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CATION RADICAL PERICYCLIC REACTIONS: CYCLOPROPANATION*

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ABSTRACT

Triarylaminium salts smoothly catalyze the cyclopropanation of dienes, styrenes and tetrasubstituted alkenes by ethyl diazoacetate. The reactions are regioselective and, in the case of additions to conjugated dienes, cyclopropane-periselective. A cation radical chain mechanism involving carbene transfer from ethyl diazoacetate to a substrate cation radical is proposed.

The cation radical chain mechanism, a fundamentally new mechanistic type, was first established by Crellin, Lambert and Ledwith in 1968 in the specific context of the cyclobutadimerization of *N*-vinylcarbazole.[1] Shortly after that (1969), Schutte and Freeman[2] and then, independently, Hammond *et al.*[3] observed the γ-radiation-induced cation radical chain Diels–Alder cyclodimerization of 1,3-cyclohexadiene. The (apparently) originally very narrow scope of the cation radical cyclobutadimerization reaction has since been appreciably extended by Farid and many others.[4] The scope and synthetic utility of the cation radical Diels–Alder reaction have been recognized and developed intensively in this laboratory.[5] The observation that a reaction which is symmetry forbidden on the neutral (uncharged) potential energy surface (i.e. cyclobutanation, a [2 + 2] cycloaddition) and one which is symmetry allowed on the neutral potential surface (i.e. Diels–Alder addition, a [4 + 2] cycloaddition), are both powerfully accelerated when executed on the cation radical potential surface led to the proposal that cation radical mechanisms might potentially represent the long-sought general catalytic principle for pericyclic reactions.[6] This proposition received significant support from a series of semi-empirical and *ab initio* SCF MO theoretical studies of cation radical pericyclic reaction paths, including not only prototype cyclobutanation[6,7] and Diels–Alder additions,[6,8] but also the Cope reaction.[6] Extraordinarily low activation barriers were calculated for all of these pericyclic reactions. Since then, not only has the cation radical Cope reaction (an allowed sigmatropic reaction) been exemplified experimentally,[9] but, in the category of forbidden sigmatropic reactions, the cation radical vinylcyclobutane rearrangement has been found to be both very facile and quite general.[10] The paper concerns experimental studies which were initiated to explore the possibility of hole catalyzed 1,3-dipolar cycloadditions to diazo compounds.[11] In reality, such reactions are found to lead to net cyclopropanation. However,

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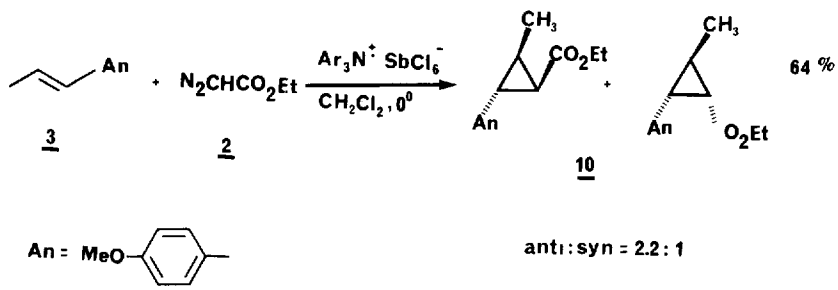
as such, they further augment the growing repertoire of useful cycloaddition types which can be executed via the cation radical format.

RESULTS

The stable aminium salt tris(4-bromophenyl)aminium hexachloroantimonate ($Ar_3N^{+\cdot}SbCl_6$, $\mathbf{1}^{+\cdot}$) has been found, in earlier studies, to be a highly effective initiator for a variety of cation radical pericyclic processes.[5] The reactions are typically carried out in dichloromethane (DCM) solvent at or below 0 °C, usually for ca 2–10 min. They normally require 3–10 mol-% of $\mathbf{1}^{+\cdot}$ as initiator. Organic substrates which are sufficiently ionizable to produce the requisite small amounts of chain-carrying cation radicals by electron transfer to $\mathbf{1}^{+\cdot}$ include a variety of conjugated dienes, styrenes and electron-rich alkenes (e.g. vinyl ethers, vinyl sulfides and *N*-vinylamides). It is noted that an exothermic initiation step is unnecessary and undesirable (high concentrations of cation radicals lead to chain termination[5f]). Indeed, most of the substrates induced by $\mathbf{1}^{+\cdot}$ to undergo efficient cation radical chain pericyclic reactions have oxidation potentials from 0·2 to 0·5 V more positive than **1** (the neutral triarylamine, Ar_3N:) Ethyl diazoacetate (**2**) was selected as the diazo component for these initial studies, in part because of its ready availability, but also partly because the presence of the electron-withdrawing carbethoxy function renders this diazo component much less ionizable than the typical diene, styrene or electron-rich alkene substrate.*[12] This circumstance would presumably favor a mechanism involving substrate cation radical–neutral diazo compound (a [4 + 1] cation radical cycloaddition) in preference to a neutral substrate–diazo compound cation radical mechanism (a [3 + 2] cation radical cycloaddition). This role selection mode was considered to be at least slightly preferable on the basis that the cation radical Diels–Alder is ideally symmetry allowed in the [4 + 1] role selection mode but forbidden in the [3 + 2] mode.[6]

Of the several substrates included in this study, *trans*-anethole (**3**) is the most readily ionizable ($E_{1/2}$ = 1·11 V). When 10 mol-% of $\mathbf{1}^{+\cdot}$–DCM was added over 5 min to a 1:1 molar ratio of **3** and ethyl diazoacetate (**2**) in DCM at 0 °C, decolorization of the aminium salt occurred rapidly and was accompanied by vigorous nitrogen evolution. Two cyclopropane adducts (Scheme 1) were formed, but were accompanied by large amounts of the *trans, anti,trans* head-to-head cyclobutane dimer of **3**.[13] The formation of this latter product,



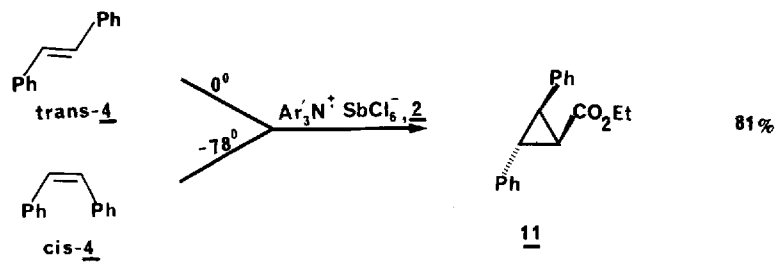
Scheme 1

*The oxidation potential of 2, corrected to S.C.E., is found to be 2·10 V, at least 0·5 V higher than the typical substrate of this study and fully 1 V greater than that of 1.

incidentally, decisively confirms the presence of $3^{+\cdot}$, and the predominance of the cyclodimer of **3** over the cyclopropane adducts suggests that the caticophilicity (reactivity toward a cation radical) of **3** toward $3^{+\cdot}$ is greater than that of **2** toward $3^{+\cdot}$. This undesirable competition is, however, largely suppressed by using a 5:1 molar ratio of **2**:**3**, under which conditions a 64% yield of cyclopropanation products is achieved. The possibility of a Brønsted acid-catalyzed reaction under aminium salt conditions is definitively excluded by the observation that the same cyclopropane adducts are formed, and in the same *anti*:*syn* ratio (2·2:1), in the presence of added 2,6-bis(*tert*-butyl)pyridine.[14] A cation radical mechanism is further indicated by the observation of formation of the same cycloadduct mixture under PET (photosensitized electron transfer) conditions.[5g] The specific involvement of the cation radical $3^{+\cdot}$ is supported not only by the formation of the cyclobutadimer of **3** in major amounts when **3** and **2** are present in equimolar proportions, but also by the observation that **2** alone does not decolorize the aminium salt, nor is it significantly decomposed or converted to detectable products within the usual reaction interval.

