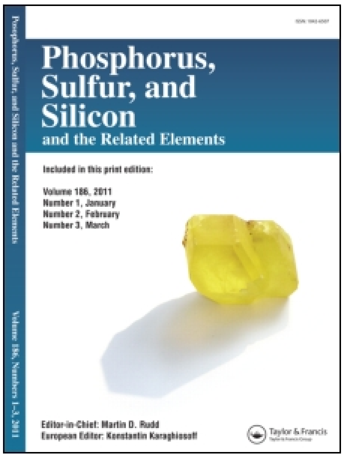

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Microwave-Assisted Reaction of Dimethyl H-Phosphonate with Cyclohexene and Alkene Oxides

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Microwave-assisted reaction of dimethyl H-phosphonate with cyclohexene-, 1,2-butene-, and 1,2-decene oxides furnishes 8, 5, and 17 compounds, respectively. The probable mechanism of the formation of the various compounds via free radical reactions and their GC-MS characterization are presented in this article.

Keywords Butyl and decyl derivatives; cyclohexyl; deoxygenation; diastereomeric phosphonates and pyrophosphates; dimethyl H-phosphonate; free radical reaction; mass spectral breakdown behavior

INTRODUCTION

Oxiranes comprise an extremely versatile group of highly useful intermediates and as such have attracted considerable interest.[1] Because of their ready availability and exceptional reactivity, the epoxides have found varied applications as a versatile functional group in synthetic organic chemistry. The oxirane ring can be opened under almost all conditions: electrophilic, nucleophilic, neutral, gas-phase, thermal, and free radical conditions. An excellent review on the preparation and synthetic applications of the oxiranes has appeared.[1f] Figure 1 shows various modes of the cleavage of the oxirane ring.[1a] Recently we investigated the free radical cleavage of styrene oxide with trifluoromethylthiocopper and reported the formation of products arising from the C—C and C—O bond fissions.[2] However, their use in the reactions with phosphorus compounds has found only a limited number of applications including their routine utilization in the Michaelis–Becker reaction to prepare phosphinates.[3,4] Thus, phosphorus azide reacted with propylene oxide

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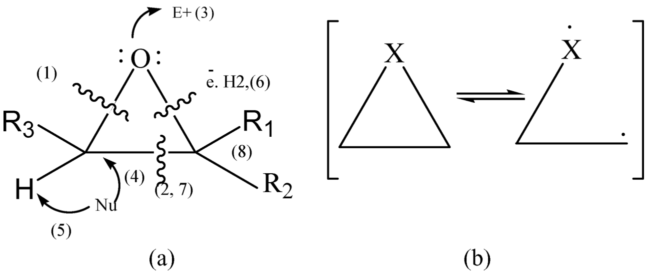

FIGURE 1 (A) Types of oxirane cleavages and reactions: (1, 2): homolytic cleavages (free radical, photolytic, thermal), (3): electrophilic attack on oxygen of the ring, (4): nucleophilic attack on the ring carbon, (5): nucleophilic attack on ring hydrogen, (6): reactions with electrons and on the surface, (7): cycloadditions, (8): reactions of the substituents. (B) hybrid structures of oxirane and thiirane (X = S or O).

to furnish cyclic oxazaphoranes as well as acyclic compounds.[5] Also, the in situ–formed, highly reactive metaphosphates have been described to open the oxirane ring to yield isomeric 1,3,2-dioxaphospholane-2-oxide derivatives.[6]

The in situ–generated energy from microwaves has been used to induce chemical reactions. This type of energy transformation depends on the molecular properties of the reacting species.[7] Due to the advent of commercially available household microwave cookers, the microwave process is finding increasing and interesting applications in synthetic organic chemistry.[8, 9a] The popularity of microwave-induced chemistry appears to rest primarily on its dramatic reduction of the reaction time and the possibility of carrying out neat reactions in "dry media" (solid phase). In fact, the latter appears to have significantly contributed to its enhanced usage.[9] The use of dielectric solvents seems to facilitate the transfer of the in situ–generated thermal energy to chemical reactants.[9b]

We became interested in adopting microwave chemistry for two reasons, namely the possibility of micro-scale chemistry and reduction and/or elimination of the generation of the hazardous waste during the normal work-up and its consequent disposal problems.

In continuation of our interest in the chemistry of the oxirane cleavage reactions,[10] the microwave-assisted oxirane ring opening, and our desire to explore the potential use of inexpensive epoxides in the decontamination and destruction of the chemical warfare agents such as the mustard gas and organophopshporus agents,[11a] the reaction of the oxirane ring of cyclohexene-, 1,2-butene-, and 1,2,-decene oxides with dimethyl H-phosphonate (1) has been examined and observed to lead to the formation of unusual ring cleavage products. This article describes the nature of the compounds thus formed, the probable mechanism of their formation, and GC-MS characterization.

RESULTS AND DISCUSSION

H-phosphonates have attracted considerable attention and have found useful applications in phosphorylation reactions.[4, 12] The presence of the readily removable hydrogen at the phosphorus center of the H-phosphonates appears to be the genesis of its reactivity.[13] In this context, it is worth mentioning that the P-H bond is rather a weak bond and readily lends itself to homolytic cleavages.[14a] In addition, H-phosphonates are known to be involved in addition reactions to (i) multiple bonds,[14a] (ii) carbonyl group,[14b] and (iii) in trans-esterifications.[14c] Dealkylations have also been noted.[14b] Both P–O and C–O bond cleavages have been observed.[14d] Methyl radicals have been stated to react with trimethylphosphite, albeit sluggishly, to give trimethylphosphonate.[15]

Deoxygenation of organic peroxides with phosphites has been recorded.[16] However, epoxides have also been stated to remain unaffected in the presence of phosphites.[17] It has also been stated that phosphites deoxygenate epoxides to furnish alkenes.[18] Thus, there seems to be some contradiction regarding the reaction of epoxides with phosphites. Phosphorus-stabilized carbanions are said to give various products on reacting with oxiranes. Thus, the formation of alkenes, cyclopropanes, and ketones has been rationalized.[19a] Significant formation of the ketones was observed via hydrogen migration.[19b] However, the treatment of styrene oxide with benzylidene trimethylphosphorane yielded (2-phenylethyl)ketone as the minor product and cis- and trans-1,3-diphenylpropene as the major product.[19b] With methylene triphenyl-phosphorane, styrene oxide gave a ketone and triphenylphosphine. The reaction of styrene oxide with ethoxycarbonyl triphenylphosphorane has been reported to give cyclopropanoids.[19d–19e] Three different types of P-centered radicals have been described.[4] Because of the multiple valence states of P, various types of P-centered radicals are frequently encountered. Added to this is the stability of the P-centered radicals.[13] Thus, these properties appear to enhance the reactivity of 1. In the present work, the reaction of H-dimethylphosphonate (**1**) with cyclohexene-, 1,2-butene-, and 1,2-decene oxides, has been examined and the results thus obtained are presented and discussed below.

