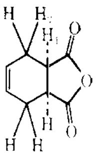
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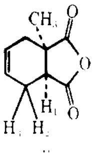
ii

(13) L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Elmsford, N.Y., 1969, p 281.

(14) B. D. N. Rao and J. D. Baldeschweiler, *J. Mol. Spectrosc.*, **11**, 440 (1963).

(15) J. J. Bloomfield and S. L. Lee, *J. Org. Chem.*, **32**, 3919 (1967); I. N. Nazarov and V. F. Kucherov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 265–273 (1955).

(16) Analogues of **8b**, **4a**, and **4b**, where *p*-anisyl has been replaced by phenyl, *p*-tolyl, *p*-chlorophenyl and 2,4-dimethoxyphenyl groups, have since been synthesized (unpublished work of Jeffrey Lang, Jill O'Donnell, and Edgar Leone). These exhibited a similar trend in the carbonyl region.

(17) For a *trans*-indanone, see P. S. Venkataramani, J. E. Karoglan, and W. Reusch, *J. Am. Chem. Soc.*, **93**, 269 (1971).

(18) K. N. Campbell, J. A. Cella, and B. K. Campbell, *J. Am. Chem. Soc.*, **75**, 4681 (1953).

(19) (a) H. O. House and J. K. Larson, *J. Org. Chem.*, **33**, 448 (1968); (b) W. S. Johnson and W. E. Shelberg, *J. Am. Chem. Soc.*, **67**, 1853 (1945); W. S. Johnson and H. J. Glenn, *ibid.*, **71**, 1092 (1949); J. Sam and J. N. Plampin, *ibid.*, **82**, 5205 (1960).

(20) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Wiley, New York, 1958, pp 137–138.

(21) H. O. House, J. K. Larson, and H. C. Muller, *J. Org. Chem.*, **33**, 961 (1968).

(22) T. Hori and K. Nakanishi, *Chem. Commun.*, 528 (1969).

(23) H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *J. Am. Chem. Soc.*, **82**, 1457 (1960).

Mechanism of Conversion of 1:1 Anion–Radical Salts of Tetracyano-*p*-quinodimethane to Their 1:2 Analogues

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Some anion–radical salts of TCNQ with composition $D^+TCNQ^-\cdot$ can be converted to their complex analogues, $D^+TCNQ^-\cdot TCNQ^0$, by simple recrystallization from pure acetonitrile. This conversion proceeds through disproportionation of $TCNQ^-\cdot$, which produces $TCNQ^0$ and $TCNQ^{2-}$. $TCNQ^0$ is incorporated into $D^+TCNQ^-\cdot$ forming the 1:2 salt. $TCNQ^{2-}$ is irreversibly oxidized to α,α-dicyano-*p*-toluoyl ion, $DCTC^-$, a process which comprises the driving force for the overall conversion mechanism. In cases where some formation of a 1:2 analogue occurs in the attempted synthesis of a 1:1 salt, rigorous exclusion of O_2 from the preparation causes exclusive production of the simple analogue.

The preparation of 1:2 donor–acceptor salts of the acceptor tetracyano-*p*-quinodimethane, TCNQ, is a process of great interest. This interest derives from the fact that in anion–radical salts of TCNQ, the 1:2 or "complex" species is, with rare exceptions,[1,2] a better conductor than the 1:1 or "simple" species with a common donor.[3,4]

Complex anion–radical salts with 1:2 stoichiometry conform to the formula $D^+TCNQ^-\cdot TCNQ^0$. The usual qualitative reason given for the enhanced conductivity of these compounds relative to their simple $D^+TCNQ^-\cdot$ counterparts is that the presence of $TCNQ^0$ in the crystal lattice creates a greater number of sites than conducting electrons, providing a mechanism of conduction which never necessitates double occupancy of a TCNQ moiety.[5] The net result of this phenomenon is a substantial decrease in unfavorable Coulombic interactions between mobile electrons, creating a reduced energy gap between the valence and conduction bands. In ideal cases of close, uniform, segregated TCNQ stacking, the bands may overlap, resulting in a semimetal.[6]

Generally, three methods for the preparation of 1:2 anion–radical salts of TCNQ are presently in use. They are: direct combination of equimolar amounts of $Li^+TCNQ^-\cdot$, $TCNQ^0$, and donor in near boiling 50% ethanolic acetonitrile; recrystallization of the 1:1 salt from acetonitrile containing an equimolar equivalent of $TCNQ^0$; and recrystallization of the 1:1 salt from pure acetonitrile, i.e., in the absence of any added $TCNQ^0$.

