88. This adduct was found to dissociate to TTF and triphenylphosphine thioxide by heating. The structure of this adduct might be assigned as III.



III

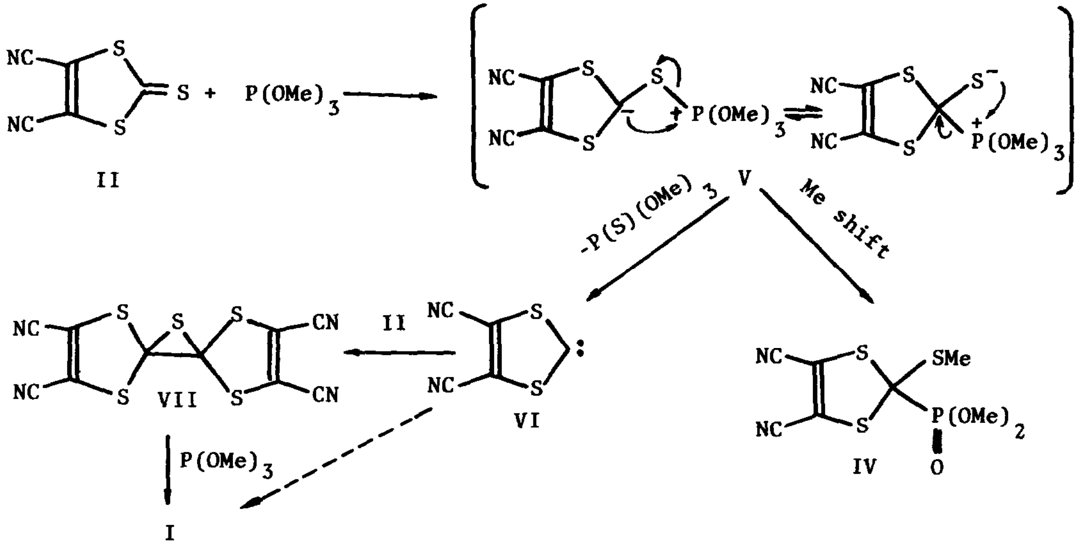
On the other hand, the reactions of II with trialkylphosphites were found to give I accompaning with formation of other products (eg. IV): A solution of II and excess trimethyl phosphite in toluene was refluxed under nitrogen atomosphere for 18 hrs. After the solvent was removed, the residue was chromatographed and recrystallized from methylene chloride-ether to give dark purple needles (I) in 10% yield; m.p. 264-265°C (dec.). The structure of I was determined on the basis of the spectral and analytical data: IR (KBr) 2218 cm^{-1} (CN stretching), 1534 (C=C stretching), 1182 (C=C-S, C-S stretching) mass: m/e 304 (M^+). Anal. Calcd for $C_{10}N_4S_4$: C, 39.46; N, 18.41; S, 42.14. Found: C, 39.06; N, 18.38; S, 42.37. In this reaction, the pale yellow solid (IV) was also obtained: m.p. 140-141°C; IR (KBr): 2950 cm^{-1} (S-CH_3, C-H stretching), 2850 (O-CH_3, C-H stretching), 2220 (CN stretching), 1504 (C=C stretching), 1240 (P=O stretching), 1173 (P-O-CH_3, CH_3 bending), 1054, 1012 (P-O-CH_3 assymmetric stretch); PMR ($CDCl_3$) δ 2.75 (s, 3H, S-CH_3), 3.83 (d, J=11.2 Hz, 6H, P-O-CH_3); Mass: m/e 261 (M^+ – SCH_3). The formation of IV could be accounted for by the mechanism *via* betaine intermediate (V)[7] from which 1,3-dithiolium carbene (VI) could be generated to give I (see Scheme).

Quantitative formation of the stable orange solid (III) is presumably explained by the reaction of VII with triphenylphosphine and impossibility of V → IV type phenyl shift in the reaction of II with triphenylphosphine.

The V → IV type alkyl rearrangement has been recently found in the reaction of alicyclic thione with trialkyl phosphite.[7] Such a rearrangement results in the decreased yield of I.

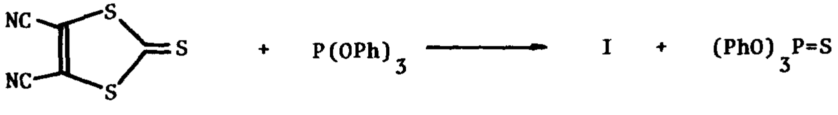
In accord with this consideration, the yield of I in the reaction of II

Scheme



with other trialkyl phosphites also does not exceed 10%.

In order to inhibit the alkyl rearrangement and to enhance the yield of I, the desulfurization of II with triphenyl phosphite was attempted in the same condition as in the case of the reaction with trimethyl phosphite. As a result, I was exclusively obtained in high yield (> 70%).



II

The compound I is soluble in solvents such as benzene, methylene chloride, methanol and acetonitrile and the solution is colored to pink. The electronic spectral data in various solvents are summarized in the Table.

A-band is assigned as an intramolecular CT band, because A-band significantly shifts to shorter wave-length when changing a solvent from nonpolar benzene to polar methanol. B- and C-bands in the Table are rather insensitive to the polarity of the solvents.

Table Electronic Spectra (λ_{max} in nm and log ε_{max}) of I

Solvent	A-band	B-band	C-band
Benzene	502 (3.30)	328 (4.18)	
Methylene chloride	500 (3.36)	325 (4.20)	262 (4.41)
Acetonitrile	492 (3.30)	323 (4.16)	261 (4.33)
Methanol	480 (3.39)	320 (4.04)	261 (4.20)

The color of I in the crystalline state is dark purple, being quite different from the pink color of the solution of I, which suggests that intermolecular CT occurs in the crystalline state of I. More detailed investigation is now in progress in our laboratory.

REFERENCES

1. J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, J. Amer. Chem. Soc., 95, 948 (1973).
2. L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito and A. J. Heeger, Solid State Commun., 12, 1125 (1973).
3. H. D. Hartzler, J. Amer. Chem. Soc., 95, 4379 (1973).
4. J. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, Tetrahedron Lett., 2553 (1973).
5. R. Mayer and B. Gebhardt, Chem. Ber., 97, 1298 (1964).
6. During preparation of this manuscript, Miles, Wilson, Dahm and Wagenknecht have reported the preparation of I by the reaction of 4,5-dicyano-1,3-dithiole-2-one with trimethyl phosphite (Chem. Commun., 751 (1974)).
7. Z. Yoshida, T. Kawase and S. Yoneda, Tetrahedron Lett., in press (1974).