The reaction of **2** with a second substrate of the general styrene type, viz. *trans*-stilbene (**4**), was also investigated, this time using the more powerful initiator tris(2,4-dibromophenyl)-aminium hexachlorantimonate ($Ar_3N^{+\cdot} = 5^{+\cdot}$, $E_{1/2} = 1{\cdot}47$ V). In this case, a single cyclopropane isomer was isolated in 81% yield (Scheme 2). Reaction with *cis*-stilbene also gives the same product in identical yield, and quenching of this reaction at early or intermediate reaction times (after incomplete reaction) reveals no *trans*-stilbene. Although it is possible that the cyclopropanation reaction is simply non-stereospecific and highly *trans*-stereoselective, it must be noted that cation radicals of the *cis*-stilbene type are known to rearrange rapidly to the more stable *trans* isomer, and it is considered highly possible that this unimolecular reaction may indeed be considerably faster than the bimolecular cyclopropanation.[15] That *trans*-**4** is not detected in the *cis*-stilbene reaction mixtures after partial reaction is also not surprising, since quenching of *trans*-$4^{+\cdot}$ by electron transfer from *cis*-**4** is substantially endothermic. *Trans*-$4^{+\cdot}$ would therefore be likely to persist until cyclopropanation occurs, but would be unlikely to be converted to neutral *trans*-**4** and *cis*-$4^{+\cdot}$ via electron transfer from *cis*-**4**.

Although the generation of cation radicals of organic substrates by electron transfer to $1^{+\cdot}$ and $5^{+\cdot}$ is well known, an experiment in which a persistent cation radical is generated by use of the aminium salt and then subsequently cyclopropanated by **2** would be most attractive. The more powerful hole catalyst ($5^{+\cdot}$) used in the previous experiment makes the generation of such a persistent cation radical feasible. Reaction of $5^{+\cdot}$ with 1,1,2,2-tetraphenylethene (TPE) produces the well known cation radical $TPE^{+\cdot}$, identified by optical spectroscopy.[16] This cation radical is, of course, highly stabilized by conjugative and steric effects. Subsequent addition of **2**, however, fails to effect cyclopropanation of TPE, indicating that even cation

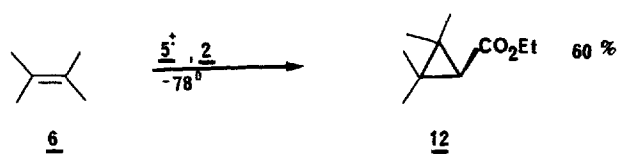


Scheme 2

radical/neutral reactions can have substantial activation energies when the cation radical is highly stabilized.

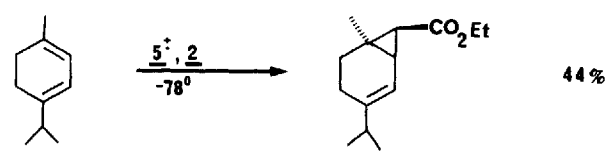
Simple olefins, including tetraalkyl-substituted ethenes, are unreactive toward **2** in the presence of the mild catalyst $\mathbf{1}^{+\cdot}$, but $\mathbf{5}^{+\cdot}$ induces a smooth cyclopropanation of 2,3-dimethyl-2-butene (**6**, Scheme 3). Cyclohexene and tetrachloroethene, both more difficult to ionize alkenes than **6**, are unreactive even under the more stringent conditions (using $\mathbf{5}^{+\cdot}$). An inverse correlation of cyclopropanation reactivity with substrate oxidation potential relative to initiator oxidation potential emerges (styrenes, dienes > **6** > cyclohexene, tetrachloroethene) and is construed as additional evidence for the obligatory involvement of a substrate cation radical–neutral diazo compound mechanism. Further, if the ionization of **2** were feasible using $\mathbf{1}^{+\cdot}$ under the conditions of a typical successful cyclopropanation reaction, it should also be feasible in the presence of cyclohexene, a less readily ionized substrate than those successfully cyclopropanated by the $\mathbf{1}^{+\cdot} + 2$ system. It would then be difficult to explain the complete unreactivity of cyclohexene, in contrast to the facile reactivity of **6** toward $\mathbf{2}^{+\cdot}$. The unreactivity of cyclohexene also rules out the intermediacy of carbethoxycarbene and, in all likelihood, its cation radical. These cation radical cyclopropanations are, incidently, extremely clean with regard to products volatile enough to be detected by gas chromatography (GC). Specifically, they produce none of the diethyl maleate and fumarate formed, e.g. in the rhodium acetate-catalyzed reaction of **6** and **2**, and which are considered to be derived from free or complexed carbethoxycarbene. Moreover, the insertion reactions expected of a free carbene are also absent in the cation radical reaction. Synthetically, the dependence of reactivity on ionization potential sharply distinguishes the new cyclopropanation reaction from transition metal-catalyzed cyclopropanations in general in that the latter typically exhibit high reactivity toward both electron-rich and electron-deficient π bonds.[17] Further, in carbene transfer reactions to neutral substrates, such as are involved in the Simmons–Smith reaction, tetrasubstituted alkenes have slightly diminished reactivity, as a result of steric effects, compared with trisubstituted alkenes and are only slightly more reactive than disubstituted alkenes.[18]

The remainder of the substrates which were successfully cyclopropanated in the study are conjugated dienes. The reaction with α-terpinene (**7**) is particularly interesting in relation to