This study is focused upon the last method of synthesis described above. The source of $TCNQ^0$ ultimately incorporated into the $D^+TCNQ^-\cdot$ structure under those experimental conditions is not immediately obvious, nor has it been satisfactorily explained even though the reaction has been known for some time.[1,7]

Results and Discussion

Recrystallization of 1-benzyl-3-cyanopyridinium tetracyano-*p*-quinodimethane (B-3CN-1) and 1-benzyl-4-cyanopyridinium tetracyano-*p*-quinodimethane (B-4CN-1) from pure acetonitrile affords their 1:2 analogues, 1-benzyl-3-cyanopyridinium bis(tetracyano-*p*-quinodimethane) (B-3CN-2) and 1-benzyl-4-cyanopyridinium bis(tetracyano-*p*-quinodimethane) (B-4CN-2), respectively. During the conversions, the originally dark green solutions develop a reddish cast, producing an absorption maximum at 480 nm, an anomaly in the visible spectra of the 1:1 and 1:2 salts.[7,8,9] This is shown in Figure 1 for the B-3CN-1 to B-3CN-2 conversion. The filtrates which result from complete precipitation of the complex salts are markedly reddish in color and exhibit only the absorption maximum at 480 nm. These results are consistent with the presence of α,α-dicyano-*p*-toluoylcyanide ion, $DCTC^-$, first prepared and characterized as its sodium salt by Hertler et al.[10] Recently, Suchanski and VanDuyne showed that in acetonitrile solutions containing ionic species of TCNQ, $DCTC^-$ arises as an oxygen decay product of $TCNQ^{2-}$.[11] Thus, we suggest the mechanism shown in Scheme I for the conversion of simple salts of pyridinium tetracyano-*p*-quinodimethane ($Py^+TCNQ^-\cdot$) to their complex analogues ($Py^+TCNQ^-\cdot TCNQ^0$) during recrystallization from pure acetonitrile.

Disproportionation of $TCNQ^-\cdot$ readily accounts for the $TCNQ^0$ required for complex salt formation, and for $TCNQ^{2-}$, the direct precursor of $DCTC^-$. The mechanism only requires that disproportionation maintain an equilibrium concentration of $TCNQ^{2-}$ sufficient to allow its irreversible oxidation to drive the reaction to completion. This proposal is strongly supported by studies on other organic anion–radicals pub-

