Reaction of Dinitrogen Tetraoxide with Hydrophilic Olefins: Synthesis of Citric and 2-Hydroxy-2-methylbutanedioic Acids

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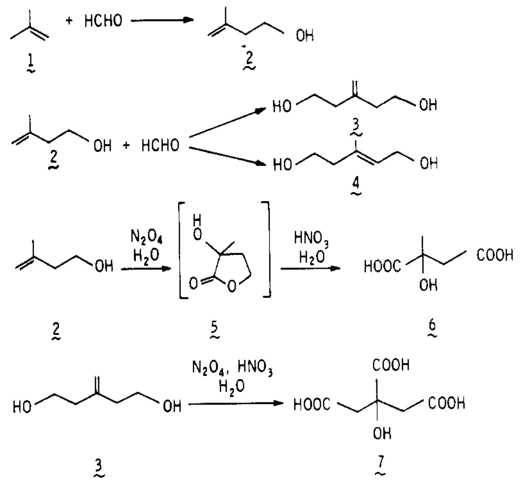
Liquid olefins typically react with N_2O_4 by free-radical reactions to form dinitro and nitronitrite derivatives. Introduction of hydrophilic substituents into 1-olefins altered the course of the reaction of the olefins with N_2O_4 in aqueous HNO_3. Citric acid was formed in 64 mol % yield by the reaction of 3-methylene-1,5-pentanediol with N_2O_4 in aqueous HNO_3. Similarly, 2-hydroxy-2-methylbutanedioic acid was made from 3-methyl-3-buten-1-ol in 88% yield. These results are explained by solution of the hydrophilic olefins in aqueous HNO_3–N_2O_4 and addition of N_2O_4 to the double bond as NO^+ and NO_3^- ions to yield nitrosonitrates, which react further to give the final products.

Addition of dinitrogen tetraoxide to 1-olefins or oxidation of the olefins with dilute nitric acid usually gives dinitro and nitronitrite compounds as the major products.[1] These can be converted into nitronitrates, nitro alcohols, nitro ketones, nitro olefins, or carboxylic acids under appropriate reaction conditions. Propene and 2-methylpropene react differently with N_2O_4. Good yields of 2-hydroxypropanoic acid or 2-hydroxy-2-methylpropanoic acid can be obtained[2] by passing the vaporized olefins into N_2O_4 or its solution in nitric acid at temperatures below 20 °C. The reactions of these two olefins to form hydroxy acids are the subject of an extensive patent literature. A few additional examples of reactions of olefins with N_2O_4 to form hydroxy acids or their nitrate esters have been reported. Ustavshchikov[3] and co-workers report reactions of this type with 1-butene, 2-methyl-1-butene, 2-methyl-1-pentene, and 3-chloro-2-methyl-1-propene but give no experimental details. Other Russian workers[4] have reported forming nitrato acids from 1-butene and 1-pentene by passing the gaseous olefins into N_2O_4 at 15–20 °C. The nitrate esters of α-hydroxy acids appear to have been made from linear 1-olefins containing from 5 to 20 carbon atoms[5] by spraying the finely divided olefins along with oxygen into N_2O_4 maintained at 0–15 °C.

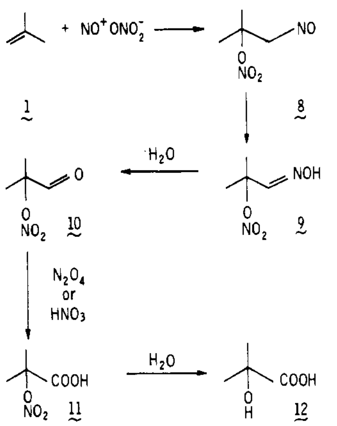
We have found that the scope of the reaction of N_2O_4 with olefins to form hydroxy acids or their nitrate esters is much broader than previously reported. Hydroxy acids were prepared in high yields by reactions of solutions of N_2O_4 in nitric acid with 1-olefins which are made hydrophilic by hydroxyl substituents. Oxidation of primary alcohol groups can be carried out in the same process to give polycarboxylic acids in good yields. These reactions of N_2O_4 with hydrophilic 1-olefins occur over a considerably greater temperature range and a greater range of reactant ratios than has been found possible when simple alkenes were used.

The application of these reactions to make citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid, **7**) as shown in Scheme I is of particular significance as it provides a potentially commercial synthetic chemical route to citric acid, which is now produced commercially only by microbiological methods. In this process, the olefinic diol **3** can be made in a single step by condensation of 2 mol of formaldehyde with 2-methylpropene. Reaction of **3** with N_2O_4 and nitric acid produces citric acid directly. A similar reaction sequence produces 2-hydroxy-2-methylbutanedioic acid, **6** (DL-citramalic acid), the racemic modification of a common natural product. Synthesis of **6** has previously been time-consuming and erratic.

