Ion Radicals. 43. Addition of Thianthrene and Phenoxathiin Cation Radicals to Alkenes and Alkynes[1,2]

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Thianthrene and phenoxathiin cation radical perchlorates have been found to form adducts with a number of alkenes and alkynes in excellent yield. Alkanedisulfonium diperchlorates were obtained from alkenes, while alkenedisulfonium perchlorates were obtained from alkynes. The products were colorless crystalline solids, explosively sensitive to heating, but characterizable by elemental analysis in some cases and ^{1}H NMR in others.

Although organic cation radicals are now known to react with a variety of nucleophiles,[5] not much is known about reactions with alkenes and alkynes. The largest body of information in the literature is comprised of aminium radical reactions, and for the most part these are of dialkylamine cation radicals ($R_2NH^+\cdot$). Such cation radicals are usually made by the ferrous ion reduction of an *N*-chloroamine in acid solution, or by the photolysis of an *N*-chloro- or *N*-nitrosoamine in acid solution. When these reactions occur in the presence of an alkene, addition may occur, for example, as in the sequence of eq 1–3 (X = Cl, NO). Analogous reactions occur with al-

$$R_2N^+HX \xrightarrow{h\nu} R_2NH^{+\cdot} + X\cdot \quad (1)$$

$$R_2NH^{+\cdot} + R'CH{=}CHR' \longrightarrow R_2\overset{+}{N}H\text{–}CH(R')\text{–}\dot{C}HR \quad (2)$$

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$$1 + X\cdot \longrightarrow R_2\overset{+}{N}H\text{–}CH(R')\text{–}CH(X)\text{–}R' \quad (3)$$

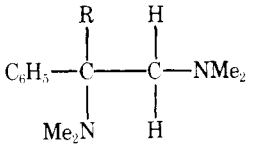
kynes, and an enamine is formed, say $R_2N^+HCH{=}C(X)R'$ from $R'C{\equiv}CH$. The reactions have been reviewed at various times;[6-9] the radical X· may be free (NO) or complexed ($FeCl^{2+}$). Alternatively, an atom-transfer sequence between 1 and R_2NHX^+ (X = Cl) may be involved.[9]

Most recently, Chow has shown that the photolysis of tetramethyltetrazene (TMT) in acetonitrile containing trifluoroacetic acid also gives the aminium radical ($Me_2NH^+\cdot$), which adds to alkenes (e.g., cyclohexene), and the adduct cation radical can be trapped with oxygen. Chow points out that the character of an aminium radical is its electrophilicity in comparison with its neutral counterpart. Thus, $Me_2N\cdot$ is indifferent to addition to alkenes.[10]

Two other types of cation radical have been shown to add to alkenes. Photolysis of di-*tert*-butyl peroxide or *tert*-butyl peracetate in solutions containing trifluoroacetic acid and an alkene at low temperatures led to trapping of the protonated *tert*-butoxy radical. ESR spectra of, for example, *t*-$BuO^+(H)CH_2CH_2\cdot$ and *t*-$BuO^+(H)CH_2\dot{C}HCH_3$ were obtained with ethene and propene. Davies has pointed out also that the protonated radical is more electrophilic than *t*-BuO·, the former adding to propene rather than abstracting a hydrogen atom.[11] Thus, *t*-$BuOH^+\cdot$ and $R_2NH^+\cdot$ have a common feature in their electrophilicity.

Some examples of the addition of an alkene cation radical to the parent alkene are known. These additions lead by further reaction to cyclobutane derivatives, e.g., with *N*-vinylcarbazole.[5] Polymerization of alkenes initiated by *addition* of a cation radical is not a common reaction, however.[5]

In all of these reactions one cation radical adds to the alkene (or alkyne) and is followed usually by the addition of another radical (e.g., X· in eq 3). Addition of *two* cation radicals has not been clearly documented, but is to be found in the reactions of TMT. TMT forms a complex with $ZnCl_2$, and if the complex is heated in THF containing either styrene or α-methylstyrene (in the absence of oxygen), adducts of the type **2** (R = H, Me) are obtained in about 30% yield. Michejda has attributed the formation of these products to the reaction of a diradical (**3**), which is itself formed by the decomposition of



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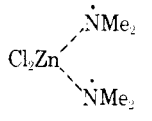

