Reactions of Methylpyrylium, Thiapyrylium, and Flavylium Salts with Tetracyanoethylene

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The reaction of 2- or 4-methyl-2,6-diphenylpyrylium perchlorate with tetracyanoethylene (TCNE) in pyridine gives 2- or 4-(2,3,3-tricyanopropylidene)-2,6-diphenylpyran in good yield. Similar results are obtained from 2- or 4-methyl-2,6-diphenylthiapyrylium and 4-methylflavylium perchlorates. In one case a stable charge-transfer salt is isolated from the reaction of a methylene base and TCNE. The reaction mechanism of dye formation is discussed.

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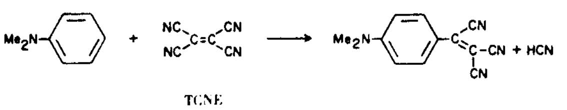
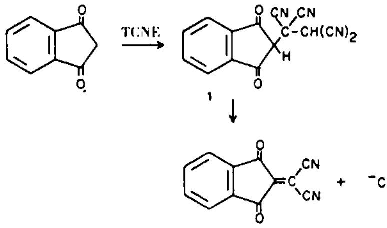
Introduction

The reactions of tetracyanoethylene (TCNE) with electron donors are usually divided into two major classes: formation of charge-transfer complexes/salts or cycloaddition, addition-elimination reactions (1). In the latter class, if a stable cycloadduct is not formed, a cyano group is usually eliminated yielding a 1,1,2-tricyano vinyl moiety as in the reaction of *N*,*N*-dimethylaniline with TCNE (Equation 1). A different kind of addition-elimination reaction has been shown to occur as illustrated by the reaction of 1,3-indanedione with TCNE (Equation 2) (2).



(1)

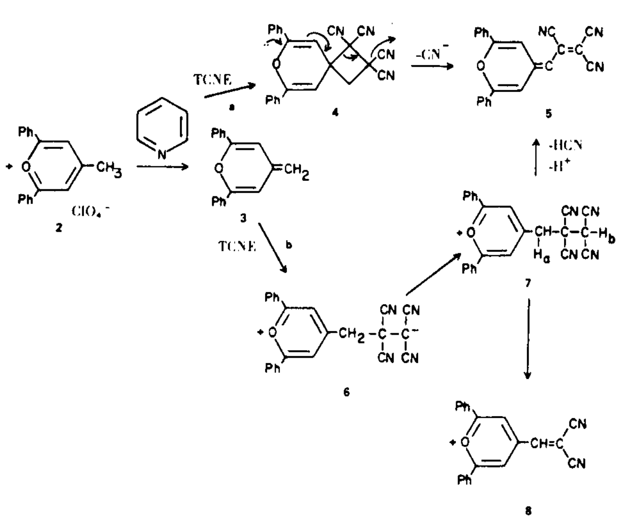


(2)

The initial adduct **1** undergoes a retro-Michael reaction resulting in expulsion of malononitrile anion thus introducing a dicyanomethylene substituent into the 2-position of the indanedione rather than a tricyanoethylene moiety as in the case of dimethylaniline (Equation 1).

We were interested therefore to observe which reaction path the methylene bases of 2- or 4-methylpyrylium salts would follow when allowed to react with TCNE. We envisaged two possible products which are depicted in Scheme 1 by 2,6-diphenyl-4-methylpyrylium perchlorate (**2**). The methylene base **3**, formed *in situ*, could react with TCNE *via* a 2 + 2 cycloaddition reaction (path **a**) forming tetracyanocyclobutane **4**. Ring opening of **4** with elimination of cyanide ion would give **5**, a tricyano-vinyl substituted pyrone. However, if path **b**, also a viable alternative as indicated by literature precedent (2), were followed, the addition product **6** could either lose cyanide ion forming **5** or protonate giving the Michael product **7**. Whether elimination of malononitrile anion from **7** to give **8** occurs, probably will depend upon the relative acidities of H_a *vs.* H_b (see Scheme 1). If H_a is the more acidic proton, **8** will be formed, otherwise **7** would eliminate hydrogen cyanide along with a proton giving **5**. *A priori* either path is conceivable based on literature precedents