REACTION OF CYCLOHEXENE OXIDE (2) WITH H-DIMETHYLPHOSPHONATE (1)

Microwave-assisted reaction of cyclohexene oxide (**2**, Figure 2) with dimethyl H-phosphonate (**1**) has now been investigated and found to furnish eight compounds excluding the starting materials. H-dimethylphosphonate (**1**) itself gives rise to trimethylphosphate (3). There is nothing unusual about this,[4] for such compounds are usually formed during the oxidation and/or free radical reactions of dimethyl H-phosphonate (**1**). Six of the compounds have both the cyclohexyl- and phosphorus-containing moieties, while one contains only the phosphoryl group, and the remaining one has only the cyclohexyl entity. It appears that the compounds identified herein are formed via non-specific free radical processes. Figure 3 attempts to describe the probable mechanism of formation of compounds described in the narrative. Table I discusses their GC-MS characterization based on their fragmentation behavior.

The dimethylphosphoranyl radical formed from dimethyl H-phosphonate (**1**) attacks the cyclohexene oxide (**2**) to yield the cyclohexyl radical intermediate (**11**), which abstracts hydrogen to give O-cyclohexyl-O,O'-dimethylphosphate (**12**). The latter in turn splits off a methylene moiety to form O-cyclohexyl-O-methylphosphate (**4**). Compound 1 itself can give rise to methyl and phosphoryl radical intermediate (cf. Figure 3). The methyl radical attacks **2** to give 2-methoxycyclohexyl radical intermediate (**14**), which loses hydrogen to yield 2-methoxy-1-cyclohexene (**5**). Or, the methyl radical can react with the diradical (**2A**) formed from cyclohexene oxide (**2**) and then give **5**. The involvement of such diradical species from the

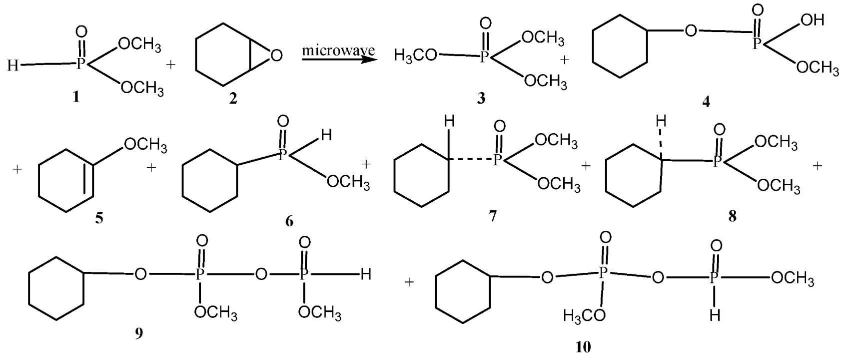

FIGURE 2 Microwave catalyzed reaction of cyclohexene oxide with $(H_3CO)_2P(O)H$.

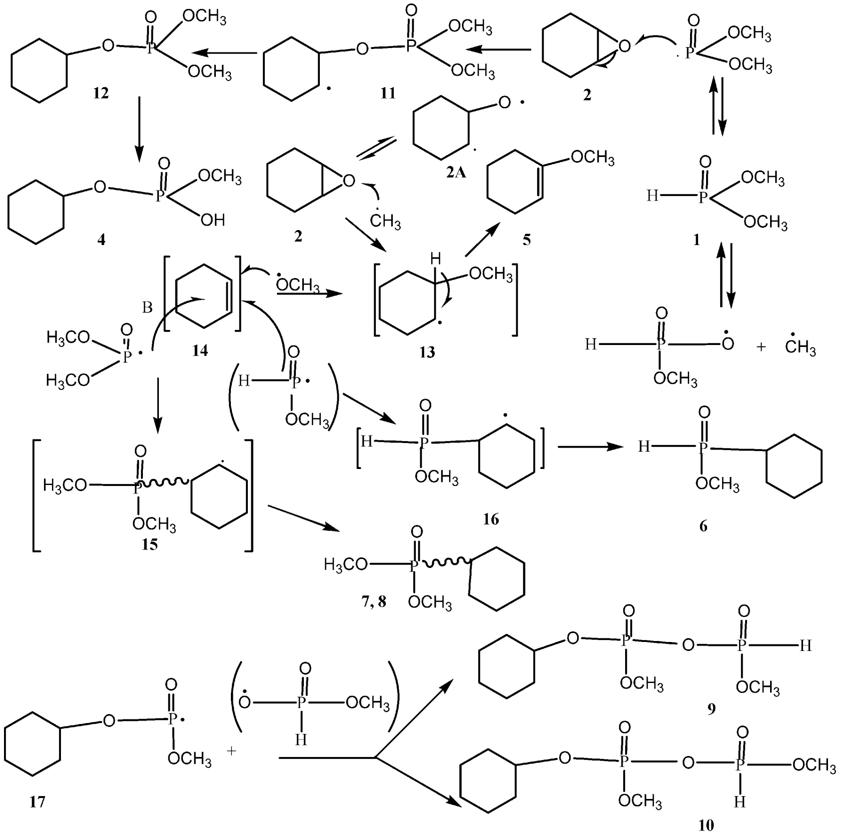

FIGURE 3 Probable mechanism of formation of compounds cited in the text.