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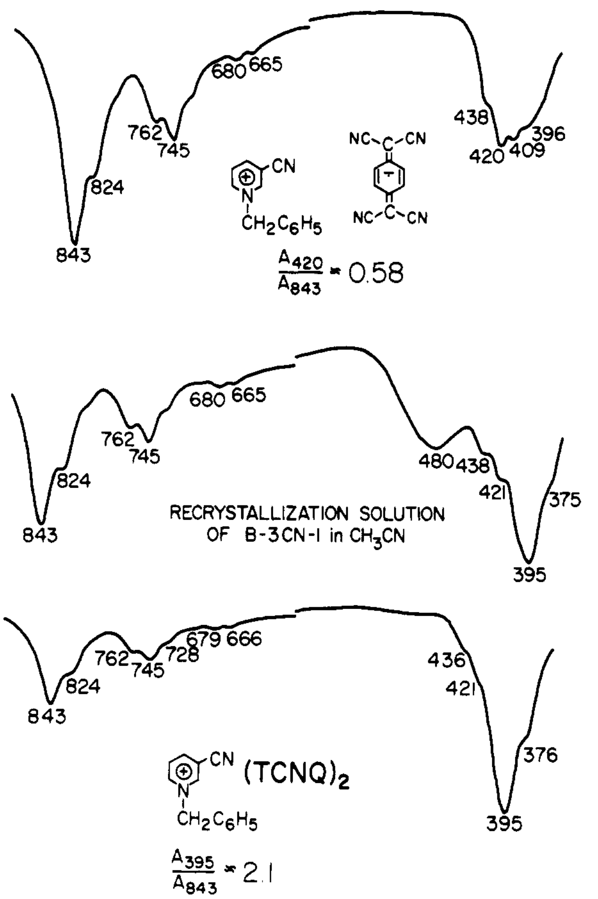
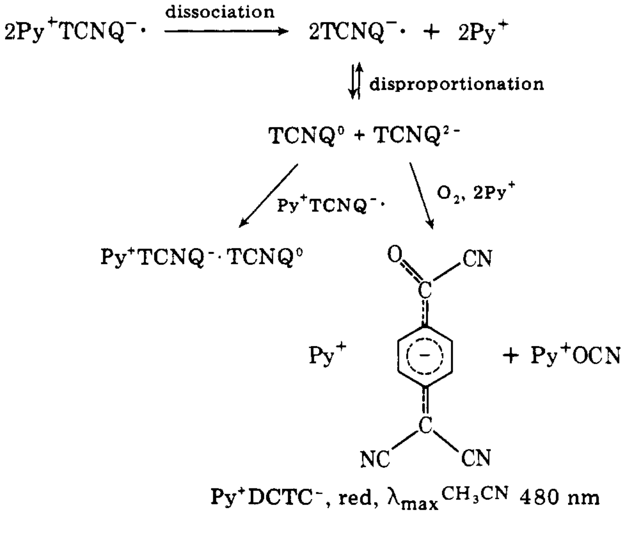


Figure 1. Electronic spectra of B-3CN-1, recrystallization solution of B-3CN-1, and B-3CN-2 in acetonitrile. Peak intensity ratios reflect compositions[8,9] and absorption maximum at 480 nm indicates presence of DCTC$^-$.

lished by Swarc and co-workers. They have shown that protonation of perylene anion–radical (Pe$^-\cdot$) by alcohols and water in THF and of anthracene anion–radical (An$^-\cdot$) by *tert*-butyl alcohol in DME occurs via Pe$^-\cdot$ and An$^-\cdot$ disproportionation followed by attack of H$^+$ on the dianions thus produced.[12,13] The reported equilibrium constants for Pe$^-\cdot$ and An$^-\cdot$ disproportionation ($K_{eq}{}^{dispro}$) are approximately 10^{-6} and 10^{-8}, respectively. Using reduction potentials of TCNQ^0 and TCNQ$^-\cdot$ reported by Suchanski and VanDuyne[11] we calculate that $K_{eq}{}^{dispro}$ of TCNQ$^-\cdot$ is 10^{-9}. The similar range of these $K_{eq}{}^{dispro}$ values and the close mechanistic analogy with the protonation scheme confirm the thermodynamic feasibility of TCNQ$^-\cdot$ disproportionation as a reasonable step in the conversion process.[14,16]

Scheme I



Py$^+$DCTC$^-$, red, $\lambda_{max}{}^{CH_3CN}$ 480 nm

The oxygen requirement for complex salt formation in the absence of external TCNQ^0 was proven by recrystallizations carried out with rigorous exclusion of oxygen (see Experimental Section for details). Under these conditions, no DCTC$^-$ formation is observed and a quantitative recovery of 1:1 salts is realized. Reheating large aliquots of the degassed mixtures to boiling and allowing them to cool in air produce the reddish cast in 2 h. Visible spectra of the exposed solutions contain the anomalous 480-nm absorption, and crystals precipitated from them are the complex salts.