6 12

Scheme 3

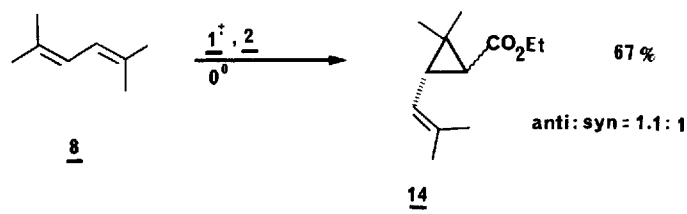


7 13

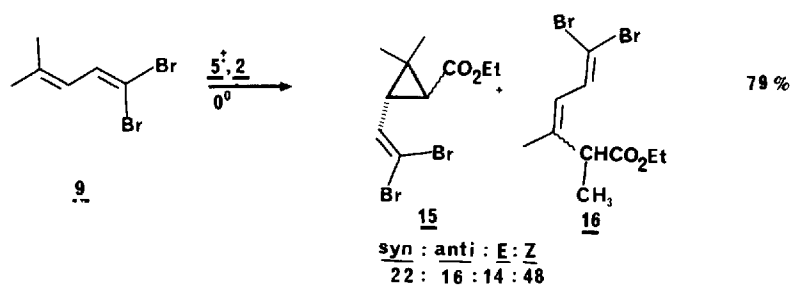
Scheme 4

regioselectivity. The cyclopropanation of **7** occurs smoothly (71%) with either $\mathbf{1}^{+\cdot}$ or $\mathbf{5}^{+\cdot}$ (Scheme 4). Incidentally, the much greater solubility of $\mathbf{5}^{+\cdot}$ than $\mathbf{1}^{+\cdot}$ in DCM makes it possible to effect this cyclopropanation at $-78\,^{\circ}C$ when the former initiator is used. Under either set of conditions ($\mathbf{1}^{+\cdot}$, $0\,^{\circ}C$; $\mathbf{5}^{+\cdot}$, $-78\,^{\circ}C$) the reaction is essentially completely regioselective for the less sterically hindered double bond. It is also of interest that this highly ionizable, rigidly *s-cis*-diene is not susceptible to aminium salt-catalyzed cation radical Diels–Alder cyclodimerization, apparently as a result of severe steric retardation. The reaction of **7** and **2**, incidentally fails to yield any of the bicyclo[2·2·1]heptene product which would result from concerted or stepwise conjugate addition to **7**. This observation suggests that a purely acyclic allylic intermediate, which could cyclize to either a vinylcyclopropane or a cyclopentene is not involved in this reaction. Further diagnostic studies were carried out with this interesting substrate. Lorenz and Bauld[5f] have established that added neutral triarylamine (Ar_3N) is a specific inhibitor for cation radical chain reactions. The cyclopropanation of **7** in the presence of $\mathbf{5}^{+\cdot}$ is indeed rendered less efficient (45% yield) in the presence of 100 mol-% (relative to **7**) of **5**. As shown by Lorenz and Bauld,[5f] this inhibition involves the quenching of chain-carrying cation radicals by electron transfer from the neutral amine. They also established that the triarylamine is not sufficiently basic to inhibit Brønsted acid-catalyzed reactions. On the other hand, 2,6-bis(*tert*-butyl)pyridine does suppress Brønsted acid-catalyzed reactions,[13] but does not suppress cyclopropanation of **7** by **2** (using $\mathbf{1}^{+\cdot}$ as initiator).

Cyclopropanation of the hindered *s-trans*-diene, 2,5-dimethyl-2,4-hexadiene (**8**) is also facile, even using $\mathbf{1}^{+\cdot}$ as initiator (67% yield; Scheme 5). The *anti* isomer of the product mixture is ethyl chrysanthemate, the acidic component of which is that present in pyrethrin I, a potent and mammal-safe, natural insecticide.[19] An even more potent pyrethroid insecticide is *syn*-**15**, which is produced (together with the corresponding *anti* isomer) in the regiospecific cyclopropanation of diene **9** (Scheme 6). A second, methyl migration, product (**16**), however, also accompanies these cyclopropanes. The cyclopropanation of **9** is feasible only when $\mathbf{5}^{+\cdot}$ is



Scheme 5



Scheme 6

used as the initiator, since the electron-withdrawing bromo substituents on the diene elevate its oxidation potential. Even $\mathbf{5}^{+\cdot}$, however, is ineffective in promoting the cyclopropanation of hexachloro-1,3-butadiene.

The final class of substrates surveyed in this study, the electron-rich alkenes, proved not to be amenable to efficient cyclopropanation. Phenyl vinyl ether, phenyl vinyl sulfide and 1-methoxycyclopentene, among others, caused immediate decolorization of the aminium salt (indicating electron transfer) and nitrogen evolution, but no cyclopropane or other volatile products were formed in significant amounts. Two potential problems have previously been noted in aminium salt-initiated cation radical cycloadditions involving such functionalities.[5g] First, the enol ethers and vinyl sulfides are exceptionally effective caticophiles, so that any cation radicals formed are most likely to react with the neutral enol ether or vinyl sulfide. Since cyclopropanation reactions appear to involve substrate (as opposed to diazo compound) cation radicals, a highly probable result is cyclodimerization of the substrate, in preference to or in competition with cyclopropanes. Secondly, the presence of a directly attached heteroatom donor substituent on the cyclopropane product may well render these products unstable to both electron-transfer agents ($Ar_3N^{+\cdot}$) and to the Brønsted acid present during aminium salt-initiated cation radical cycloadditions.[5]

DISCUSSION

Synthetic aspects

The scope of the new, cation radical cyclopropanation reaction appears reasonably well defined by the present reasearch. In a general sense, olefinic π bonds which have oxidation potentials less than about 1·6 V (vs SCE) are potentially susceptible to cyclopropanation by **2**, when the mild initiator $\mathbf{1}^{+\cdot}$ is used. In a synthetic context, this includes a variety of styrenes and conjugated dienes, the oxidation potentials of which are not elevated by an electron-withdrawing substituent and which, preferably, have a number of alkyl substituents attached to the conjugated functionality. In the case of styrenes, donor groups attached to the aromatic ring are especially advantageous. When the stronger intiator $\mathbf{5}^{+\cdot}$ is used, the scope is further extended to include tetraalkyl-substituted simple olefins, but apparently not olefins which have fewer alkyl substituents. Conjugated dienes containing one or two electron-withdrawing substituents can also be cyclopropanated using $\mathbf{5}^{+\cdot}$. This latter initiator is not only valuable for the cyclopropanation of less readily ionizable olefinic functionalities, but is also uniquely useful for reactions which must be run at $-78\,^{\circ}C$, e.g. for enhanced selectivity or for the preservation of thermally unstable functionalities. The special effectiveness of $\mathbf{5}^{+\cdot}$ in this context is based on its much greater solubility than $\mathbf{1}^{+\cdot}$ at such low temperatures and on the greater rates of initiation achieved by $\mathbf{5}^{+\cdot}$.

The cation radical cyclopropanations are frequently characterized by high regiospecificity, as has been established with **7** and **9**. These reactions, respectively, reveal the sensitivity of the reaction to steric effects and to charge distribution in the cation radical. With **7**, the positive charge in the dienic cation radical ($\mathbf{7}^{+\cdot}$) is presumably nearly equivalent at the two dienic termini, so that differential steric effects prevail in determining regioselection. In $\mathbf{9}^{+\cdot}$ the methylated terminus is undoubtedly the site of greater positive charge density and this factor evidently prevails against both opposing steric effects and product development character in the transition state. Although site selectivity in the case of multiple isolated olefinic functionalities has not been studied in this present work, this element may be considered to be potentially the

strongest aspect of the selectivity profile of cation radical cyclopropanation. Assuming the validity of the mechanism proposed here, site selection should be determined by site ionizability and thus should be both predictable and highly developed.

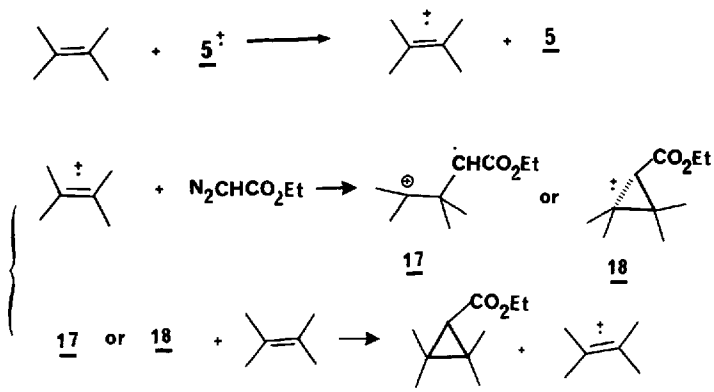
The reactions presented in this paper occur in yields that are comparable to those attainable by transition metal-catalyzed cyclopropanation, e.g. the rhodium acetate-catalyzed procedure, and the regioselectivities of the two reactions appear to be parallel.[17] As mentioned previously, site selectivity in molecules containing more than one alkene function is predicted to be superior in the cation radical version, although this remains to be demonstrated experimentally. The ability to execute the reaction at $-78\ ^{\circ}C$ has potential advantages in terms of selectivity and the preservation of thermally unstable functionalities. On the other hand, the rhodium-catalyzed procedure appears to be compatible with a wider range of alkenic functionality (e.g. electron-rich alkenes and strained alkenes).