homolytic fission of the oxirane ring has been previously described.[21] It is conceivable that deoxygenation of **2** can lead to cyclohexene (**13**), which then reacts with the methoxyl radical formed from **1** and gives intermediate **14**. The latter, as stated earlier, fragments off hydrogen to finally furnish compound **5**. The phosphinyl radical formed along with the methyl radical can add to **13** to yield cyclohexyl O-methyl H-phosphonyl radical intermediate (**16**). The latter then abstracts hydrogen and forms cyclohexyl-O-methyl H-phosphinate (**6**). The dimethylphopshoranyl radical formed from **1**, in principle, can attack **13** either from top side or from below to yield dimethylphosphoranyl cyclohexyl radical (**15**), which in turn abstracts hydrogen and forms the two isomeric compounds, **7** and **8**. Compound **6** undergoes homolytic α-fission to form the O-cyclohexyl-O-methylphosphoranyl radical (**17**). The intermediate **17** reacts with methyl H-phosporanyl radical

TABLE I Mass Spectral Fragmentation of Compounds Described in Figure 1

1. Dimethyl hydrogenphosphonate (**1**): ($M^+ = 110$).
2. Cyclohexene oxide (**2**): ($M^+ = 98$).
3. Trimethylphosphate (**3**): ($M^+ = 140$).
4. Cyclohexyl methylphosphoric acid (**4**): $M^+ = 194$ (r. t. = 8.57 min, 1.8%); 166 ($M-C_2H_4$); 151 ($166-CH_3$); 137 ($M-C_4H_9$); 123 ($137-CH_2$); 113 ($M-C_6H_9$); 98 ($M—PO_3CH_5$); 97 (113-O, 100%); 79 (C_6H_7); 70 (C_5H_{10}); 57 (C_4H_9); and 47 (PO).
5. 1-Methoxy-l-cyclohexene (**5**): $M^+ = 112$ (r. t. = 871 min, 0.4%); 97 ($M-CH_3$); 84 ($M-C_2H_4$); 80 (C_6H_8); 79 (C_6H_7 or 97 - H_2O); 77 (C_6H_5); 70 (C_5H_{10}); 69 (C_5H_9); 55 (C_4H_7) and 53(C_4H_5).
6. Cyclohexyl -O-methyl hydrogenphophinate (6): $M^+ = 162$ (r. t. = 8.77 min, 2.6%); 134 ($M-C_2H_4$); 121 $M-C_3H_5$); 112 ($C_7H_{12}O$); 106 ($M-C_4H_8$); 97 ($112—CH_3$); 83 (C_6H_{11}); 80 [$PH_2(O)(OCH_3)$]; 79 (C_6H_7); 70 (C_5H_{10}); 69 (C_5H_9); 57 (C_4H_9); and 47(PO).
7. O-Cyclohexyl-O,O-dimethylphophate (**7**): $M^+ = 208$ (r. t. = 9.39 min, 0.3%); 153 ($M-C_4H_7$); 127 [$PH(O)(OH)(OCH_3)_2$ 100%]; 109 [($P(O)(OCH_3)_2$)]; 99(M $C_6H_{11}O$); 95 [($P(O)(OH)(CH_3)$)]; 83 (C_6H_{11}); 79 (C_6H_7); 69 (C_5H_9); 57 (C_4H_9) and 47 (PO).
8. Cyclohexyl-O,O-dimethylphophonate (**8**): $M^+ = 208$ (r. t. = 9.48 min, 2.8%); 153($M-C_4H_7$); 127 [$PH(O)(OH)(OCH_3)_2$]; 113 ($C_7H_{13}O$, 100%); 99 ($C_6H_{11}O$); 95 [$P(O)(OH)(OCH_3)$)]; 83 (C_6H_{11}); 79 (C_6H_7); 69 (C_5H_9); 67 (C5H7); 55 (C_4H_7) and4 (PO).
9. O-Cyclohexyl -O,O'-dimethylhydrogenpyrophophate (**9**): $M^+ = 272$ (r. t. = 12.12 min, 2.1%); 271 (M−H); 193 [M-$PH(O)(OCH_3)$]; 191 (193—2H);); 176 [$C_6H_{11}OP(O)OCH_2$)]); 97 [PH_2 $(O)OH(OCH_3)$, 100%]; 81(C_6H_9);; 79 (C_6H_7); 70 (C_5H_{10}) and 47(PO).
10. O-Cyclohexyl -O,O'-dimethylhydrogenpyrophophate (**10**): $M^+ = 272$ (r. t. = 12.22 min, 2.0%); 271 (M−H); 193 [M -$PH(O)(OCH_3)$]; 191 (193—2H);); 176 [$C_6H_UOP(O)OCH_2$)]); 97 [PH_2 $(O)OH(OCH_3)$, 100%]; 81(C_6H_9);; 79 (C_6H_7); 70 (C_5H_{10}) and 47 (PO). Isomer of 9 and fragmentation is strikingly similar to 9.

to give rise to another pair of diasteremeric compounds **9** and **10** (cf. Figure 3). Since the mixed pyrophosphate derivatives **9** and **10** are formed in almost equal amounts, it would be safe to assume that both are present in the reaction mixture to the same extent. They are diastereomers. What is unusual about the reaction described above is the non-specific nature of radical formation processes from the homolytic fission of dimethyl-H-phosphonate.

Reaction of 1,2-Butene Oxide (18) with H-Dimethylphosphonate (1)

The microwave-assisted reaction of 1,2-butene oxide (**18**) with H-dimethylphosphonate (**1**) gives five compounds (Figure 4). Three of them have both the alkyl- and phosphorus-containing moieties, while the remaining two compounds possess only

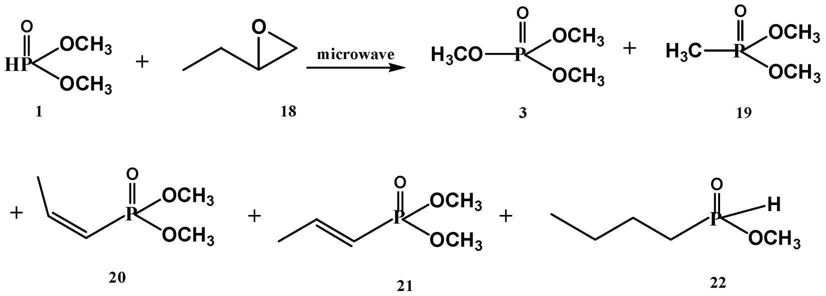

FIGURE 4 Reaction of 1,2-butene oxide (**18**) with demethyl H-phosphonate (**1**).

the latter group. The three compounds having both groups are (i) 1-(cis-2-propenyl)dimethylphosphonate (**20**), (ii) 1-(trans-2-propenyl)dimethylphosphonate (**21**), and (iii) n-butyl hydrogen methylphosphinate (**22**). There is nothing unusual about the presence of compounds **3** and **19**, for such compounds are usually formed during the oxidation and/or free radical reactions of dimethyl H-phosphonate (**1**).[4] Trimethylphosphonate (**19**) arises from the reaction of the methyl radical with the phopshoryl radical. It appears that the compounds identified herein are formed via free radical processes.