Further support for the proposed conversion mechanism comes from identification of the predicted products remaining in the filtrates. Evaporation of the acetonitrile from B-3CN-2 filtrates leaves a red oil. When redissolved in acetonitrile or ethanol this material gives a UV–visible spectrum with absorption maxima at 280 nm, indicative of the *N*-benzyl-3-cyanopyridinium ion[18,19] (B-3CN-Py$^+$) and DCTC$^-$,[10] and at 480 nm, the principal absorption of DCTC$^-\cdot$. Mixed solutions of B-3CN-Py$^+$Cl$^-$ and Na$^+$DCTC$^-$ give spectra which only approximate this. However, solutions of Na$^+$DCTC$^-$ and B-3CN-Py$^+$OCN$^-$[18] produce spectra identical with that of the red oil. This strongly suggests that its composition is the same as that of the soluble product mixture predicted by the conversion mechanism.

Attempts to crystallize the red material in hopes of obtaining its pure components for unambiguous characterization were unsuccessful. However, an independent synthesis of B-3CN-Py$^+$DCTC$^-$, also a red oil, revealed it to be a major constituent. The ^{1}H NMR spectrum of the synthesized compound confirmed its structure[18,20] (see Experimental Section for details) and is identical with the ^{1}H NMR spectrum of the red oil obtained from recrystallization of B-3CN-1 in the presence of oxygen. Furthermore, the UV–visible spectrum of B-3CN-Py$^+$DCTC$^-$ is the same as that of mixed solutions of Na$^+$DCTC$^-$ and B-3CN-Py$^+$Cl$^-$, and is rendered identical with that of the soluble recrystallization product mixture by addition of K$^+$OCN$^-$. Thus, while it is unfortunate that neither the red oil obtained from conversion of a 1:1 salt to its 1:2 analogue nor that obtained in an independent synthesis of B-3CN-Py$^+$DCTC$^-$ could be crystallized, much spectroscopic evidence exists that shows they are both substantially comprised of B-3CN-Py$^+$DCTC$^-$, a required product of the disproportionation mechanism.

In summary, the mechanism we propose for the conversion of simple salts of pyridinium tetracyano-*p*-quinodimethane to their complex analogues by recrystallization from pure acetonitrile in the presence of oxygen is completely consistent with all observations made during the process and with results of experiments designed to test its validity. Thus, it appears reasonable to propose that the conversion proceeds via disproportionation of TCNQ$^-\cdot$ driven by irreversible oxidation of TCNQ^{2-} thereby produced.

It should be emphasized that recrystallization of 1:1 salts in the absence of oxygen provides a practical method of purification and may be utilized in growing pure single crystals of simple anion–radical salts. In fact, it is advisable to rigorously exclude oxygen when originally preparing 1:1 salts if complex salt formation is a possibility. The purity of these materials is of utmost importance, since even small amounts of contamination, deliberate or otherwise, can cause appreciable changes in their solid-state properties.

Experimental Section

Materials. TCNQ was obtained from K and K laboratories and Aldrich Chemical Co. It was purified before use by sublimation at 200 °C under high vacuum. Aldrich Spectroquality acetonitrile was used in most preparative procedures without further purification. Other grades of acetonitrile were distilled from P_2O_5 before use. 3-Cyanopyridine and 4-cyanopyridine were obtained from Aldrich Chemical Co.

Analyses. All microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Spectra. UV-visible-near-IR solution spectra were obtained on a Cary Model 14 spectrophotometer. Peak intensity ratios were used as preliminary indications of salt compositions[8,9] (e.g., Figure 1). UV-visible spectra were also obtained with a Perkin-Elmer Model 202 spectrophotometer when appropriate. ^1H NMR spectra were taken on a JEOL C-60HL high-resolution NMR spectrometer. Spectra run in acetone-d_6 and D_2O utilized Me_4Si and DSS, respectively, as internal standards. All infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrometer using KBr pellets.