Mechanistic aspects

The cation radical mechanism of these cyclopropanation reactions is affirmed by several independent observations. First, two well established cation radical initiating systems, the aminium salt and PET systems, afford the same cyclopropanation products and in essentially the same isomer ratios.[5g] Hindered bases, which completely suppress Brønsted acid-catalyzed reactions, fail to suppress these cyclopropanations.[14] Moreover, a specific diagnostic test for cation radical chain reactions, developed in this laboratory, and applied to cation radical Diels–Alder cycloadditions, has also been applied to cation radical cyclopropanation.[5f] The neutral triarylamine corresponding to the aminium salt initiator used was found to inhibit cation radical cyclopropanation. These triarylamines have previously been established as being too non-basic to retard Brønsted acid-catalyzed reactions. The chain nature of the cation radical mechanism is clearly reflected by the catalytic quantities of initiator which suffice in these reactions.

That the initiation step of the cation radical chain reaction involves ionization of the substrate as opposed to ethyl diazoacetate (**2**) is strongly indicated not only by the relative oxidation potentials of **2** and the various substrates studied, but also by several independent observations. First, in instances where the substrate is subject to cation radical chain cyclodimerization (e.g. *trans*-anethole) via the substrate cation radical, these cyclodimerization products are observed in major quantities when the substrate and diazo compound are present in equimolar amounts. The use of a 5:1 excess of diazo compound suppresses the formation of the cyclodimer in these cases. Secondly, although each of the substrates successfully cyclopropanated in this study decolorizes and quenches the appropriate aminium salt catalyst in the absence of **2**, **2** does not quench $\mathbf{1}^{+\cdot}$ and is not extensively decomposed during the approximately 10 min reaction time typical of cyclopropanation. Finally, the relative order of substrate reactivities is that of a reaction which succeeds when the substrate oxidation potential is within 0·5 V of the oxidation potential of the initiator. The reactivity behavior is therefore parallel to cation radical chain oxidation, a cation radical chain process which undoubtedly involves substrate cation radicals.[20] For a hypothetical mechansim involving diazo compound cation radical, moreover, it does not appear reasonable to expect that the reaction between **2** and a specific substrate should depend on the initiator ionization potential.

The previous analysis characterizes the aminium salt initiated cyclopropanation reaction essentially as a cation radical chain carbene transfer to a substrate cation radical (Scheme 7). The further details of the reaction path, such as its concerted or stepwise nature, are less clear and cannot be unambiguously assigned at present. The product studies do, however, provide



Scheme 7

some valuable insights into some aspects of this reaction path. Especially interesting is the observation of 1,2-rearrangement (methyl migration) in the case of **9**. This competing reaction suggests that carbene transfer to the substrate cation radical ($9^{+\cdot}$) does not occur in a wholly concerted manner to give an intact cyclopropane cation radical, at least in these instances. Rather, an intermediate, either an acyclic propanediyl cation radical (**17**) or a long-bond cyclopropane cation radical (**18**), appears to be implied. Either of these might plausibly explain the observed competition between methyl migration and closure to a cyclopropane adduct. The choice between these two alternatives is influenced by the observation that cation radical carbene transfer reactions appear to be highly cyclopropane pericyclic when, as in additions to cisoid dienes such as **7**, either vinylcyclopropane or cyclopentene adducts could be formed. This selectivity appears most consistent with an intermediate which, at least for **7**, is at least not purely acyclic, but which maintains a significant interaction between the cation and radical sites. Nevertheless, the complexity of cation radical energy surfaces and the concomitant mechanistic diversity suggest that it is highly inappropriate to generalize the proposed mechanism or to be more precise about the nature or strength of the interaction between the cation and radical sites. The stereochemical information provided by the *cis*/*trans*-stilbene cyclopropanation study appears irrelevant to the pericyclic step, so that additional stereochemical studies will be of interest. It appears to follow from the tentatively proposed long-bond mechanism that suprafacial stereospecificity is the predominant expectation. Nevertheless, if the long bond is indeed weak, a small random stereochemical component may well be introduced in at least some systems as a result of thermal dissociation of the long bond, rotation and re-closure of the long bond. No information is available on the possible intervention of other intermediates, such as a diazonium cation radical (**19**), and such intermediates are not necessarily presumed here, i.e. concerted formation of a long-bond cyclopropane cation radical is most simply consistent with the present data.

The incorporation of pericyclic reactions into radical chain processes is one of the noteworthy features of cation radical chain pericyclic reactions, including the present cyclopropanation reaction. Detailed kinetic studies have previously established activation enthalpies of 0·8 and 1·8 kcal mol^{-1} for the pericyclic step of the cyclobutadimerization of *trans*-anethole and the Diels–Alder cyclodimerization of 1,3-cyclohexadiene.[5f] Presumably the constraints of radical chain processes militate against any propagation step with a barrier of more than a few kilocalories per mole.

EXPERIMENTAL

Analysis

Proton magnetic resonance (PMR) spectra were recorded in deuterated chloroform or carbon tetrachloride on either a Varian EM-390 spectrometer for routine spectra at 90 MHz or a Nicolet NT-200 multi-nuclear spectrometer for 200 MHz Fourier transform (FT) spectra and proton decoupling NMR studies. High-field and COSY (2D NMR) spectra were recorded on a General Electric GN-500 for 500 MHz FT spectra. PMR chemical shifts are reported as δ (ppm) downfield from an internal tetramethylsilane standard. Carbon magnetic resonance (CMR) spectra were determined in deuterated chloroform on either a Varian FT-80A for routine spectra or a Bruker WH-90 FT spectrometer for smaller amounts requiring a greater accumulation of transients for acceptable spectra. Again, chemical shifts are reported as δ (ppm) downfield from tetramethylsilane.

Low-resolution mass spectra (LRMS) were obtained on a DuPont 21-471 mass spectrometer. High-resolution mass spectra (HRMS) were recorded from a DuPont (CED) 21-110B mass spectrometer. Gas chromatography–mass spectrometry (GC–MS) was performed on a Finnigan El-Cl instrument using an SE-30 coated 50 m capillary column with helium as carrier gas. LRMS and GC–MS data processing was performed on an INCOS data system. .

Analytical GC analyses were obtained either on a Gow-Mac Series 550 gas chromatograph (thermal conductivity detection and helium as carrier gas) using a 4 ft × 1/8 in i.d. column of 5% OV-101 on Chromosorb P, or on a Varian Model 3700 gas chromatograph (flame ionization detector with nitrogen as carrier gas) using a 4 ft × 1/8 in i.d. column of 5% OV-101 on Chromosorb G-HP. Preparative GC was performed on the Gow-Mac instrument utilizing a 5 ft × 1/4 in i.d. column of 10% SE-30 on Chromosorb W. GC yields were calculated with the aid of a Hewlett-Packard 3390A reporting integrator (Gow-Mac GC) or a Varian SP4270 integrator (Varian GC). Capillary GC analyses were conducted on the same Varian Model 3700 gas chromatograph equipped with an SE-30 coated 25 m column.