The oxirane-diradical equivalent[20] (**18A**) of 1,2-butene oxide (**18**) reacts with the phosphoryl radical, which is itself formed from the homolytic cleavage of the P—H bond of **1** to give intermediate **23**. The latter splits off formaldehyde (CH_2O) to form the propyl radical intermediate (**24**), which goes on to lose hydrogen and to yield cis- and trans-isomers, **20** and **21**. The substrate (**18**) undergoes deoxygenation during the course of the reaction to give 1-butene (**25**), which then reacts with methyl H-phosphinyl radical and forms the intermediate **26**. The latter abstracts hydrogen and gives n-butyl O-methyl H-phosphinate (**22**). The lower part of Figure 5 describes the free radicals formed from **1**. Table II describes the mass spectral breakdown of compounds cited in Figure 4.

Reaction of H-Dimethylphosphonate (1) with 1,2-Decene Oxide (27)

Figure 6 describes the products formed from the reaction of **1** with 1,2-decene oxide (**27**). This reaction is highly complex and gives rise to 17 compounds formed from the fragmentation of two and four carbon moieties, a pair of rearranged epoxides, a deoxygenation product, the compounds formed from free radical attack on the oxygen of the oxirane

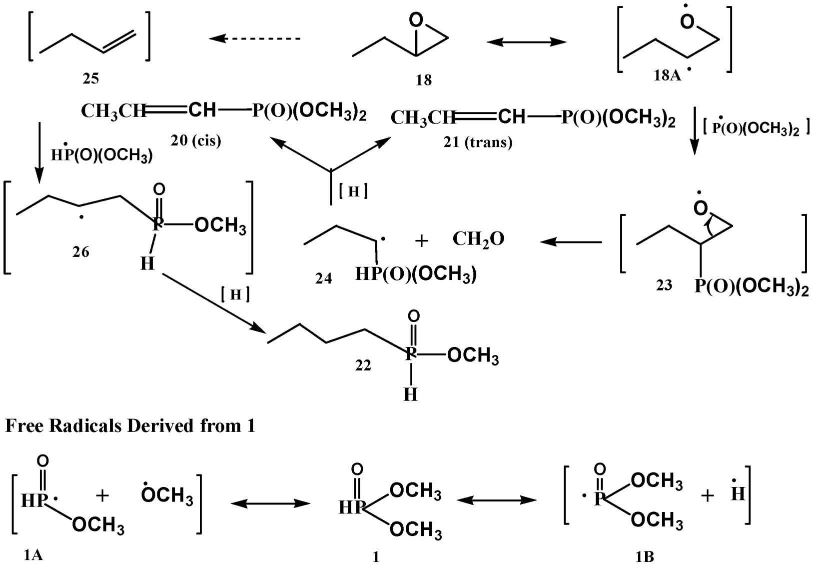

FIGURE 5 Probable mechanism of the formation of compounds (**5**, **6**, and **7**).

ring, the cleavage of the oxirane ring, etc (cf. Figure 6). Included in the above list are (i) hexane (**28**, M$^+$ = 86, 1.1%, r.t. = 1.61 min) and (ii) hexene (**29**, M$^+$ = 84, 1.1%, r.t. = 1.68 min), which are considered to

TABLE II Mass Spectral Fragmentation of Compounds Described in Figure 4

1. 1,2-Epoxybutane (**18**): M$^+$ = 72 (8.3%, r.t. = 1.62 min); 71 (M−H); 57 (M−CH_3, 100%); 55 (C_3H_3O or M−OH) and 45 (C_2H_5O or M−C_2H_5).

2. $P(O)H(OCH_3)_2$ (**1**): M$^+$ = 110 (78.7%, r.t. = 2.44 min).*

3. $P(O)CH_3(OCH_3)_2$ (**19**: M$^+$ = 124 (78.7%), 0.2%, r.t. = 3.01 min).*

4. $P(O)(OCH_3)_3$ (**3**): M$^+$ = 140 (1.2%, r.t. = 3.42 min).*

5. O, O-Dimethyl cis-propenylphosphonate (**20**): M$^+$ = 150 (0.3%, r.t. = 3.74 min); 135 (M−CH_3); 123 (M−C_2H_3); 121 (135—CH_2). 120 (M−OCH_2); 110 (M−C_3H_4). 105 (120—CH_3); 96 [PH(0)(OH)(OCH_3), 100%] 91 [$C_3H_8P(O)$]; 89 (C_3H_6PO); 79 [PH(O)(OCH_3)]; 65 [P(O)H(OH)]; 62 [P(O)CH_3]; 55 C_4H_7); 53 (C_4H_5) and 47 (PO).

6. O, O-Dimethyl trans-propenylphosphonate (**21**): M$^+$ = 150 (9.7%, r.t. = 3.70 min); 135 (M -CH3); 123 (M−C_2H_3); 121 (135—CH_2). 120 (M−OCH_2); 110 (M−C_3H_4). 105 (120—CH_3); 96 [PH(O)(OH)(OCH_3), 100%] 91 [$C_3H_8P(O)$]; 89 (C_3H_6PO); 79 [PH(O)(OCH_3)]; 65 [P(O)H(OH)]; 62 [P(O)CH_3]; 55 C_4H_7); 53 (C_4H_5) and 47 (PO).

7. n-Butyl O-methylphosphinate **22**): M$^+$ = 136, (1.8%, r.t = 3.94 min); 135 (M−H); 121 (M -CH_3); 107 (M−C_2H_5, 100%); 106 (M−OCH_2 or 107−H).; 89 (C_3H_6PO); 79 (M−C_4H_7); 65 [P(0)H(OH)]; 54 (C_4H_6); 48[P(O)H]) and 47 (PO).