Preparations. 1-Benzyl-3-cyanopyridinium Chloride (B-3CN-Py^+Cl^-) and 1-Benzyl-4-cyanopyridinium Chloride (B-4CN-Py^+Cl^-). The pyridinium salts were prepared by refluxing 3- and 4-cyanopyridine with benzyl chloride in equimolar amounts in absolute ethanol for 20–22 h. No precipitation occurred upon cooling. Small amounts were removed from each solution and ether was added to them until precipitates formed. These were added back to the reaction solutions for seeding, and overnight cooling caused precipitation of the pyridinium salts. The salts were obtained by vacuum filtration and recrystallized from 1:1 ethanol–water: yields, 55–65%; mp B-3CN-Py^+Cl^-, 292–295 °C dec; mp B-4CN-Py^+Cl^-, 209–212 °C dec. Structures were confirmed by UV, IR, and ^1H NMR spectra.[18]

$Li^+TCNQ^-\cdot$. This compound was prepared by the method of Melby et al.[7]

1-Benzyl-3-cyanopyridinium Tetracyano-*p*-quinodimethane (B-3CN-1) and 1-Benzyl-4-cyanopyridinium Tetracyano-*p*-quinodimethane (B-4CN-1). The simple anion–radical salts were prepared by metathesis of the pyridinium salts with an equimolar amount of $Li^+TCNQ^-\cdot$ as previously described.[7] In a typical run, a hot ethanolic solution of pyridinium salt was added to a boiling filtered solution of $Li^+TCNQ^-\cdot$ in ethanol. In the case of B-4CN-1, there was such a strong tendency for it to convert to B-4CN-2 that the solvents used in its preparation had to be degassed by complete flushing with N_2. Even with this precaution taken, B-4CN-2 was an unavoidable contaminant as reflected in the poor elemental analysis (see below) and the anomalously high conductivity of B-4CN-1 (published elsewhere).[21] However, the visible spectrum of the product of metathesis showed it to be predominantly B-4CN-1. Complete suppression of B-4CN-2 formation is achieved by degassing the solvent with freeze-pumping and running the synthesis under N_2 atmosphere. Purple crystals of the simple salts precipitated from solution after 2 days and were collected by vacuum filtration. They were washed with cold acetonitrile and ether, and air-dried: yields, 55–60%; mp B-3CN-1, 148–155 °C dec; mp B-4CN-1, 155–165 °C dec. Anal. Calcd for $C_{25}H_{15}N_6$: C, 75.25; H, 3.76; N, 21.05. Found for B-3CN-1: C, 74.92; H, 3.78; N, 20.88. Found for B-4CN-1: C, 74.59; H, 3.60; N, 21.76.

1-Benzyl-3-cyanopyridinium Bis(tetracyano-*p*-quinodimethane) (B-3CN-2) and 1-Benzyl-4-cyanopyridinium Bis(tetracyano-*p*-quinodimethane) (B-4CN-2). Saturated solutions of the simple salts in acetonitrile were prepared by dissolving 7.5 mmol in 125 mL of boiling acetonitrile. The solutions were allowed to stand under a bell jar for 20–40 h. Precipitation of the complex salts was assumed to be complete when the visible spectrum of the reddish-green mother liquor contained a single maximum at 480 nm and no bands characteristic of either simple or complex salt. The 1:2 salts were recovered by vacuum filtration, washed with cold acetonitrile and ether, and air-dried: Yields of both were typically 40–45%: mp B-3CN-2, 146–152 °C dec; mp B-4CN-2, 159–164 °C dec. B-3CN-2 was blue-black parallelepipeds having a metallic sheen (long axis length ~0.5 cm). B-4CN-2 was rectangular prisms also blue-black in color with metallic sheen (long axis legnth ~0.3 cm). The solution electronic spectra showed the following peak absorptions: λ_{max} (CH_3CN) 843, 824, 762, 745, 728, 679, 666, 436, 421, 395, and 376 nm. The ratio of peak intensities given by $A_{395}/A_{843} \approx 2$ was a preliminary indication of the 1:2 composition.

Anal. Calcd for $C_{37}H_{19}N_{10}$: C, 73.56; H, 3.15; N, 23.19. Found for B-3CN-2: C, 73.80; H, 3.21; N, 22.96. Found for B-4CN-2: C, 73.57; H, 3.23; N, 23.16.