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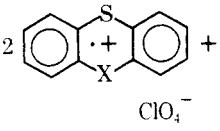
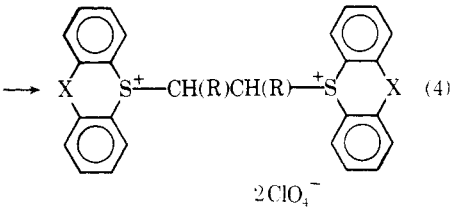
the TMT–$ZnCl_2$ complex.[12] It is clear, however, that the dimethylamino parts of **3** must have cationic character from complexing with $ZnCl_2$, so that these reactions are also akin to cation radical additions.

Apart from these examples, the clear-cut twofold addition of cation radicals to alkenes and alkynes has not been reported. We have found, however, that thianthrene (**4**) and phenoxathiin cation radicals (**5**) add to a number of alkenes



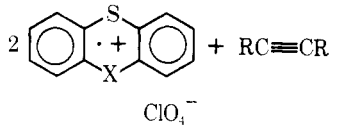
ClO_4^-

4, X = S
5, X = O

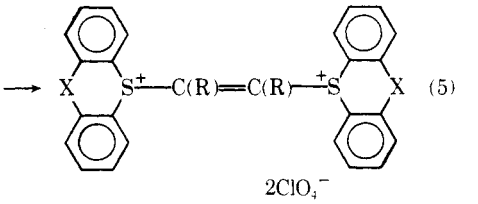


$2ClO_4^-$

6, X = S
7, X = O



ClO_4^-



$2ClO_4^-$

8, X = S
9, X = O

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and alkynes according to the stoichiometry shown in eq 4 and 5. As indicated in eq 4 and 5, the configuration of the adducts is not known.

Results and Discussion

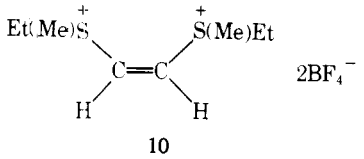
Addition of the cation radicals **4** and **5** to simple alkenes and alkynes appears to occur readily although somewhat slowly. The products are, respectively, alkane- and alkenedisulfonium ions which are easily isolated as the diperchlorates. Reaction occurs in acetonitrile solution from which the diperchlorate sometimes precipitates. No attempt was made to optimize yields, which for the most part are in the range of 70 to 100%. The only poor yield was of **8a** from reaction of **4** with acetylene. This reaction was also very slow, being incomplete under the conditions used, even after 10 days.

The Experimental Section reports products from reactions with cyclopentene, cyclohexene, 1-octene, acetylene, propyne, butyne, and phenyl- and diphenylacetylene. Reactions with some alkenes and alkynes containing electron-withdrawing groups were not successful. Some years ago it was found that solutions of **4** in acrylonitrile were stable for months.[13] Presently, we have found that reactions of **4** with ethyl propiolate, dimethyl acetylenedicarboxylate, and propargyl chloride were too slow to be studied, the reactions appearing to be incomplete during 3 or 4 weeks.

Thus, the additions are electrophilic, in analogy with those of the aminium radicals and t-BuOH^{+}·. To our knowledge no analogous twofold additions of cation radicals to alkenes and alkynes have been reported except for Michejda's work with the $ZnCl_2$ complex of TMT and styrene and α-methylstyrene.[12] In these additions, however, although the dimethylamino moieties have positive character while complexed with $ZnCl_2$, the final products are neutral, bis(dimethylamino)alkanes. How much positive charge character the dimethylamino radicals have at the time of addition is, of course, unknown.

The diperchlorates which we have isolated are sensitive to heat but otherwise appeared to be safe to handle. Nevertheless, much caution was used in handling the products. The alkyne adducts were the more sensitive of the two types of product, their thermal decomposition being explosive. Nevertheless, it was possible to determine so-called melting points and to carry out elemental analyses.[14] It was also possible to characterize some of the products by ^{1}H NMR. There was a tendency for some of the products to give low concentrations of the parent cation radical when being recrystallized. Therefore, crystallization was occasionally carried out in the presence of some of the unsaturated reactant. The product (**8e**) of reaction of **4** with diphenylacetylene appeared to dissociate particularly extensively, preventing characterization by NMR.