*Mass spectral breakdown has been previously described (cf. Ref. 20).

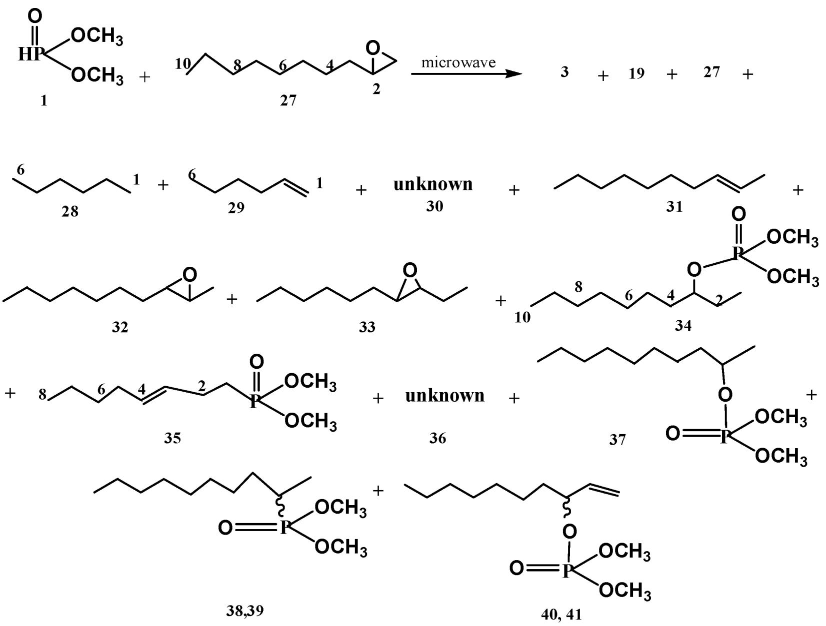

FIGURE 6 Reaction of 1,2-epoxydecane with dimethyl H-phosphonate.

have been formed from the fission of the carbon–carbon bond of the alkyl chain of the substrate, followed by hydrogen abstraction and loss of hydrogen respectively (cf. Figure 7).

Of the remaining 15 compounds, two components, namely **3** and **19**, are derived from **1**, and their origin has previously been described.[11a-b, 21] Six compounds, namely **28–33**, originate from the substrate (**27**). The origin of compounds **28** and **29**, as implied earlier, is ascribed to the β-fission of **31** and to the formation of the hexyl radical (cf. Figure 7). The correct structures of **30** and **36** could not be ascertained with certainty from their mass spectra (both EI and CI-modes), for they undergo extensive degradation before their molecular ions are recorded. Compound **31** arises from the deoxygenation of **27** and migration of the double bond from C_1 to C_2. Or, it could have been formed from deoxygenation of **32** as suggested below. The presence of 2,3- and 3,4-decene oxides (**32** and **33**) is attributed to the rearrangement of the substrate, namely **27**. This observation is supported by the characterization of three components, all exhibiting the same molecular weight of 156: (i) r.t. = 5.63 min, 0.4%, (ii) r.t. = 5.92 min, 0.2%, and (iii) r.t. = 6.24 min, 0.4%. These are considered to be isomeric decene oxides. They exhibit similar peaks corresponding to the same m/e ions, though

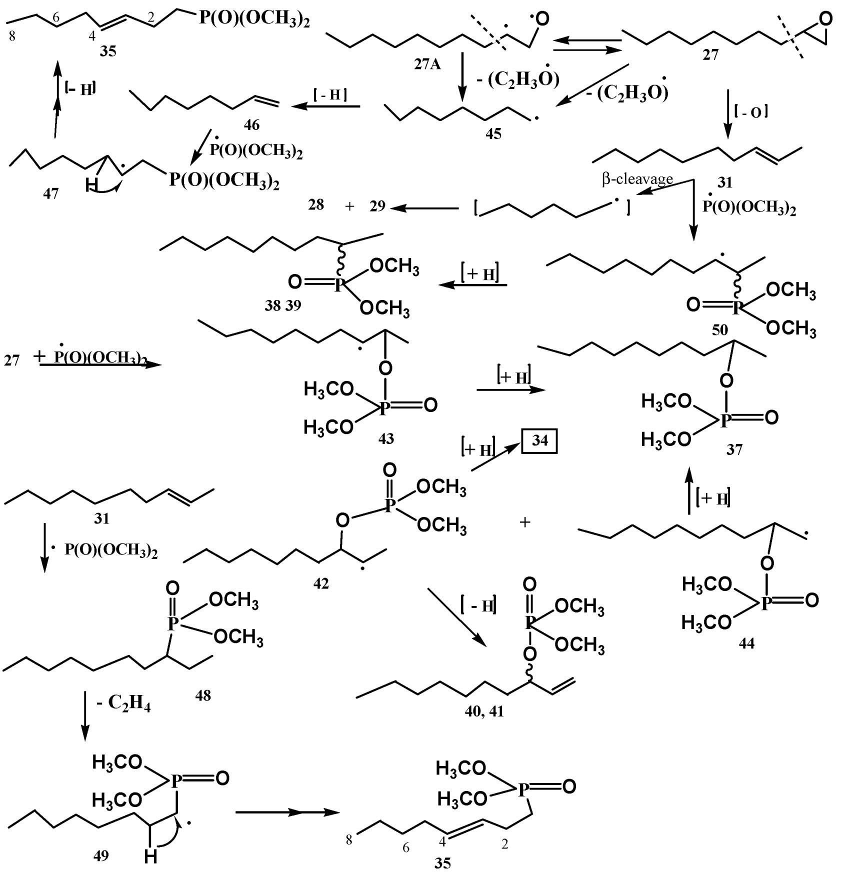

FIGURE 7 Probable mechanism of formation of compounds cited in Figure 6.

of differing intensities. They are presumed to have been formed either during the course of the reaction or on the gas-chromatographic column. These are known rearrangement reactions of the oxiranes. This suggestion is supported by published reports.[1,11a–b,21]

In principle, deoxygenation of **27** should yield 1-decene, while deoxygenation of 2,3-decene oxide (**32**) ought to give 2-decene (**31**). The former has a mono-substituted carbon–carbon double bond, while latter has a disubstituted bond. The latter, being more stable than the former, is easily formed. Compounds **34** and **37** are formed from the attack of the phosphoryl radical on the oxygen of the epoxides, **32** via intermediates **42** and **43**, followed by hydrogen abstraction. Similar observations have been previously described.[21] A second pathway for

37 starts from **27**. The attack of the phosphoryl radical on the oxygen of **27** leads to the intermediate **44**, which then abstracts hydrogen and furnishes **37**.