Evaporation of solvent from the filtrate of B-3CN-2 preparation yielded a red oil (see Results and Discussion). This material resisted crystallization attempts from methylene chloride, ethyl alcohol, acetone, and combinations of these solvents with ethyl ether. Its UV–visible spectrum gave the following absorptions: λ_{max} (CH_3CN) 280, 480 nm. Its ^1H NMR spectrum in acetone-d_6 is identical with that of B-3CN-Py^+DCTC^- described below.

Recrystallization of B-3CN-1 from Acetonitrile in the Absence of O_2. Acetonitrile (150 mL) was degassed in a 500-mL, three-neck, round-bottom flask fitted with a stopper and two right-angle stopcock adapters, one of them connected to an Hg U tube. Three cycles of liquid N_2 freezing pump thawing were utilized. B-3CN-1 (4 mmol) was added under a positive pressure of N_2. After resealing, the connection to the U tube was opened and the mixture was heated at 80 °C until the B-3CN-1 dissolved. Heating was reduced over a 5-h period to room temperature and the solution was allowed to stand under static N_2 atmosphere for 3 days. At daily intervals, samples were removed under positive N_2 pressure and their visible spectra were recorded. Each sample showed no 480-nm absorption in the acetonitrile solution spectrum of the 1:1 salt. After 3 days, one-half of the solution was removed, reheated to 80 °C, and allowed to stand in air. After 2 h a spectrum of this solution displayed absorption at 480 nm. Upon complete evaporation of the solvent from this sample, well-defined crystals of the 1:2 salt were obtained as was determined by the characteristic solution electronic spectrum and crystal morphology. Finally, when the degassed solution sample, maintained under N_2, was partially evaporated with an N_2 stream, a sample of recovered crystals produced a spectrum of the 1:1 salt with no 480-nm absorption.

Preparation of 1-Benzyl-3-cyanopyridinium α,α-Dicyano-*p*-toluoylcyanide (B-3CN-Py^+DCTC^-). Na^+DCTC^- was prepared as previously described.[10] Its ^1H NMR spectrum in acetone-d_6 consists of a symmetrical pair of doublets centered at 6.90 and 7.67 ppm.

Spectroquality acetonitrile (75 mL) was added to 0.275 g (12 mmol) of B-3CN-Py^+Cl^- in a 125-mL Erlenmeyer flask and heated on a steam cone. When the pyridinium salt dissolved, 0.26 g (12 mmol) of Na^+DCTC^- was added as the solid to the hot solution and heating was continued for 15 min. The Na^+DCTC^- did not dissolve completely, so the flask was transferred to a heating–magnetic stirring plate where vigorous magnetic stirring and heating at 60 °C were allowed to proceed for 1 h. The dark red-orange solution was then allowed to stand at room temperature overnight. In that time a fine tan precipitate formed which was removed by filtration and discarded. The solvent was evaporated from the filtrate using a rotary evaporator, leaving a red oil. Repeated attempts to crystallize this oil from methylene chloride and acetone always failed. Its UV–visible spectrum contains the following absorptions: λ_{max} (CH_3CN) 275, 483 nm. Its ^1H NMR spectrum, taken in acetone-d_6, contains the following assigned signals: 6.90 and 7.67 (ring protons of $DCTC^-$), 8.55, 9.20, 9.65, and 10.07 (pyridinium ring protons at C-5, C-6, C-4, and C-2, respectively)[18,20] and 6.2 and 7.4 ppm (methylene and phenyl ring protons, respectively, of benzyl group).

Acknowledgments. Our thanks are extended to the National Science Foundation for support of this research through Grant DMR74-24208. Thanks are also extended to the Division of Sponsored Research, Florida Atlantic University, for partial support for A.L. during the summer quarter, 1977. We also acknowledge Drs. J. S. Blakemore, J. B. McGuire, F. A. Schultz, and D. A. Woodbury and Mr. J. E. Lane for their invaluable assistance throughout the course of this work.