Infrared (IR) spectra were recorded on a Beckman Acculab 7 infrared spectrometer using polystyrene film as a standard. Melting points were determined on a Mel-Temp capillary melting point apparatus. All melting points and boiling points reported are uncorrected.

UV–visible spectra and kinetic results were obtained on a Hewlett-Packard Model 8450A diode-array spectrometer equipped with an HP 98100A temperature controller and an HP 89101A thermostated cuvette holder (with a dry nitrogen purge and chilled water).

High-performance liquid chromatography (HPLC) was performed on a Waters Model 6000A solvent delivery system equipped with a Waters Model R401 differential refractometer.

Preparation of reagents and standards

The dichloromethane (DCM) (Aldrich, HPLC grade) used in these studies as a solvent was distilled from P_2O_5 (Aldrich) under dry nitrogen. It was then stored over 4 Å molecular sieves (Aldrich, 8–12 mesh) in an aluminium foil-wrapped round-bottomed flask. The flask was kept in a desiccator between uses.

Tris(*p*-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^{+\cdot}$) (Aldrich) was washed with anhydrous diethyl ether (Fisher) prior to its use to remove traces of acid. The tris(*p*-bromophenyl)aminium (**1**) (Aldrich) was recrystallized from hot ethanol and vacuum dried before use. All substrates and ethyl diazoacetate were of reagent grade (Aldrich).

Tris(2,4-dibromophenyl)amine (**5**) was prepared according to literature procedures.[21] The

white precipitate obtained was purified by Soxhlet extraction and recrystallized from ethanol: m.p. 214–216 °C (lit., 216–218 °C), $l_{max} = 301$ nm (lit., 301·5 nm).[21]

Tris(2,4-dibromophenyl)aminium hexachloroantimonate ($5^{+\cdot}$) was prepared according to a literature procedure.[22] The only modification was that the aminium salt was precipitated and washed with pentane rather than diethyl ether. The green crystals were stored in a light-proof bottle in a desiccator: $l_{max} > 800$ nm (lit.,[20] 880 nm).

Generalized aminium salt-initiated cyclopropanation procedure

To a flame-dried 10 ml round-bottomed flask containing a magnetic stirrer bar and with a dry nitrogen purge is added 0·3–0·5 mmol of the substrate to be cyclopropanated, a 3–4-fold excess of ethyl diazoacetate (ETDA) (Aldrich), and 3–5 ml of freshly distilled DCM via a syringe. The solution is cooled to 0 °C in an ice–salt bath while stirring. A sufficient portion of the aminium salt (10–40 mol-%) is added by spatula (or powder addition funnel, if available) in small portions. The nitrogen purge is used to exclude adventitious water during the additions of aminium salt. As a portion of the salt is added, decolorization of the salt and concurrent evolution of nitrogen bubbles (as a by-product of the cyclopropanation) from the solution will be observed as a positive sign of the desired reaction. When evolution of the nitrogen slows or ceases, a second portion of the salt may be added. The amount of salt ultimately added will depend on the efficiency of cyclopropanation.

Work-up proceeds as in other aminium salt-initiated reactions. The solution is quenched with the addition of a solution of sodium methoxide in methanol. More DCM is added to dissolve all of the products and the reaction mixture is extracted in a separating funnel successively with water, saturated sodium chloride solution and water. The DCM solution is then dried and filtered by passing it through a plug of cotton. The solution is concentrated on a rotary evaporator and the product mixture analyzed by GC using a 1 ft column of 5% OV-101 for separations.

The GC analysis (typically with a thermal gradient program from 100 to 250 °C at 25 °C min^{-1}) reveals that a successful cyclopropanation reaction shows a decrease or absence of starting olefin or diene, concurrent with a new peak(s) at longer retention times. However, these new products generally have shorter retention times than competing dimerizations or oligomerizations of the olefin or diene. The last component to elute generally is the tris(2,4-dibromophenyl)amine.

The GC analysis, if promising, is followed by preparative thin-layer chromatography (TLC) to remove both excess of ETDA and the free amine. (Some of the free amine can be removed by decanting the product mixture from the precipitated free amine. The insolubility of the free amine becomes evident as the solution is concentrated and subsequently cooled. In large-scale syntheses the recovered free amine can be recycled to the aminium salt.) The product usually runs at R_F values between that of the front-running free amine and the lagging ETDA. Isolation of the product fractions is effected by cutting the product-impregnated band of silica gel from the TLC plate and eluting the product from the silica gel with chloroform. Evaporation of the chloroform is followed by characterization with three or more of the following methods: PMR, COSY PMR, CMR, GC–MS, HRMS and IR.

In some cases, a comparative cyclopropanation reaction is run using a known catalyst for cyclopropanations with ETDA. The catalyst, rhodium(II)acetate, is known for carbene-type additions of ETDA; however, a major side-reaction to these reactions is coupling of ETDA carbenes to give both diethyl fumarate and diethyl maleate. This comparison is useful in determining the utility and scope of the cation radical cyclopropanation (CRCP) procedure.

Cyclopropanations of 2,3-dimethyl-2-butene (6)

As described in the generalized procedure above, 250 μl (2·13 mmol) of 2,3-dimethyl-2-butane, 880 μl (8·37 mmol) of ETDA, 12 ml of DCM and 665 mg (30 mol-%) of the aminium salt were combined and the reaction was initiated at 0 °C. The aminium salt was instantly decolorized together with the evolution of copious amounts of nitrogen. GC analysis (90–250 °C at 10 °C min^{-1}) of the reaction mixture shows one new product at a retention time of 1·77 min.

The work-up was as described above. Isolation of the product was performed by preparative GC on a 4 ft × 1/4 in i.d. SE-30 column at 80 °C (isothermal). Using exactly 33% of the homogeneous reaction mixture, the second GC fraction was collected as the product fraction, giving 50·0 mg of sample. In this way a projected isolated yield of 150·0 mg (41·95% yield) of a clear, mobile, pleasant-smelling oil was obtained. Analytical GC of this oil attested it to be greater than 95% pure. PMR and CMR spectra confirmed the identity of the product as ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate (**12**).

The product (9·1 mg, $5·345 \times 10^{-5}$ mol), once confirmed to be pure, was prepared as a solution with 3·1 mg ($2·01 \times 10^{-5}$ mol) of biphenyl (Eastman) as an internal standard. A GC detector response factor of 0·742 was determined for the cyclopropane ester relative to the biphenyl. This value was used to obtain a GC yield of 60·3% in a parallel run using 50 ml (0·421 mmol) of **10**, 176 ml (1·67 mmol) of ETDA, 2 ml of DCM and 443 mg (41 mol-%) of the aminium salt. The reaction in this case was initiated at −78% C and allowed to warm to 0 °C before GC analysis. PMR ($CDCl_3$): δ 4·025 (q, 2H, $J = 7·2$ Hz), 1·20 (t, 3H), 1·195 (s, 6H), 1·133 (s, 6H), 1·12 (s, 1H) (lit.[23]). CMR ($CDCl_3$): δ 172·08, 59·38, 35·7, 29·66, 23·41, 16·39, 14·24. HRMS: ($C_{10}H_{18}O_2$) *m/z* calculated 170·13067, measured 170·13103 amu, error 0·36/2·1 AMU ppm^{-1}. LRMS *m/z* [% of base peak (B)]: 170 [1·11 (*M*)], 125 (21·2), 109 (20·7), 97 (B, $-CO_2Et$), 55 (69·04).

