

SYNTHESIS OF ANION-RADICAL SALTS BY HYDRIDE TRANSFER REACTIONS

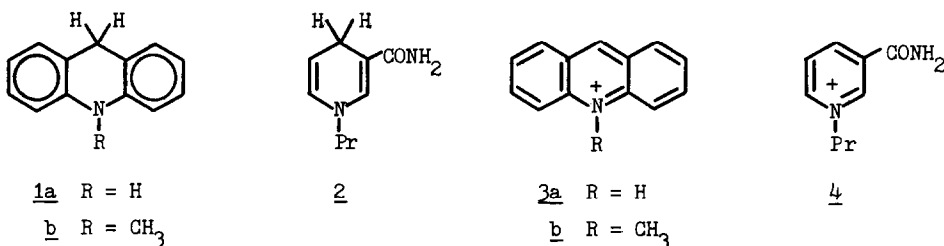
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Crystalline anion-radical salts of heterocyclic cations are of interest as organic conductors.² While both simple and complex anion-radical salts derived from 7,7,8,8-tetracyanoquinodimethane (TCNQ) have been extensively studied,^{2,3} salts derived from other π acceptors have received much less attention.

In the course of an investigation of the mechanisms of hydride transfer reactions between dihydropyridine analogs and π acceptors⁴ we observed that reaction of acridan (1a), N-methylacridan (1b), and N-propyl-1,4-dihydropyridinamide (2) with strong π acceptors, A, led



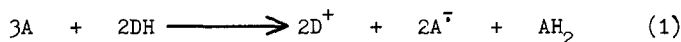
to anion-radical salts (eg., 3^+A^-) of the corresponding acridinium (3) and pyridinium (4) cations. We describe here the application of this method to the preparation of several known and new crystalline anion-radical salts derived from TCNQ, 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ), 2,3-dicyano-1,4-naphthoquinone (DCNQ), 2,3-dicyano-5-nitro-1,4-naphthoquinone (DCNNQ), 9-dicyanomethylene-2,4,7-trinitrofluorenone (DTNF), and 9-dicyanomethylene-2,4,5,7-tetranitrofluorenone (DTENF).

The reactions were carried out in anhydrous benzene, ether, or acetonitrile, the salt crystallizing from the reaction mixture. In a typical preparation 0.0505 g (2.47×10^{-4} mol) of DDQ in 20 ml of ether was added to 0.0195 g (1.00×10^{-4} mol) of 2b in 2 ml of ether. A black solid separated which was washed with acetonitrile and then ether to yield 0.0418 g (99%) of 3^+DDQ^- .

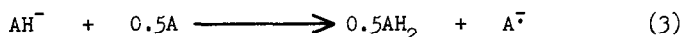
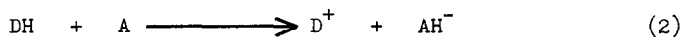
Analytical data for this and several other salts prepared in a similar manner are presented in the Table, with the solvents and molar ratios of reactants used in their preparation. The examples listed include both simple (1:1) and complex (1:2 and 2:3) salts. The influence of reaction conditions on the compositions of the salts was not investigated in detail. We note, however, that reaction of 1a with molar ratios of TCNQ ranging from 1.0 to 2.5 in acetonitrile yielded only the complex salt $\underline{3a}^+(\text{TCNQ})_2^-$, and reaction of 1b with molar ratios of DDQ ranging from 1.0 to 2.2 in ether led only to the simple salt $\underline{3b}^+\text{DDQ}^-$. Further, reaction of 1b with DCNQ in benzene led to the simple salt while the same reaction in ether led to the complex salt $\underline{3b}^+(\text{DCNQ})_2^-$. Only the 1:2 salt or salts of indefinite composition could be obtained by the conventional method³ from Li^+DCNQ^- or Na^+DCNQ^- and $\underline{3b}^+\text{I}^-$ in acetone.

The products were characterized by elemental analysis, and by comparison of their infrared and uv-visible spectra with those of the halide salts of $\underline{3a}^+$, $\underline{3b}^+$ and $\underline{4}^+$, and the alkali metal anion-radical salts of the six acceptors prepared by the method of Torrey and Hunter.⁵ Spectra of TCNQ^- ,³ DDQ^- ,⁶ and DCNQ^- ⁷ salts agreed well with published spectra; spectra of DTNF^- ,⁸ and DTENF^- ,^{8b} salts were consistent with published spectral data. The previously-unreported K^+DCNNQ^- showed major absorption maxima at 580, 547, ca 460, 434, 412 and 390 nm in the uv-visible, and a characteristic intense absorption ($\text{C}\equiv\text{N}$ stretch) at 2200 cm^{-1} . The $\text{C}\equiv\text{N}$ stretching absorption in DCNNQ^- ⁹ appears at 2210 cm^{-1} and is much weaker. Of the salts listed in the Table, $\underline{3a}^+(\text{TCNQ})_2^-$,¹⁰ $\underline{3b}^+(\text{TCNQ})_2^-$,^{3b} and $\underline{3a}^+\text{DTENF}^-$ ^{8b} have been reported previously; the others are, to our knowledge, new.