Registry No.—B-3CN-Py^+Cl^-, 14535-08-1; B-4CN-Py^+Cl^-, 1966-86-5; B-3CN-1, 68297-64-3; B-4CN-1, 68297-66-5; B-3CN-2, 68297-67-6; B-4CN-2, 68297-68-7; B-3CN-Py^+DCTC^-, 68297-69-8; Na^+DCTC^-, 57379-38-1; 3-cyanopyridine, 100-54-9; 4-cyanopyridine, 100-48-1; benzyl chloride, 25168-05-2; $Li^+TCNQ^-\cdot$, 1283-90-5.

References and Notes

(1) L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965).
(2) W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963).
(3) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).
(4) H. Meier, "Organic Semiconductors", Verlag Chemie, Weinheim, Germany, 1973, p 199, and references cited therein.
(5) J. B. Torrance, B. A. Scott, and F. B. Kaufmann, *Solid State Commun.*, **17**, 1369 (1975).
(6) O. H. LeBlanc, Jr., in "Physics and Chemistry of the Organic Solid State", Vol. III, D. Fox, M. Labes, and A. Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1967, p 190.
(7) L. R. Melby et al., *J. Am. Chem. Soc.*, **84**, 3374 (1962).
(8) A. Rembaum, A. M. Hermann, F. E. Stewart, and F. Gutman, *J. Phys. Chem.*, **73**, 513 (1969).
(9) M. Murakami and S. Yoshimura, *Bull. Chem. Soc. Jpn.*, **48**, 157 (1975).
(10) W. R. Hertler, H. D. Hartzler, D. S. Acker, and R. F. Benson, *J. Am. Chem. Soc.*, **84**, 3387 (1962).
(11) M. R. Suchanski and R. P. VanDuyne, *J. Am. Chem. Soc.*, **98**, 250 (1976).

(12) G. Levin, C. Sutphen, and M. Swarc, *J. Am. Chem. Soc.*, **94**, 2652 (1972).
(13) A. Rainis, R. Tung, and M. Swarc, *J. Am. Chem. Soc.*, **95**, 659 (1973).
(14) The calculation of K_{eq}^{dispro} of TCNQ$^-\cdot$ was suggested by a reviewer who also proposed the mechanism shown below as a possible alternative to TCNQ$^-\cdot$ disproportionation.

$$2(Py^+TCNQ^-\cdot) + O_2 \rightleftarrows Py^+O_2^-\cdot + Py^+TCNQ^-\cdot TCNQ^0$$

$$Py^+TCNQ^-\cdot + Py^+O_2^-\cdot \rightarrow Py^+DCTC^- + Py^{+-}OCN$$

It was shown to be thermodynamically unfavorable by calculation of K_{eq} for the first step, reduction of O_2 by TCNQ$^-\cdot$.[11,15] K_{eq} is approximately 10^{-18}.
(15) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970, pp 497–505.
(16) It should also be noted that oxidation of TCNQ$^-\cdot$ by Py$^+$ as a source of TCNQ^0, a process observed by Ashwell and co-workers in bipyridyl tetracyano-*p*-quinodimethane salts,[17] does not appear to be operative here. It cannot account for TCNQ^{2-} formation and no dihydropyridine derivatives nor their degradation products are observed.
(17) G. J. Ashwell, D. D. Eley, and M. R. Willis, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1227 (1975).
(18) A. Lombardo, Ph.D. Thesis, Syracuse University, 1967.
(19) E. M. Kosower, "Molecular Biochemistry", McGraw-Hill, New York, N.Y., 1962, p 172.
(20) W. S. Caughey and K. A. Schellenberg, *J. Org. Chem.*, **31**, 1978 (1966).
(21) J. E. Lane, T. R. Fico, A. Lombardo, and J. S. Blakemore, *J. Chem. Phys.*, **69**, 3981 (1978).