Cyclopropanation of *cis*- and *trans*- stilbene (4)

As in the generalized procedure, 102 mg (0·566 mmol) of *cis*-stilbene (Aldrich), 250 μl (2·38 mmol) of ETDA, 3 ml of DCM and 230 mg (40 mol-%) of the aminium salt were combined and initiated at −78 °C, then allowed to warm to 0 °C. The aminium salt was gradually decolorized, followed by nitrogen evolution to given an orange–yellow solution. GC analysis (80)–250 °C at 10 °C min^{-1}) showed a new peak at a retention time of 12·94 min.

Work-up proceeded as usual, with isolation being performed by preparative TLC, using carbon tetrachloride–chloroform (4:1) to elute the sample. After stripping the isolated band of silica gel with chloroform, and subsequent evaporation of the solvent, 121·9 mg (80·8% yield) of a clear, mobile oil was isolated. This compound was identified by PMR, IR, LRMS and HRMS to be ethyl *trans*-2,3-diphenylcyclopropanecarboxylate (**11**).

In a parallel run, using 34 mg (0·189 mmol) of *trans*-stilbene (Aldrich), 80 μl (0·761 mmol) of ETDA, 2 ml of DCM and 79·6 mg (40 mol-%) of the aminium salt, combined and initiated at 5 °C, an identical product was obtained (established by GC spiking with the previously isolated sample). In addition, all of the starting *trans*-stilbene was completely gone. No attempt was made to isolate this product: PMR ($CDCl_3$): d 7·30 (s, 10H), 3·93 (q, 2H, $J = 7·5$ Hz), 3·20 (dd, 1H, $J = 5·25, 6·75$), 2·86 (dd, 1H, $J = 6·75, 9·8$), 2·25 (dd, 1H, $J = 5·25, 9·8$), 0·99 (t, 3H, $J = 7·5$ Hz). IR (CCl_4): 3075, 3040 cm^{-1} (cycloprop.−H), 2995 cm^{-1} (C−H), 1730 cm^{-1} (C=O); 1603 cm^{-1}, 1500 cm^{-1} (C=C, aromatic), 1180 cm^{-1} (C−O), 780 cm^{-1} (C−H, aromatic). LRMS: *m/z* (% of base peak): 266 [4·22 (*M*)], 237 (4·88), 221 (9·01), 193

(B), 115 (77·63), 91 (19·6). HRMS: ($C_{18}H_{18}O_2$) m/z calculated 266·13067 amu, measured 266·13030 amu, error −0·37/ −1·4 mamu ppm^{-1}.

Attempted cyclopropanation of cyclohexene

As in the generalized procedure, 18 μl (0·178 mmol) of cyclohexene (MCB), 75 μl (0·712 mmol) of ETDA, 1·5 ml of DCM and 47 mg (25 mol-%) of the aminium salt were combined and initiated at 0 °C. There was no decolorization of the aminium salt, and no apparant nitrogen evolution. GC analysis (100–250 °C at 10 °C min^{-1}) showed only starting material and the free amine.

Attempted cyclopropanation of ethyl vinyl ether

As in the generalized procedure, 25 μl (0·126 mmol) of ethyl vinyl ether (Aldrich), 94·5 μl (0·899 mmol) of ETDA, 2 ml of DCM and ca 35 mg (12·7 mol-%) of the aminium salt were combined and initiated at 0 °C. There was little apparent reaction from either visual or GC (100–250 °C at 10 °C min^{-1}) analysis.

Attempted cyclopropanation of phenyl vinyl ether

As in the generalized procedure, 20 μl (0·163 mol) of phenyl vinyl ether (PolySciences), 50 ml (0·475 mmol) of ETDA, 2 ml of DCM and ca 35 mg (20·4 mol-%) of the aminium salt were combined and initiated at 0 °C. There was decolorization of the aminium salt and some nitrogen evolution; however, GC analysis (80–250 °C at 10 °C min^{-1}) showed no evidence of any products, and the ETDA was significantly decomposed.

Attempted cyclopropanation of 1-methoxycyclopentene

As in the generalized procedure, 35 μl (0·30 mmol) of the vinyl ether,[24] 150 μl (1·425 mmol) of ETDA, 2 ml of DCM and 80 mg (40 mol-%) of the aminium salt were combined and initiated at 0 °C. Decolorization of the aminium salt and vigorous evolution of nitrogen occurred; however, GC analysis (100–250 °C at 25 °C min^{-1}) showed only long retention time, oligomeric (multiple, low-intensity) peaks and decomposition of the starting vinyl ether.

Attempted cyclopropanation of 1,1,2,2,-tetraphenylethene (TPE)

As in the generalized procedure, 63 mg (0·189 mmol) of tetraphenylethene (Commercial Organic Chemical), 100 μl (0·95 mmol) of ETDA, 2 ml of DCM and 80 mg (40 mol-%) of the aminium salt were combined and initiated at 5 °C. The aminium salt was instantly decolorized, being replaced by a deep purple color. In addition there was no nitrogen evolution from the reaction mixture. GC analysis (100–260 °C at 25 °C min^{-1}) confirmed that no products were formed and the starting materials remained intact. A UV–visible spectrum of the solution revealed the formation of a compound that has a maximum absorption at 480 nm and a weak broad absorption at ca 600 nm. This is in accord with cited values for the cation radical of 1,1,2,2-tetraphenylethene, which is a metastable species in DCM.[25]

Attempted cyclopropanation of 1,1,2,2-tetrachloroethene (11)

As in the generalized procedure, 35 μl (0·343 mmol) of the tetrachloroethene (J. T. Baker), 100 ml (0·95 mmol) of ETDA, 2 ml of DCM and 50 mg (15 mol-%) of the aminium salt were combined and initiated at −78 °C. No decolorization of the aminium salt or apparent nitrogen evolution occurred. No attempt at GC analysis was made.

Attempted cyclopropanation of phenyl vinyl sulfide

As in the generalized procedure, 20 μl (0·153 mmol) of phenyl vinyl sulfide (Aldrich), 50 μl (0·475 mmol) of ETDA, 2 ml of DCM and 40 mg (25 mol-%) of the aminium salt were combined and initiated at 0 °C. Decolorization of the aminium salt and nitrogen evolution occurred; however, GC analysis (80–250 °C at 10 °C min^{-1}) showed that the only peaks which appeared are at too long retention times (9–10 min) to be seriously considered as cyclopropanation products. No attempt was made at isolation.

Cyclopropanation of α-terpinene (7)

As in the generalized procedure, 500 mg (3·67 mmol) of **17** (Aldrich), 1·675 g (14·6 mmol) of ETDA, 5 ml of DCM and 1·932 g (50 mol-%) of the aminium salt were combined and initiated at −78 °C. Immediate decolorization of the aminium salt and vigorous nitrogen evolution were observed. The solution was allowed to warm to 0 °C to complete the reaction and then quenched and worked up in the usual way. GC analysis (100–250 °C at 20 °C min^{-1}) showed only two potential product peaks.