Scheme I



Scheme II



The formation of hydroxy acids from N_2O_4 and the hydrophilic olefins used in this work probably proceeds in the same manner as the reaction of 2-methylpropene[2] with N_2O_4, which is outlined in Scheme II. In this case, N_2O_4, probably in the form of the ions NO^+ and NO_3^-, adds rapidly to the double bond of the olefin to give the nitrosonitrate **8** and its dimer. The nitroso group can isomerize to the oxime **9**. The oxidation of this intermediate could proceed by several paths, depending on reaction

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conditions. Compounds **10** and **11** have been isolated from reaction mixtures and are reasonable intermediates. The presence of a large amount of N_2O_4 is essential for good yields in this reaction. The yield of **12** was found to decrease rapidly[2b] as the ratio of N_2O_4 to olefin is decreased below 3:1. The optimum temperature for this reaction appeared to be about 10 °C. The patent literature shows that considerable care is required in hydrolysis of the nitrate ester made by reaction of N_2O_4 with propene, as the secondary alcohols are readily oxidized to ketones by nitric acid.

The product of addition of N_2O_4 to 2-methylpropene can be detonated.[2a] The oxygen balance for decomposition of the nitrosonitrate derivatives of **2** and **3** indicates that detonation of these compounds may also be possible. The use of aqueous nitric acid as a reaction medium dilutes these potentially hazardous compounds. When the reaction is carried out at 50–60 °C and the hydrophilic olefin gradually added to the nitric acid solution, oxidation of the nitroso group to a carboxyl group and at least partial hydrolysis of the nitrate ester occurs during the addition of the olefin. This procedure keeps the concentration of nitrosonitrate compounds below that which is likely to be hazardous. At the same time, a considerable fraction of the primary alcohol groups of **2** or **3** are oxidized to carboxyl groups with concurrent formation of additional N_2O_4. The N_2O_4 formed in the oxidation of the primary alcohol groups can react with the fresh hydrophilic olefin feed. Alternatively, N_2O_4 solution may be reacted with the hydrophilic olefins at −5 to 20 °C. The temperature can subsequently be increased to hydrolyze the nitrate ester and oxidize the primary alcohols to the acids.

The olefin structures which react with N_2O_4 to yield hydroxy acids under the reaction conditions have not been fully defined. This investigation was limited to reactions of olefinic alcohols which contain vinylidene groups and which are readily formed by the ene reactions[6] of 2-methylpropene with formaldehyde. Preliminary results also showed that the alkenylsuccinic anhydrides which are formed by the ene reactions of 2-methylpropene and 2-methylbut-2-ene with 2,5-furandione do not form significant amounts of nitro derivatives upon reaction with N_2O_4 in aqueous HNO_3, as would have been predicted from the previously known reactions of liquid olefins with N_2O_4. Evidence from IR and ^1H NMR showed that the products may be mainly lactone dicarboxylic acids, but the product structures have not been definitely established.

Experimental Section

Olefinic Alcohols from 2-Methylpropene. The reaction of formaldehyde and **1** was initially carried out in a 1-L magnetically stirred autoclave in a solvent of acetic acid and acetic anhydride as described by Blomquist and Verdol.[7] Subsequently, larger amounts of **2** and **3** were prepared by reaction of **1** or **2** or their mixtures in 2-propanol with buffered solutions of aqueous methanolic formaldehyde.[8] Products were recovered as described in the references. Distilling crude **2** through a 20-tray Oldershaw perforated bubble tray distillation column gave **2** in 96–97% purity; bp 129–130 °C.

Reaction of **2** with formaldehyde following the procedures in both ref 7 and 8 gave both **3** and substantial amounts of the previously unreported stereoisomers of 3-methyl-2-pentene-1,5-diol, **4**. A number of unidentified compounds were also formed. The crude olefinic diols obtained by the method of ref 8 first received a simple rapid distillation at 10–40 torr after recovery of **2**. The diols were then distilled at 20 torr through a 16- or 40-cm distilling column packed with 3.2-mm protruded packing which had been deactivated by treatment with $(NH_4)_2S$ solution. A small amount of K_2CO_3 was added to the distillation vessel to avoid decomposition of **4**. Complete separation of the diols was not attained by distillation, as the boiling point of **3** was 145–146 °C at 20 torr while the boiling point of the isomers of **4** was about 148–152 °C at 20 torr. Product purities and identities were established by GC, IR, and ^1H NMR analyses.