The class of products **8** and **9** appears to be uncommon. A few years ago Braun and Amann reported the preparation of the hitherto unknown *cis*-vinylenedisulfonium tetrafluoroborate (**10**) by reaction of *cis*-1,2-bis(methylthio)ethene with



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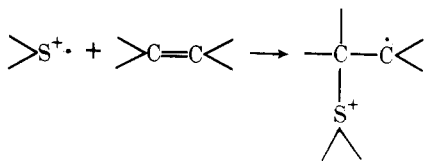
triethyloxonium tetrafluoroborate. Photochemical isomerization of **10** gave the trans isomer.[15] We are not aware of other reports of disulfonium salts of this type.

The formation of the two classes of disulfonium adducts must be stepwise in nature (e.g., eq 6 and 7). The difference between these additions and most of those of aminium radicals is that in the latter another radical (NO, Cl) is available for additon and the concentration of aminium radicals is probably



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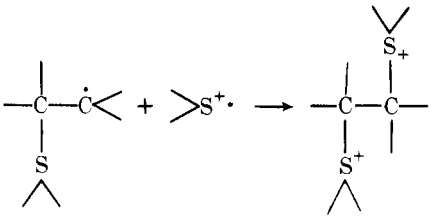

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low at all times. In our own case there is no other route to radical addition to compete with that of eq 7, except perhaps dimerization of the first adduct (eq 6), and this does not seem to occur.

The reactions are also interesting in another respect. The majority of reactions of organosulfur (and other) cation radicals with nucleophiles follows the stoichiometry of eq 8 and 9, where for convenience the nucleophile is written as an anion. That is, equal amounts of adduct and parent sulfide (eq 9) are obtained. This appears not to be the case in the alkene and alkyne reactions. Electron transfer (e.g., eq 9) between, say, **11** and the cation radical appears not to be a competing path of reaction.

$$>S^{+}\cdot + Nu^{-} \rightleftarrows >S^{\cdot}\text{–}Nu \quad (8)$$

$$>S^{\cdot}\text{–}Nu + >S^{+}\cdot \rightleftarrows >S^{+}\text{–}Nu + >S \quad (9)$$

For this reason, also, perhaps the reaction with alkenes differs from the reactions of **4** and **5** with ketones. These follow, for example, eq 10, and although the mechanism of reaction has not been established, it is thought that the cation radical adds to the enolic form of the ketone (eq 11).[16] Loss of a proton from the adduct **13** is thought to occur either before, after, or during the electron transfer step from which the parent sulfide (eq 10) is obtained. The adducts **11** and **13** then are similar in form but enjoy different fates. The mechanisms of these several reactions and the reasons for their differences are being sought.

$$2>S^{+}\cdot + CH_3COCH_3 \rightarrow >S^{+}CH_2COCH_3 + >S + H^{+} \quad (10)$$

$$>S^{+}\cdot + CH_2{=}C(OH)CH_3 \rightleftarrows >S^{+}CH_2\dot{C}(OH)CH_3 \quad (11)$$

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Experimental Section

Reactions were carried out in Eastman's anhydrous grade acetonitrile stored over molecular sieves. Commercial alkenes and alkynes were used mostly without further purification. Commercial acetylene, however, was passed through consecutive traps cooled in dry ice and traps of sulfuric acid in order to remove acetone. Thianthrene (**4**) and phenoxathiin cation radical perchlorate (**5**) were made as described earlier.[13,17] These compounds[18] and the perchlorate products of their reactions may explode and should be handled with care.

Reactions of 5 with Alkenes. With Cyclopentene. A suspension of 1.164 g (3.88 mmol) of **5** in 50 mL of acetonitrile was stirred for 20 min, and to it was added 2 mL (~23 mmol) of cyclopentene (Phillips Petroleum Co., pure grade). The dark purple solution lost much of its color within 2 min but remained colored for 30 min, and therefore a further 2 mL of cyclopentene was added. After being stirred for 3 h, the solution was yellow. The solvent was removed on a rotary evaporator, and the residue was washed well with chloroform, leaving 980 mg (1.47 mmol, 75.8%) of white solid, assumed to be the adduct **7a**, mp 160–161 °C dec after crystallizing from nitromethane–ether.

Anal. Calcd for $C_{29}H_{24}S_2Cl_2O_{10}$ (**7a**): C, 52.2; H, 3.62; S, 9.61; Cl, 10.6. Found: C, 52.8; H, 3.99; S, 9.70; Cl, 10.0.