The products were isolated by flash chromatography on silica gel (Kieselgel 60, 230–400 mesh, EM Reagents) using carbon tetrachloride–chloroform (5:1). The second fraction (R_F 0·26) was collected as the product fraction. Capillary GC (100–250 °C at 20 °C min^{-1}) on a 25 ft SE-30 column showed that predominantly one isomer was collected. After evaporation of the solvent, 355 mg (43·5% yield) of a pale yellow oil were obtained. PMR analysis of product showed the presence of only one olefinic proton, which indicated selective cyclopropanation of one of the double bonds.

After PMR [200 MHz, 500 MHz (with COSY)], CMR and IR analyses, one isomer was characterized as the cyclopropanation product **13**. This regioisomer at the methyl-substituted double bond with an *anti* configuration (relative to the two protons on the cyclopropyl ring) was the only adduct eluted.

The GC response factor using 27·0 mg (0·1214 mmol) of the cyclopropyl compound and 19·5 mg (0·1094 mmol) of phenanthrene (Aldrich) was determined to be 0·8475 for the cyclopropane ester. A parallel run was carried out, using 30 ml (0·184 mmol) of **7**, 77·5 ml (0·737 mmol) of ETDA, 2 ml of DCM and 76 mg (40 mol-%) of the aminium salt. Utilizing the calculated response factor, a GC yield of 72·0% was obtained. PMR ($CDCl_3$): δ 5·63 (dd, 1H, J = 5·6 Hz, 1·0 Hz), 4·09 (mult./500 MHz), q, 90 MHz, 2H), 2·10 (septet, 1H, J = 6·9 Hz), 1·96 (m, 1H), 1·91 (m, 1H), 1·72 (m, 1H), 1·52 (m, 1H), 1·87 (d, 1H, J = 4·2 Hz), 1·73 (t, 1H, J = 3·2 Hz), 1·29 (s, 3H), 1·24 (t, 3H, J = 9·6 Hz), 0·94 (d, 3H, J = 2·1 Hz), 0·92 (d, 3H, J = 2·1 Hz). CMR ($CDCl_3$): 172·36, 141·94, 117·06, 60·14, 34·85, 29·30, 28·88, 28·49, 27·54, 23·08, 21·25, 20·83, 18·6, 14·41 HRMS: ($C_{14}H_{22}O$) m/z calculated 222·16197 amu, measured 222·16239 amu, error 0·42/1·9 mamu ppm^{-1}. LRMS: m/z (% of base peak) 222 [18·9 (M)], 149 (59·9), 105 (B), 93 (72). IR (CCl_4): 3050 cm^{-1} (cyclopropyl C−H), 2960, 2920, 2870 cm^{-1} (aliphatic C−H), 1725 cm^{-1} (C=O), 1155 cm^{-1} (C−O); 770 cm^{-1} (=C−H), *cis*); 1645 cm^{-1} (C=C, *cis*, v. weak).

Control experiments for the cyclopropanation of α-terpinene (7)

Addition of tris(2,4-dibromophenyl)amine.

As in the generalized procedure, 30 μl (0·1843 mmol) of α-terpinene, 77·5 μl (0·737 mmol) of ETDA, 132·4 mg (100 mol-%) of tris(2,4-dibromophenyl)amine, 77.6 mg (40 mol – %) of the aminium salt and 2 ml of DCM were combined and initiated at −78 °C. The aminium salt was decolorized and nitrogen evolution was observed. The reaction was run for 10 min and quenched, as in the generalized procedure. To the reaction mixture were added 14 mg (0·079 mmol) of phenanthrene as an internal standard. GC analysis (100–250 °C at 25 °C min^{-1}) produced a GC yield of 44·7%

*GC yield with tris(*p*-bromophenyl)aminium hexachloroantimonate.*

As in the generalized procedure, 30 μl (0·1843 mmol) of α-terpinene, 77·5 μl (0·737 mmol) of ETDA, 77·6 mg (40 mol-%) of tris(*p*-bromophenyl)aminium hexachloroantimonate (Aldrich) and 2 ml of DCM were combined and initiated at −78 °C and allowed to warm to 0 °C over a 10 min period. The decolorization of the aminium salt was slower than the corresponding experiment using the dibromophenylaminium salt, and evolution of nitrogen was not as vigorous. The usual quenching and addition of 20 mg (0·112 mmol) of phenanthrene, followed by GC analysis (100–250 °C at 25 °C min^{-1}), showed a 71·3% GC yield of the desired product.

*Addition of 2,5-di-*tert*-butylpyridine.*

As in the generalized procedure, 30 μl (0·1843 mmol) of α-terpinene, 77·5 μl (0·737 mmol) of ETDA, 23 mg (65 mol-%) of 2,5-di-*tert*-butylpyridine, 63 mg (42 mol-%) of tris(*p*-bromophenyl)aminium hexachloroantimonate (Aldrich) and 2 ml of DCM were combined and initiated at 5 °C. Decolorization of the aminium salt was slow and nitrogen evolution was decreased. The reaction was quenched after 10 min, and 11 mg (0·062 mmol) of phenanthrene were added. GC analysis (100–250 °C at 25 °C min^{-1}) produced a 3·8% GC yield of the desired product.

Attempted CRCP of 1,1,2,3,4,4-hexachloro-1,3-butadiene

As in the generalized procedure, 37 μl (0·236 mmol) of the hexachlorobutadiene (Aldrich), 100 ml (0·951 mmol) of ETDA, 75 mg (30 mol-%) of the aminium salt and 2 ml of DCM were combined and initiated at 0 °C. No decolorization or nitrogen evolution was observed. No attempt was made at GC analysis.

Synthesis of 3-methylcrotonaldehyde

A literature procedure was used to oxidize 3-methylbut-2-en-1-ol to the corresponding aldehyde.[26] To a flame-dried three-necked flask, equipped with a magnetic stir bar, a dry nitrogen purge (through a calcium chloride drying tube outlet) and an addition funnel were added 200 ml of dry DCM. The DCM was cooled to 0 °C in an ice-bath while 37·5 g (0·174 mol) of pyridinium chlorochromate (PCC)[27] were dissolved in the reaction flask. To the

addition funnel were added 30 ml of DCM and 10 g (0·116 mol) of 3-methylbut-2-en-1-ol (Aldrich). The alcohol solution was added quickly to the PCC solution with rapid stirring. The reaction was monitored by analytical GC (80 °C, isothermal), which showed the product at a retention time of 0·59 min.

The work-up proceeded by extraction with anhydrous diethyl ether (Fisher) and filtration of the solid residue and ether eluate through a plug of cotton. The ether was subsequently passed through a pad of Florisil and concentrated to a volume of ca 30 ml. Finally, distillation of the solution under a water aspirator vacuum (60–70 °C) gave 5·45 g (56% yield) of a yellow oil whose PMR spectrum was consistent with 3-methylcrotonaldehyde [lit.,[28] b.p. 66 °C (65 mmHg)]. PMR ($CDCl_3$: δ 9·91 (d, 1H), 5·82 (d, 1H), 2·19 (s, 3H), 1·97 (s, 3H).

Synthesis of 1,1-dibromo-4-methylpenta-1,3-diene (9)

A literature procedure[29] for the addition of the dibromomethylene unit was used . The reaction proceeded by adding 24·97 g (95·2 mmol) of triphenylphosphine (Aldrich), 11·55 g (47·6 mmol) of carbon tetrabromide (Eastman) and 200 ml of dry DCM to a flame-dried three-necked flask equipped with a magnetic stirrer bar and a dry nitrogen purge. This solution was stirred for 30 min while a solution of 2·0 g (23·8 mmol) of 3-methlycrotonaldehyde and 25 ml of DCM was prepared. The aldehyde solution was then syringed slowly into the red betaine solution, resulting in a deep red–brown solution in which a white precipitate (triphenylphosphine oxide) was readily visible. The solution was stirred for an additional 30 min.