Syntheses with *F*-Alkyl Radicals from *F*-Alkyl Iodides: Amine and Amine Salt Induced Addition to Alkenes[1]

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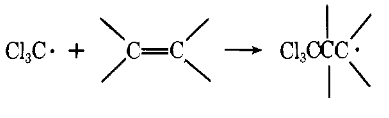
July 6, 1978

Free radical induced reactions of 1-iodo-*F*-alkanes (R_FI) with diallyl ether, *N*-methyldiallylamine, and 1-heptene, using an amine or amine salt as initiator at 120–140 °C, are described. Copper(I) or copper(II) ions appear to inhibit the reaction, while copper ion and an amine or amine salt in no case gave faster reaction than amine or amine salt alone. These results are contrasted with CCl_4 additions which are strongly accelerated by this initiating system. The best initiator found for R_FI addition was benzyltriethylammonium chloride, which gave 94% conversion of diallyl ether to adducts at 135 °C in 3 h. An azonitrile initiator would be preferred, however, for most R_FI additions which can be carried out at 50–110 °C.

Free radical addition of *F*-alkyl iodides (R_FI) to unsaturated compounds is by now a well-known process.[2] Azonitrile initiators, peroxides, and of course heat and irradiation have been used to initiate these reactions. Other polyhalogenated substances such as CCl_4 also add to double bonds and one of the best methods employs a metal salt–amine system of initiation.[3,4] Monomers such as acrylate esters, which telomerize with CCl_4, gave simple 1:1 adducts in high yield when metal salts, an amine, and amine hydrochloride are used. This was attributed to more efficient transfer from a metal complex according to the simplified mechanism, in which M^+ represents a metal ion, e.g., Cu^+ or Fe^{2+}.[3b] The amine salt apparently catalyzes the chain transfer step 2, making it faster than direct transfer on CCl_4.[3b] Carbon tetrachloride and 1,6-heptadiene gave a five-membered ring cyclization product, confirming the free radical nature of the process.[5] Peroxides[6] or other free radical generating systems[7] have subsequently been used in similar additions of CCl_4 to diallyl ether[6] or for the telomerization of diallylamine derivatives.[7-9] For reactions of R_FI initiated by copper salts or amines, the nature of the process is not clear, as copper(II) iodide does not appear to exist. Thus, Burton and Kehoe[10] in a study of several polyhalogenated compounds refluxed 1-octene and 1-iodo-*F*-propane with copper(I) chloride (1%) and 2-aminoethanol (50 mol %) and isolated both adduct and dehydrohalogenated product in modest yield.[11] Jaeger[12] heated a mixture of R_FI and various alkenes with a catalytic amount of copper or other metal salt and an amine at 140–180 °C. However, at these temperatures thermally induced addition of R_FI is likely to occur.[13,14]



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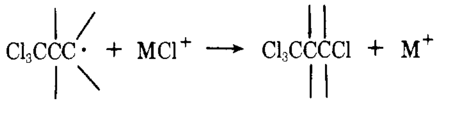


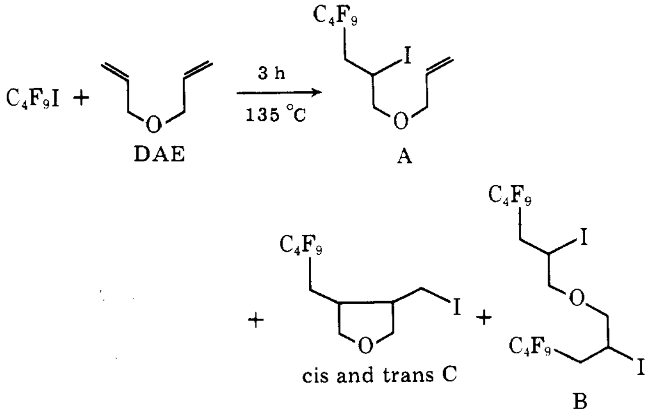
(2)

$$M^+ + Cl_3C{-}Cl \longrightarrow MCl^+ + Cl_3C\cdot \qquad (3)$$

It is the purpose of this paper to describe new and more efficient methods for the initiation of free radical additions of R_FI, involving amines and amine derivatives. The role of amine and copper salt in reactions of CCl_4 will be contrasted with reactions of R_FI. Preparation and stereochemistry of cyclization products from R_FI and diallyl ether will be described in some detail.

Results and Discussion

Reaction of 1-iodo-*F*-butane with diallyl ether (DAE) was chosen for initial study because the free radical nature of the process could be readily proved by the structure of the prod-



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