Scheme 1



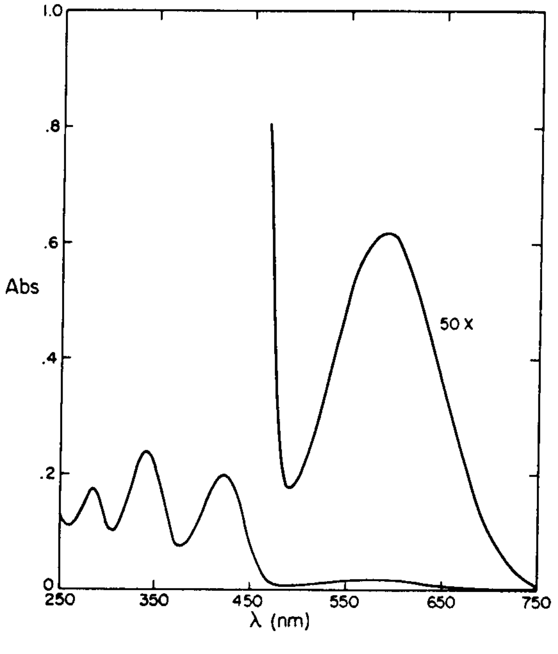
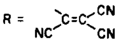
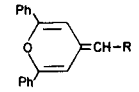
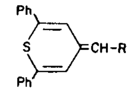
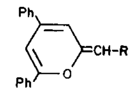
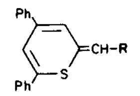
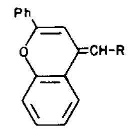


Figure 1. Uv-visible spectrum of **3**·TCNE in acetonitrile.

Table I

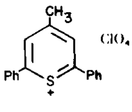
R =


Compound No.		λ max Acetonitrile nm (log E)	M.p. °C	% Yield	Empirical Formula	Anal. Calcd./Found C	H	N
5		555 (4.89) 523 (4.79)	308-310	75	$C_{23}H_{13}N_3O$	79.5 79.2	3.8 4.0	12.1 12.2
12		590 (4.82) 560 (4.76)	275-277	66	$C_{23}H_{13}N_3S$	76.0 76.0	3.6 3.5	11.6 11.7
14		625 (S) (4.46) 595 (4.58) 510 (S) (4.46)	299-301	58	$C_{23}H_{13}N_3O$	79.5 79.8	3.8 4.0	12.1 12.4
15		665 (S) (4.22) 620 (4.37) 585 (S)	208-210 dec.	41	$C_{23}H_{13}N_3S$	76.0 76.3	3.6 4.0	11.6 11.4
13		555 (4.654) 528 (4.679)	238-240	78	$C_{21}H_{11}N_3O$	78.5 78.2	3.5 3.2	13.1 13.1
	3·TCNE	585 (3.21)	326-330 dec.	80	$C_{24}H_{14}N_4O$	77.0 76.8	3.8 3.5	15.0 15.0

involving the chemistry of TCNE (1,2).

We have found that when **2** and TCNE are dissolved in excess pyridine an exothermic reaction occurs which deposits crystals of **5** within a few minutes in 75% yield. Also, addition of one equivalent of pyridine or triethylamine to **2** in methanol followed quickly by TCNE results in a rapid formation of **5**. However, when the amine is omitted and methanol is utilized as solvent, a blue-black, highly reflective crystalline solid soon precipitates from solution. Analyses and spectra (see Figure 1 for uv-visible) indicate the blue-black solid is the 1:1 charge-transfer salt formed from the reaction of **3** and TCNE. Apparently methanol is acting as a base to form **3** from **2** which, acting as a good donor, complexes with TCNE.

We also have obtained similar results from reaction of the thiapyrylium **10** and flavylium **11** with TCNE in pyridine: the formation of tricyanovinyl dyes **12** and **13**.