The loss of hydrogen from intermediate **42** leads to a pair of diastereomers, namely **40** and **41**. It then remains for us to rationalize the origins of **35**, **38**, and **39**. Two options can be advanced to explain the formation of **35**. First, **27** undergoes α-cleavage as shown by the dotted line to yield octene (**46**) via the octyl radical (**45**). The reaction of the phosphoryl radical with **46** gives radical intermediate **47**, which through hydrogen migration and elimination yields **35**. The second option involves the reaction of the phosphoryl radical with 2-decene (**31**) to form intermediate **48**. The latter fragments off a C_2H_4 moiety and forms intermediate **49**, which eventually leads to **35**. The formation of the diastereromeric pair, **38** and **39**, is ascribed to the reaction of the phopshoryl radical with **31** to give intermediate **50**, which then abstracts hydrogen and yields the pair of diastereomers. Thus, pathways have been proposed to rationalize the presence of the two pairs of the diastereomers, namely **38–41** (Figure 7).

The mass spectral fragmentation of **28** and **29** is straightforward. The mass spectral breakdown behavior of aliphatic oxiranes using labeled precursors and substrates has shown that frequently isomeric fragments appear in their mass spectra.[22a] Three types of fissions—single bond cleavages, rearrangement reactions such as “inside McLafferty” and “outside McLafferty,” and transannular fissions—usually observed in the mass spectra of the epoxides have been discussed in detail.[22b] The noticeable feature in the mass spectrum of **32** is the presence of ions m/e = 141 and 111, which corresponds to ($M–CH_3$) and ($M–OC_2H_5$) entities. Compound **33** shows ions m/e = 99 ($M–OC_3H_5$) and m/e = 86 ($M–OC_4H_6$). 1,2-Epoxydeacne (27) forms about 50% of the reaction mixture and has the most intense peak at m/e = 71 [(C_5H_{11}) or (C_4H_7O)]. The presence of two ions, m/e = 171 ($M–C_2H_5$) and m/e = 71 (C_4H_7O) fragments, supports this inference. The mass spectra of **1**, **3**, and **19** have been previously described.[21, 23]

Compounds **34** and **37** are isomers with $M^+ = 266$. The mass spectrum of **34** has three characteristic ions: m/e = 141 [$M–OP(O)(OCH_3)_2$], m/e = 79 ($PH(O)(OCH_3)$, and m/e = 97 C_7H_{13}). While that of **37** has m/e = 157 [$M–P(O)(OCH_3)_2$], m/e = 125 [$P(O)(OCH_3)_2$], and m/e = 69 (C_5H_9). The mass spectra of **38** and **39** are almost identical. They are stereomers having $M^+ = 250$. This suggests that they have one oxygen atom less than compounds **34** and **37**. Compound **36** has four prominent ions in its partial mass spectrum: m/e = 137, 113, 113, and 85 corresponding to [$C_6H_4P(O)(OCH_3)_2$], (C_8H1_7), [$P(O)(OCH_3)_2$], and (C_6H_{13}) fragments, respectively. Since it degrades rapidly before its

M^+-ion gets recorded under both EI- and CI-modes, its structure could not be identified. Compound **35** contains a C_8-chain (octyl moiety) instead of the decyl chain. As stated elsewhere, its origin can be attributed two sources. It can arise from the addition of the phosphoryl moiety to octene (**46**). This inference derives its support from a precedent.[21] The mass spectra of **40** and **41** exhibit similar breakdown behavior. Both fragment off $[OP(O)(OCH_3)_2\}$ moiety and similar fissions of the alkyl chain. Additional details on the mass spectral breakdown behavior of the compounds cited in Figure 6 are given in Table III.

EXPERIMENTAL

Stoichiometric amounts of the respective reagents were mixed in glass vials or 5 mL ground joint round bottom flasks and tops, vigorously shaken on a vibro-mixer and heated in the microwave oven for a specified period. The reaction mixture was allowed to come to ambient temperature; the cooled product was first analyzed by gas chromatography and then subjected to GC-MS analysis. All solvents were dry and freshly distilled prior to use. Mass spectra were obtained using a Finnigan TSQ-7000 GC/MS/MS equipped with a 30 m × 0.25 mm i.d. DB-5 capillary column (J and W Scientific, Folsom, CA) or a Finnigan 5100 GC/MS equipped with a 15 m × 0.25 mm. i.d. Rtx-5 capillary column (Restek, Bellefonte, PA). The conditions on 5100 were: oven temperature 60–270°C at 10°C/min, injection temperature was 210°C, interface temperature 230°C and scan time 1 sec, electron energy 70 eV, emission current 500 μA. The conditions on the TSQ-7000 were oven temperature 60–270°C at 15°C/min, injection temperature 220°C, interface temperature 250°C, source temperature 150°C, electron energy 70 eV (EI) or 200 eV (CI) and emission current 400 μA (EI) or 300 μA (CI), and scan time 0.7 sec. Data were obtained in both the electron ionization mode (range 45–450 da) and chemical ionization mode (mass range 60–450 da). Ultrahigh purity methane was used as the CI agent gas with a source pressure of 0.5 Torr (5100) or 4 Torr (TSQ-7100). Routine GC analyses were accomplished with a Hewlett-Packard 5890A gas chromatograph equipped with a J and W Scientific 30 m × 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA).