The stoichiometry of the reaction for formation of simple anion-radical salts is as represented by eq. 1, where DH is the hydride donor and A the acceptor.⁴ Evidence presented



elsewhere⁴ indicates that the reaction proceeds by a slow hydride transfer (eq. 2) followed by rapid reaction of the AH^- with unreacted acceptor (eq. 3). Reaction 3 is well known for



benzoquinone acceptors.¹¹

The requirements for isolation of anion-radical salts in high yield and purity by this method have not been investigated in detail. The product obtained must depend, among other things, on the concentration of anion-radical in solution. Reaction of 1b with chloranil or 2,3-dichloro-5-nitro-1,4-naphthoquinone under conditions similar to those described above led to mixtures containing the hydroquinone monoanion. Under strongly acidic conditions the anion-radical concentration will be negligible.^{3a, 11c} Reid et al¹² have reported that reaction of 1a with DDQ in acetic acid leads to the hydroquinone monoanion salt $\underline{3a}^+\text{DDQH}^-$.

The method described in the present work is similar to that described by Melby et al^{3a} for preparation of salts of the type $\text{R}_3\text{NH}^+(\text{TCNQ})_2^-$ by reaction of trialkylamines with TCNQ. In

Table. Preparation and Properties of Anion-Radical Salts

Salt	Analyses, %						Solvent	Molar Ratio of Acceptor to Donor	Color
	Calculated			Found					
	C	H	N	C	H	N			
$2a^+(TCNQ)_2^-$	75.5	3.1	21.4	75.4	3.4	21.5	acetonitrile	1.0 - 2.5	green-black
$2b^+(TCNQ)_2^-$	75.7	3.4	20.9	76.0	3.7	21.2	acetonitrile or ether	1.0	green-black
4^+TCNQ^-	68.3	4.6	22.8	68.4	4.6	23.3	acetonitrile-ether	a	dark blue
$3a^+DDQ^-$	61.9	2.5	10.3	62.0	2.9	10.4	acetonitrile or ether	1.0	green
$2b^+DDQ^-$	62.7	2.9	10.0	61.8	3.3	10.0	acetonitrile or ether	1.0 - 2.2	dark green
$(3a^+)(DCNQ)_3^{2-}$	75.6	3.3	11.4	75.8	3.7	11.3	acetonitrile	1.5	green-black
$2b^+DCNQ^-$	77.6	4.0	10.4	77.3	4.3	10.5	benzene	1.5	green
$3b^+(DCNQ)_2^-$	74.8	3.3	11.5	74.2	4.2	10.9	ether	1.0	greenish brown-black
$(3a^+)_2(DCNQ)_3^{2-}$	66.5	2.6	13.8	67.0	3.1	13.2	benzene	1.5	black
$2b^+DCNQ^-$	69.8	3.4	12.5	69.7	4.0	12.4	ether	1.0	black
$2a^+(DITNF)_2^-$	59.6	2.2	17.0	59.4	2.6	16.6	acetonitrile	1.0	black
$2a^+DITNF^-$	59.2	2.4	16.7	58.9	3.0	17.3	acetonitrile	1.3	black

a, not measured

these reactions a portion of the amine is apparently consumed by a hydride transfer reaction but attempts to identify the presumed oxidation product were not successful. Wallenfels *et al*¹³ have reported that reaction of dihydropyridines with tetracyanoethylene (TCNE) leads to TCNE⁻ in solution, but the salt isolated contained the pentacyanopropenyl anion.

A more extensive investigation of the scope of the method, including the influence of reaction conditions on the product composition is in progress.

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REFERENCES AND NOTES

1. Present address: Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080, U.S.A.
2. (a) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, 7, 232 (1974); (b) E. M. Engler, *Chem. Tech.*, 6, 274 (1976); (c) R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, 98, 3916 (1976).
3. (a) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, 84, 3374 (1962); (b) L. R. Melby, *Can. J. Chem.*, 43, 1448 (1965).
4. (a) A. K. Colter, G. Saito, F. J. Sharom, and A. P. Hong, *J. Am. Chem. Soc.*, 98, 7833 (1976); (b) A. K. Colter, G. Saito, and F. J. Sharom, *Can. J. Chem.*, in press.
5. H. A. Torrey and W. H. Hunter, *J. Am. Chem. Soc.*, 34, 702 (1912).
6. Y. Iida, *Bull. Chem. Soc. Jap.*, 44, 1777 (1971).
7. Y. Iida, *Bull. Chem. Soc. Jap.*, 45, 624 (1972).
8. (a) T. K. Mukherjee and L. A. levasseur, *J. Org. Chem.*, 30, 644 (1965); (b) P. Dupuis and J. Néel, *C. R. Acad. Sci., Paris, Ser. C*, 268, 557 (1969).
9. K. Wallenfels, G. Bachmann, D. Hofmann, and R. Kern, *Tetrahedron*, 21, 2239 (1965).
10. P. Dupuis and J. Néel, *C. R. Acad. Sci., Paris, Ser. C*, 265, 688 (1967).
11. (a) J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, 49, 1433 (1953); (b) H. von Diebler, M. Eigen, and P. Matthies, *Z. Naturforsch.*, 16b, 629 (1961); (c) S. Carter, J. N. Murrell, E. J. Rosch, N. Trinajstić, and P. A. H. Wyatt, *J. Chem. Soc. (B)*, 447 (1967).
12. D. H. Reid, M. Fraser, B. B. Molloy, H. A. S. Payne, and R. G. Sutherland, *Tetrahedron Letters*, 530 (1961).
13. K. Wallenfels, G. Bachmann, H. Diekmann, K. Friedrich, D. Hofmann, and R. Kern, *Angew. Chem., Int. Ed. Engl.*, 3, 241 (1964).