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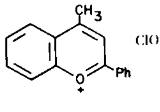
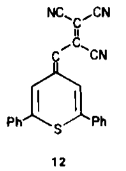
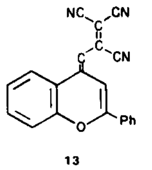


11



12



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However, charge-transfer salts from the corresponding free bases of **10** and **11** could not be obtained as crystalline solids. A color change was noted upon the addition of TCNE to a methanol solution of **10** or **11** but no precipitate appeared even upon prolonged standing. Examination of the reaction by uv spectroscopy shows, however, that complex formation is occurring. It is probably fortuitous that the charge-transfer salt from **3** crystallizes and those from **10** and **11** do not.

Reactions of 2-methyl-4,6-diphenylpyrylium and 2-methyl-4,6-diphenylthiapyrylium perchlorates with TCNE in pyridine also gave the corresponding 2-tricyanovinyl pyrylium salts **14** and **15** (see Table I).

EXPERIMENTAL (3)

Since all of the tricyanopropylidene pyrones were prepared under similar experimental conditions only one procedure will be described which can be considered general for all pyran dyes in Table I.

4-(2,3,3-Tricyanopropylidene)-2,6-diphenylpyrone (**5**).

4-Methyl-2,6-diphenylpyrylium perchlorate (**4**) (347 mg., 1 mmole) and tetracyanoethylene (127 mg., 1 mmole) were brought to reflux in pyridine (5 ml.). The solution was cooled to ambient temperature and the highly crystalline solid was collected, washed with methanol (10 ml.), and air dried to yield 4-(2,3,3-tricyanopropylidene)-2,6-diphenylpyrone (260 mg., 75%), m.p. 308-310°; ir (potassium bromide): 2180, 1620, 1500, 1410, 1335, 1320, 1215, 930 cm^{-1}; ms: (70 eV) M+ = 347; uv-visible (acetonitrile): 555 (4.89), 523 (4.79), 370 (4.18), 238 (4.31) nm (log E).

Anal. Calcd. for $C_{23}H_{13}N_3O$: C, 79.5; H, 3.8; N, 12.1. Found: C, 79.2; H, 4.0; N, 12.2.

In a similar manner use of only one equivalent of pyridine or triethylamine in methanol or acetonitrile (25 ml.) gave identical results to the above.

Charge-Transfer Salt from **3** and TCNE.

4-Methyl-2,6-diphenylpyrylium perchlorate (347 mg., 1 mmole) and tetracyanoethylene (127 mg., 1 mmole) was stirred at ambient temperature (22°) in 50% nitromethane-methanol (25 ml.) for 24 hours. The blue-black highly reflective crystalline solid was collected by filtration and washed with chloroform (20 ml.), then diethyl ether (25 ml.) and finally air dried to yield 300 mg. of a charge-transfer salt, m.p. 326-330°; ir (potassium bromide): 2180, 1615, 1480, 1200, 780 cm^{-1}; uv-visible (acetonitrile): 585 (3.21), 420 (4.42), 335 (4.50), 285 (4.37) nm (log E); nmr (TFA): Only two multiplets of equal intensity at 7.9 and 8.5 ppm from TMS.

Anal. Calcd. for $C_{24}H_{14}N_4O$: C, 77.0; H, 3.8; N, 15.0. Found: C, 76.8; H, 3.5; N, 15.0.

Acknowledgment.

The author acknowledges the generous gifts of methyl pyrylium salts from Drs. George Reynolds and James Van Allan of these laboratories as well as helpful discussions concerning the chemistry presented above.

REFERENCES AND NOTES

(1) D. N. Dhar, *Chem. Rev.*, 67, 611 (1967); also Z. Rappoport and D. Ladkani, *J. Chem. Soc.*, (C), 2595 (1974).

(2) H. Junek and H. Sterk, *Tetrahedron Letters*, 40, 4309 (1968).

(3) All melting points are uncorrected. Ir spectra were obtained with a Perkin-Elmer 137 spectrophotometer and nmr spectra with a Varian T-60 spectrometer using TMS as internal standard. Uv spectra were taken with a Cary 17 spectrophotometer.

(4) J. Kelemen and R. Wizinger, *Helv. Chim. Acta*, 45, 1908 (1962).