Chromatography of the chloroform washings on a column of silica gel gave 50 mg (0.25 mmol, 6.4%) of phenoxathiin and 10 mg (0.05 mmol, 1.3%) of phenoxathiin 5-oxide.

With Cyclohexene. Similar reaction of 1.80 g (6.0 mmol) of **5** with two 1-mL portions (~10 mmol) of cyclohexene (Phillips, pure grade) gave 1.79 g (2.63 mmol, 87.7%) of a white solid adduct **7b,** mp 156–157 °C (aqueous acetonitrile), and 128 mg (0.64 mmol, 10.7%) of phenoxathiin.

Anal. Calcd for $C_{30}H_{26}S_2Cl_2O_{10}$ (**7b**): C, 52.9; H, 3.86; S, 9.41; Cl, 10.4. Found: C, 52.3; H, 4.20; S, 8.96; Cl, 9.7.

With 1-Octene. Reaction of 677 mg (2.26 mmol) of **5** with 1 mL (~6 mmol) of 1-octene (Phillips, research grade) in 35 mL of acetonitrile was quite slow. The color of **5** persisted for many hours until discharged by addition of a further 0.5 mL of octene. Workup gave 621 mg (0.83 mmol, 73.5%) of white solid, mp 125–127 °C dec (acetone–ether), which appears to be the dihydrate of the adduct **7c.** Also obtained was 56 mg (0.28 mmol, 12.4%) of phenoxathiin and 6 mg of the 5-oxide.

Anal. Calcd for $C_{32}H_{32}S_2Cl_2O_{10}\cdot 2H_2O$ (**7c**): C, 51.4; H, 4.85; S, 8.58; Cl, 9.48. Found: C, 51.4; H, 4.80; S, 8.53; Cl, 9.60.

Reaction of Cyclohexene with 4. Reaction of 1.22 g (3.88 mmol) of **4** with 3 mL (~30 mmol) of cyclohexene in 45 mL of acetonitrile gave 1.22 g (1.70 mmol, 87.6%) of a pale brown solid after washing well with ether. Crystallization from hot acetonitrile–ether, mp 147–148 °C dec, gave what is assumed to be the adduct **6b.** The compound was not analyzed. Infrared (KBr) showed the strong, broad ClO_4^- band at 9.1–9.3 μm.

Reactions of Alkynes with 4. With Acetylene. Purified acetylene was bubbled for 1 h into a solution of 1.0 g (3.17 mmol) of **4** in 50 mL of acetonitrile. The flask was sealed, and the deep purple color of **4** faded slowly during 10 days. Ether was then added to precipitate 110 mg (0.167 mmol, 10.8%) of the adduct **8a**: mp 216 °C (expl) after crystallizing from acetonitrile; ^1H NMR (CD_3CN) δ 8.24–8.10 (m, 4 H, 1,1′, 9,9′ protons), 8.02–7.60 (m, 12 H, remaining aromatic protons), 6.72 (s, 2 H, vinylic protons). The mother liquor gave 526 mg (2.43 mmol, 77%) of thianthrene.

With Propyne. Propyne was bubbled into a similar solution of **4** for 30 s. A white solid separated out, but the color of the solution faded only after 2 days. Wet acetonitrile was added to destroy remaining **4.** Ether was added, and the white precipitate (675 mg, 1.0 mmol, 63%) was collected: mp 231 °C (expl.) (acetonitrile–ether); ^1H NMR (CD_3CN) δ 8.34–8.12 (m, 4 H), 8.02–7.62 (m, 12 H), 6.52 (s, 1 H), 2.12 (s, 3 H); Infrared band (ClO_4^-) at 9.4 μm.

Anal. Calcd for $C_{27}H_{20}S_4Cl_2O_8$ (**8b**): C, 48.3; H, 3.00; S, 19.1; Cl, 10.6 Found: C, 48.6; H, 3.38; S, 19.3; Cl, 10.7.

The mother liquor gave 190 mg (28%) of thianthrene.