Work-up proceeded by repeated extraction of the reaction solution (and the resulting solids) with portions of hexane. Concentration of the hexane extracts resulted in more of the by-product triphenylphosphine oxide, in addition to the unreacted triphenylphosphine, precipitating from the solution. In this way, three cycles of concentration, extraction and filtration gave a yellow oil after evaporation of the solvent. This oil was then flash chromatographed on silica gel (Kieselgel 60, 230–400 mesh, EM Reagents) using hexane as eluent. The product (R_F 0·41) was easily separated from the residual triphenylphosphine (R_F 0·16), giving 3·415 g (59·8% yield) of a mobile yellow oil. The PMR spectrum ($CDCl_3$) gave the expected proton absorptions for the dibromodiene, with no residual aldehyde: δ 7·1 (d, 1H, $J = 9·6$ Hz), 5·8 (br. d, 1H), 1·86 (s, 3H), 1·79 (s ,3H).

Cyclopropanation of 1,1-dibromo-4-methylpenta-1,3-diene (9)

As described in the generalized procedure, 225·0 mg (0·695 mmol) of **9**, 280 μl (2·66 mmol) of ETDA, 292 mg (40 mol-%) of the aminium salt and 8 ml of DCM were combined and initiated at 0 °C. The immediate decolorization of the aminium salt concurrent with vigorous evolution of nitrogen signaled a positive reaction. GC analysis (100–250 °C at 25 °C min^{-1}) showed that the starting diene (retention time 2·72 min) was gone and four new peaks appeared in a 22:15:14:48 ratio (retention times 3·85, 3·90, 4·28 and 4·48 min, respectively).

Work-up was as described in the generalized procedure. Isolation of the products was initiated by first passing the product mixture through a plug of silica gel (Aldrich, grade 12, 28–200 mesh) using hexane–ethyl acetate (5:1) to remove most of the unreacted starting materials, that is, the dibromodiene and the ETDA. A second chromatographic separation was done on silica gel using hexane–ethyl acetate (10:1) to isolate 193·5 mg (79·1% yield) of a light yellow oil. GC (as above) showed the four isomers to be the only compounds present. CG–MS

(100–260 °C at 25 °C min^{-1}; 25 ft SE-30 capillary column) showed that all four isomers had a parent ion of *m/z* 326 (one ^{81}Br present) in roughly equal proportions. The first two isomers showed the loss of the carbethoxy group as the first fragmentation, while the latter two isomers showed the loss of only the ethoxy radical as the first fragmentation. This product mixture was then further separated on a preparative TLC plate (Analtech, 2000 mm thickness, 200–400 mesh) using a carbon tetrachloride–chloroform (5:1) to isolate the first isomer in pure form. The other fraction was still a mixture of the four original isomers, although not much of the first isomer was present. The PMR and CMR spectra confirmed that the first isomer is the desired all *cis*-dibromomethylene cyclopropane (*cis*-**15**). The PMR and decoupled PMR (200 MHz) spectra indicated that the second isomer is the *trans*-dibromomethylenecyclopropane (*trans*-**15**) and the other two isomers are dienes in which the carbethoxymethylene component has been inserted at the 1-methyl and 1′-methyl positions [(*E*)-**16** and (*Z*)-**16**]. The ratio of cyclopropane to insertion products is 47:53 by capillary GC (as above). PMR ($CDCl_3$): *cis*-**16** δ 6·80 (d, 1H, $J = 8·4$ Hz), 4·13 (q, 2H, $J = 6·7$ Hz), 1·94 (t, 1H, $J = 8·4$ Hz), 1·83 (d, 1H, $J = 8·4$ Hz), 1·28 (t, 3H, $J = 6·7$ Hz), 1·27 (s, 3H), 1·24 (s, 3H), *trans*-**16** δ 6·16 (d, 1H, $J = 8·2$ Hz), 4·13 (q, 2H), 2·17 (dd, 1H, $J = 5·5$ and 8·2 Hz), 1·63 (d, 1H, $J = 5·5$ Hz); (*E*)-**17** δ 7·20 (d, 1H, $J = 8·62$ Hz), 5·93 (d, 1H, $J = 8·62$ Hz), 4·13 (q, 2H), 3·62 (q, 1H, $J = 7·36$ Hz), 1·76 (s, 3H); (*Z*)-**17** δ 7·13 (d, 1H, $J = 8·20$ Hz), 5·96 (d, 1H, $J = 8·20$ Hz), 4·13 (q, 2H), 3·19 (q, 1H, $J = 7·36$ Hz), 1·76 (s, 3H). CMR ($CDCl_3$; *cis*-**16** 170·47, 133·68, 89·04, 60·38, 35·48, 31·95, 28·41, 27·34, 14·29, 14·11, LRMS: *m/z* (% of base peak) 324 [4·63 (*M*)], 253 (B), 217 (34), 174 (71), 172 (73), 93 (61), 91 (55). HRMS: ($C_{10}H_{14}O_2Br_2$) *m/z* calculated 323·93604 amu, measured 323·936984 amu error 0·8/2·5 mamu/ppm^{-1}.

Cyclopropanation of *trans*-anethole (3)

To a solution of **2** (3·033 g, 26·6 mmol) and **3** (0·788 g, 5·32 mmol) in 10 ml of dry DCM at 0 °C was added $\mathbf{1}^{+\cdot}$ (0·412 g, 0·504 mmol; 9·5 mol-% of **3**) in 15 ml of dry DCM. The blue solution turned brown quickly. GC analysis showed that the cross cycloadducts were formed in a greater amount than the cyclodimer of **3**. The GC yield was 64·0% (corrected). After dry column chromatography on silica gel [Skelly B–ethyl acetate (3:1) as eluent] and preparative TLC [Skelly B–ethyl acetate (3:1) as eluent] the isomer mixture was subjected to preparative GC, which yielded **10**, with a greater than 95:5 *anti*:*syn* ratio. PMR ($CDCl_3$): δ 7·2–6·79 (q, 4H), 3·87 (q, 2H), 3·77 (s, 3H), 2·29 (dd, 1H), 2·12 (dd, 1H), 1·76 (dd, 1H), 1·26 (d, 3H), 1·05 (t, 3H). CMR ($CDCl_3$: 171·0, 158·2, 130·1, 128·7, 113·3, 60·1, 55·2, 33·6, 30·0, 19·8, 17·7, 14·1. IR ($CDCl_3$): 1720 cm^{-1} (C=O). HRMS for $C_{14}H_{18}O_3$: *m/z* (calculated) 234·125585 amu, *m/z* (measured) 234·125895 amu, error 0·31/1·32 mamu ppm^{-1}.

Cyclopropanation of 2,5-dimethyl-2,4-hexadiene (8)

To a solution of **2** (1·512 g, 13·2 mmol) and **8** (1·734 g, 15.7 mmol) in 6 ml of dry DCM at 0 °C was added $\mathbf{1}^{+\cdot}$ (1·098 g, 1·34 mmol; 8·6 mol-% of **8**) in 20 ml of dry DCM. The product isomer mixture was isolated in a yield of 67·3% using dry column chromatography.

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