Microwave-Assisted Reaction of Cyclohexene Oxide (2) with H-Dimethyl-phosphonate (1)

Stoichimetric amounts of H-dimethylphosphonate (**2**) and cyclohexrene oxide (**2**) were mixed in a glass vial or glass joint round bottom flask (**5** mL). The mixture was shaken for a few minutes using the

TABLE III Mass Spectral Fragmentation of Compounds Cited in Figure 6

1. Hexane (**28**): $M^+ = 86$ (100%) [1.1%, r.t. = l. 40 min]; 74 ($M{-}CH_2$) and 71 ($M{-}CH_3$).
2. Hexene (**29**): $M^+ = 84$ [0. 3%, r.t. = l. 69 min]; 83 (M−H.); 70 ($M{-}CH_2$); 69 ($M{-}CH_3$,100%); 68 (69- H) and 65 (C_5H_5).
3. Unknowm (30): M^+ = not recorded), (0.1%, r.t. = 2.01 min; undergoes extensive degradation.)
4. Mass spectra of compounds 1 (38.8%), 3 (0.3%) and **19** (1.1%) have been previously described (cf. Table 1).
5. 2-Decene (**31**): $M^+ = 140$ (0.1%,r.t. = 3.95 min); 111 (C_8H_{15}); 98 (C_7H_{14}); 97 (C_7H_{13}); 84 (C_6H_{12}); 83 (C_6H_9); 81 (C_6H_9); 70 (C_5H_{10}); 69 (C_5H_9); 67 (C_5H_7); 56 (97—C_3H_5, 100%); 55 (C_4H_7, 99%) and 53 (C_4H_5).
6. 2, 3-Epoxydecane (**32**): $M^+ = 156$ (0.4%, r.t. = 5.63 min); 141 ($M{-}CH_5$); 127 ($M{-}C_2H_5$); 113 ($M{-}C_3H_7$); 99 (C_7H_{15}); 95(113—H_2O);); 85($M{-}C_5H_{11}$); 83 (C_6H_{11}); 70 (C_5H_{10}); 69 (C_5H_9 100%); 57 (C_4H_9 or C_3H_5O); 55 (C_4H_7, 98%); 53 (C_4H_5) and 45 (CH_3OCH_2).
7. 3, 4-Epoxydecane (**33**): $M^+ = 156$ (0.2%, r.t. = 5.92); 141 ($M{-}CH_5$); 127 ($M{-}C_2H_5$); 113 ($M{-}C_3H_7$); 111 (127—O); 99 ($M{-}OC_3H_5$); 95(113—H_2O);); 85($M{-}C_5H_n$); 83 (C_6H_{11}); 70 (C_5H_{10}); 69 (C_5H_9); 57 (C_4H_9 or C_3H_5O); 55 (C_4H_7, 100%) and 53 (C_4H_5).
8. 1,2-Epoxydecane 1 (**27**): $M^+ = 156$ (49.9%, r.t. = 6.24 min); 127 (M−CHO); 113 ($M{-}C_3H_7$); 98 C_7H_{14}); 96 (C_6H_8O or (M -C_4H_6O); 95(C_6H_7O);); 85(C_6H_{13}); 82 (C_6H_{10}); 71(C_5H_n or C_4H_7O, 100%); 68 (C_5H_8); 56 (C_4H_8); 55 (C_4H_7) and 53 (C_4H_5).
9. 3-(Decyl)-dimethylphosphate (**34**): $M^+ = 266$ not seen, 0.4%, r.t. = 11.22 min); 170 ($M{-}C_7H_{12}$); 141 [M -$P(O)O(OCH_3)_2$]; 138 [$P(O)(OCH_3)_2C_2H_5$]; 109 [$P(O)(OCH_3)_2$]; 99 [M -$C_3H_6OP(O)(OCH_3)_2$]; 97 C_7H_{13}, 100%); 85 (C_6H_{11}); 82 (C_6H_{12}); 79 [$PH(O)OCH_3$ or $P(O_3$] and 71 (C_5H_{11}).
10. Unknown:(36, 0.4%, r.t. = 8.46 min; undergoes extensive degradation.).
11. 3-(Octenyl) -dimethylphosphonate (35): $M^+ = 220$:(2.4%, r.t. = 11.54 min); 179 ($M{-}C_3H_5$); 149[M-C_5H_{11}];123(149-C_2H_2); 109 [$P(O)(OCH_3)_2$]; 96 (C_7H_{12}); 83 (C_6H_9, 100%); 81 (C6H9); 79 [$P0_3$]; 67 (C_5H_7); 57 (C_4H_9) and 55 (C_4H_7).
12. 2-(Decyl)-dimethylphosphate (37): $M^+ = 266$ not seen,:0.2%, r.t. = 11.40 min); 170 ($M{-}C_7H_{12}$); 157 [M−P(O)(OCH3)2, 94%]; 153 (170—OH); 125 [$P(O)(OCH_3)_2$]; 110 [$P(0)H(OCH_3)_2$]; 97 C_7H_{13},); 85 (C_6H_{11}); 83 (C_6H_{11}); 79 [PO_3] and 69(C_5H_9.,100%).
13. 2-(Decyl)-O, O'-dimethylphosphonate (38): $M^+ = 250$:0.7%, r.t. = 11.96 min); 165 [$C_3H_7P(O)(OCH_3)_2$]); 153 ($M{-}C_7H_{13}$); 152 (M−C7H12); 113 (C_8H_7, 100%); 109 [$P(O)(OCH_3)_2$]; 96 [$P(O)(HO)(OCH_3)$]; 81 (C6H9); 69 (PO_3); 67 (C_5H_7); 57 (C_4H_9) and 55 (C_4H_7).
14. 2-(Decyl)-O, O'-dimethylphosphonate (39): $M^+ = 250$, (:0.4%,%, r.t. = 12.09 min), 165 ($M{-}C_6H_{13}$); 153 [$P(O)(OCH_3)(C_3H_6)$]; 137 [$CH_3CHP(O)(OCH_3)_2$]; 126 (C_9H_{18}); 113 ([P(O)H(OH)-(OCH_3) or C_9H_{15},100%]; 85 (C_6H_n); 81 (C_6H_9); 69 (C_5H_9); 69(C_5H_9); 67 (C_5H_7); 57 (C_4H_9) and 55 (C_4H_7).
15. 3-(l-Decenyl)-O, O'-dimethylphosphate (40): $M^+ = 264$, (:0.2%,%, r.t. = 12.39 min), 237 ($M{-}C_2H_3$); 139[$M{-}OP(0)(OCH_3)_2$]; 127 [(C_9H_{18}) or $PH_2O_2(OCH_3)_2$,100%]; 113 (C_8H_{17}); 99 (C_7H_{15}); 81 (C_6H_9); 81 (C_6H_9); 67 (C_5H_7); 57 (C_4H_9) and 55 (C_4H_7).
16. 3-(l-Decenyl)-O, O'-dimethylphosphate **41, isomer of 40)**: $M^+ = 264$ (:01%, r.t. = 10.65 min); isomer of 21 Fragmentaion is very similar to compound 21.