With 2-Butyne. 2-Butyne (1 mL) was added to a solution of **4** in 30 mL of acetonitrile. Workup after standing overnight gave 560 mg (0.817 mmol, 51.6%) of **8c**: mp 211–212 °C (expl.) (acetonitrile–ether); ^1H NMR (CD_3CN) δ 8.34–8.16 (m, 4 H), 8.04–7.68 (m, 12 H), 2.10 (s, 6 H).

Anal. Calcd for $C_{28}H_{22}S_4Cl_2O_8$ (**8c**): C, 49.1; H, 3.23; S, 18.7. Found: C, 49.0; H, 3.42; S, 19.0.

The mother liquor gave 329 mg (48%) of thianthrene.

With Phenylacetylene. Phenylacetylene (1 mL) was added to 760 mg (2.41 mmol) of **4** in 20 mL of acetonitrile. A white solid separated during 30 min. Workup gave 609 mg (0.831 mmol, 69%) of **8d**: mp 198 °C (expl.) (acetonitrile–ether); ^1H NMR (CD_3CN) δ 8.0–6.84 (m, 21 H), 6.52 (s, 1 H).

Anal. Calcd for $C_{32}H_{22}S_4Cl_2O_8$ (**8d**): C, 52.4; H, 3.02; S, 17.5; Cl, 9.66. Found: C, 52.8; H, 3.31; S, 17.5; Cl, 9.62.

The mother liquor gave 85 mg (16%) of thianthrene.

With Diphenylacetylene. To a solution of 930 mg (2.95 mmol) of **4** in 30 mL of acetonitrile was added 288 mg (1.62 mmol) of diphenylacetylene. Within 5 min the color had faded to light purple and a cream-colored suspension had formed. After 100 mL of ether and 30 mL of acetonitrile were added, the solid was collected, giving 1.04 g (1.29 mmol, 87.5%) of adduct **8e**, mp 162 °C (expl.) (acetonitrile–ether).

Anal. Calcd for $C_{38}H_{26}S_4Cl_2O_8$ (**8e**): C, 56.4; H, 3.23; S, 15.8; Cl, 8.75. Found: C, 55.8; H, 3.88; S, 15.8; Cl, 9.04.

This compound was very sensitive to heating, and only very small samples could be used for microanalysis.[14] The compound was not stable in acetonitrile; its solution gave on standing the purple color of **4.** For this reason NMR data could not be obtained.

From the mother liquor of the preparation was obtained 33 mg (5%) of thianthrene.

Reactions of Alkynes with 5. With Phenylacetylene. Within 1 min of adding 0.4 mL (~360 mg, 3.5 mmol) of phenylacetylene to a solution of 1.02 g (3.40 mmol) of **5** in acetonitrile, the color of the solution faded to brown-yellow. After 30 min, the yellow solution was evaporated and the residue washed with chloroform to give 1.2 g (1.71 mmol, 100%) of adduct **9d,** mp 174 °C (expl.), as pale yellow crystals from acetonitrile–ether.

Anal. Calcd for $C_{32}H_{22}S_2Cl_2O_{10}$: C, 54.8; H, 3.16; S, 9.14; Cl, 10.1. Found: C, 52.4; H, 3.15; S, 9.23; Cl, 9.44.

Analysis suggests that the product may be hydrated (for $2H_2O$: C, 52.1), but the sensitivity to explosive decomposition did not encourage further analytical work.

With Diphenylacetylene. An analogous reaction with 899 mg (3.00 mmol) of **5** and 584 mg (3.28 mmol) of diphenylacetylene gave 963 mg (1.24 mmol, 82.9%) of adduct **9e**: mp 185 °C (expl.); ^1H NMR (Me_2SO-d_6) δ 8.0–7.18 (m, 22 H, aromatic), 7.15–6.97 (m, 4 H, aromatic).

Registry No.—**4,** 35787-74-4; **5**, 55975-63-8; **6b,** 68843-17-4; **7a,** 68843-19-6; **7b,** 68843-21-0; **7c,** 68843-23-2; **8a,** 68843-25-4; **8b,** 68843-27-6; **8c,** 68867-03-8; **8d,** 68843-29-8; **8e,** 68843-31-2; **9d,** 68843-33-4; **9e,** 68867-01-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; 1-octene, 111-66-0; acetylene, 74-86-2; propyne, 74-99-7; 2-butyne, 503-17-3; phenylacetylene, 536-74-3; diphenylacetylene, 501-65-5.

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(3) Postdoctoral fellow.
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