vibro-mixer and then heated in a table top microwave oven for 2 min. The reaction mixture was cooled to ambient temperature and heated for 4 min more. Based on their mass spectral fragmentation behavior, the following compounds were characterized: (**1**) dimethyl H-phosphonate (**1**, $M^+ = 110$, 68.7%, r.t. = 2.42 min); (**2**) cyclohexrene oxide (**2**, $M^+ = 98$, 15.6%, r.t. = 2.85 min); (3) trimethylphosphate (**3**, $M^+ = 140$, 1.4%, r.t. = 3.41 min); (**4**) O-cyclohexyl methylphosphoric acid (**4**, $M^+ = 194$, 1.8%, r.t. = 8.71 min); (**5**) 1-methoxy-1-cyclohene (**5**, $M^+ = 112$, 0.4%, r.t. = 8.57 min); (6) cyclohexyl O-methyl H-phosphinate (**6**, $M^+ = 162$, 2.6%, r.t. = 8.77 min); (7) cyclohexyl–O,O'-dimethylphosphonate (**7**, $M^+ = 208$, 0.3%, r.t. = 9.39 min); (8) cyclohexyl–O,O'-dimethylphosphonate (**8**, $M^+ = 192$, 2.8%, r.t. = 9.48 min); (9) O-cyclohexyl–O,O'-dimethylhydrogenphosphate (**9**, $M^+ = 272$, 2.1%, r.t. = 12.12 min); (10) O-cyclohexyl–O,O'-dimethyl hydrogenphosphate (**10**, $M^+ = 272$, 2.0%, r.t. = 12.22 min). Their mass spectral fragmentation patterns are all described in Table I.

Microwave-Catalyzed Reaction of 1,2-Butene Oxide (18) with H-Dimethyl-phosphonate (1)

Stoichimetric amounts of H-dimethylphosphonate (**1**) and 1,2-epoxybutane (**18**) were mixed in a glass vial or glass joint round bottom flask (**5** mL). The mixture was shaken for a few minutes using the vibro-mixer and then heated in a table top microwave oven for 2 min. The reaction mixture, after cooling to ambient temperature, was heated again for 2 min more. Based on their mass spectral fragmentation behavior, the following compounds were characterized (Figure 4): (**1**) dimethyl H-phosphonate (**1**, $M^+ = 110$, 78.8%, r.t. = 2.44 min); (**2**) 1,2-butene oxide (**18**, $M^+ = 98$, 8.3%, r.t. = 1.62 min); (3) trimehtylphosphonate (**19**, $M^+ = 124$, 0.2%, r.t. = 3.01min); (**4**) trimethylphosphate (**3**, $M^+ = 140$, 1.2%, r.t. = 3.42 min); (**5**) O,O'-dimethyl cis-propenylphosphonate (20, $M^+ = 150$, 0.3%, r.t. = 3.70 min); (6) O,O'-dimethyl trans-propenylphosphonate (**21**, $M^+ = 150$, 9.7%, r.t. = 3.80 min); (7) n-butyl O-methyl H-phosphinate (**22**, $M^+ = 136$, 1.8%, r.t. = 3.94 min). Their mass spectral fragmentation patterns are all described in Table II.

Microwave-Assisted Reaction of 1,2-Decene Oxide (27) with H-Dimethyl-phosphonate (1)

Stoichimetric amounts of H-dimethylphosphonate (**1**) and 1,2-decene oxide (**27**) were mixed in a glass vial or glass joint round bottom flask (5 mL). The mixture was shaken for a few minutes using the vibro-mixer and then heated in a table top microwave oven for 2 min. The reaction mixture, after cooling to ambient temperature, was heated again for 2 min more. Based on their mass spectral fragmentation behavior, the following compounds were characterized (Figure 6): (**1**) dimethyl H-phosphonate (**1**, $M^+ = 110$, 38.7%, r.t. = 2.42 min); (**2**) trimehtylphosphonate (**19**, $M^+ = 124$, 0.3%, r.t. = 3.01 min); (3) trimethylphosphate (3, $M^+ = 140$, 1.1%, r.t. = 3.42 min); (**4**) 2-decene (12, $M^+ = 140.0$. 1%, r.t. = 3.95 min); (**5**) 2,3-decene oxide (**32**, $M^+ = 156$, 0.2%, r.t. = 5.63 min); (6) 3,4-decene oxide (33, $M^+ = 156$, 0.2%, r.t. = 5.92 min); (7) 1,2-epoxydecane (**27**, $M^+ = 156$, 49.9%, r.t. = 6.24 min); (8) 3-decyl-O,O'-dimethylphosphate (**34**, $M^+ = 266$, 0.2%, r.t. = 11.22 min); (9) unknown (**36**, 0.4%, r.t. = 8.46 min); (10) 1-(3-octenyl-O,O'-dimethylphosphonate (**35**, $M^+ = 220$, 2.4%, r.t. = 9.54 min; (**11**) 2-decyl dimethylphosphate (**37**, $M^+ = 266$, 0.2%, r.t. = 11.40 min); (12) 2-decyl–O,O'-dimethylphopshonate (**38**, $M^+ = 250$, 0.7%, r.t. = 11.96 min); (13) 2-decyl-O,O'-dimethyl-phosphonate (**39**, an isomer of 38, $M^+ = 250$, 0.4%, r.t. = 12.09 min); (14) 3-(1-decenyl)dimethylphosphate (**40**, $M^+ = 264$, 0.3%, r.t. = 12.39 min) and (15) 3-(1-deencyl) dimethylphosphonate (**42**, an isomer of 40, $M^+ = 264$, 0.2%, r.t. = 10.65 min). The mass spectral breakdown behavior of the above mentioned compounds is described in Table III.

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