Citric Acid. Oxidations of **3** were carried out in a well-agitated vessel (the height about 5 times the diameter) equipped with a number of baffles and a stirrer with multiple flat blades located opposite the baffles. A jacket through which thermostated water was circulated provided temperature control. A mixture of **3** and **4** was fed from a syringe pump and introduced below the liquid level in the reactor through a poly(fluoroethylene) tube. Ice-cold water was circulated through a reflux condenser during addition of the diol mixture to minimize loss of N_2O_4. When addition of **3** was complete, the circulation of cooling water to the condenser was stopped. Samples were taken periodically for analysis. The crude reaction product was recovered by evaporation of most of the liquid at 60 °C and 35–40 torr. Drying was completed at 70 °C under a stream of nitrogen. Water was added to hydrolyze nitrate esters and the drying repeated. Crude citric acid crystals were separated and then purified by precipitating calcium citrate and boiling this with aqueous Na_2CO_3 to form sodium citrate. The trimethyl citrate derived from the Ca salt was identical with an authentic sample by GC, IR, and ^1H NMR.

Citric Acid Analysis. The samples were evaporated to dryness at room temperature under a stream of nitrogen. For analysis, the carboxylic acids were esterified by refluxing with a mixture of 40 wt % of H_2SO_4 in methanol. This reaction product was diluted with an aqueous 26 wt % solution of $(NH_4)_2SO_4$ which served to convert the H_2SO_4 to HSO_4^- and to salt out the esters. The esters were extracted from the mixture with chloroform and analyzed by GC using a poly(ethylene glycol–adipate) column or by IR and ^1H NMR spectroscopy. GC analysis showed that several compounds in addition to citric acid were present after the initial addition of the diols to the N_2O_4–HNO_3 mixtures. These compounds were not identified. Some were apparently reaction intermediates, as the amounts of the compounds decreased as the amount of citric acid increased during the subsequent oxidation with nitric acid.

2-Hydroxy-2-methylbutanedioic Acid (6). In a manner similar to the synthesis of **7**, 42 g of **2** was added to 10 g of N_2O_4 in 600 g of 70 wt % HNO_3 at 48–55 °C over a period of 80 min. The mixture was held for 120 min at 48 °C. Most of the solvent was evaporated at 50–60 °C under water aspirator vacuum. The solvent was evaporated to dryness under a nitrogen stream. After the residual solid was dissolved in ethyl acetate, the addition of petroleum ether (bp 30–60 °C) precipitated a solid, which was filtered and dried in vacuo at 30–40 °C to give 32.8 g of **6**: mp 109.2 °C (lit. 108–109 °C); neutral equivalent 73.9, theory 74.05; ^1H NMR (D_2O) δ 1.55 (s, 3 H), 2.7 (unsym d, 1 H), 3.2 (unsym d, 1 H), consistent with racemic **6**. Destructive distillation from an oil bath of 8 g of **6** at 83–89 °C and 15 torr gave 4.9 g of 3-methyl-2,5-furandione, identical with an authentic sample by GC; mp 8–12 °C (lit. 7–8 °C).

The use of more N_2O_4 at the start of the reaction may improve yields of **6**. A 6.9-g sample of **2** was added at 50 °C to a solution of 5 g of N_2O_4 in 142 g of 70 wt % of HNO_3 over a period of 48 min. The resultant solution was reacted at 50 °C. Analysis by ^1H NMR with an internal standard of 2,2-dimethylpropionic acid showed 80 mol % yield of **6** at 30 min and 88% yield at 60 min after final addition of **2**.

Results and Discussion

The synthesis of citric acid from **3** was studied in the greatest detail. Addition of **3** to N_2O_4 in nitric acid at temperatures below 20 °C, as recommended[2,3] for reaction of **1** and of propene, followed by oxidation of the products at higher temperatures, gave the results shown in runs 1–4 of Table I. The citric acid precursor **3** used in the reactions always contained considerable amounts of the close-boiling isomers of **4**. The best yields of **7** under these

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Table I. Effect of Reaction Variables on Yields of Citric Acid

	low temp N_2O_4-olefin reacn				additn of olefin at oxidizing temp					
	1[e]	2[e]	3[e]	4[e]	5[e]	6[e]	7[e]	8[e]	9[e]	10[e]
moles of N_2O_4/mole of **3** + **4**	2.9	2.7	1.5	2.7	3.4	1.9	0.5[a]	0.6	0.5[b]	1.7
nitric acid										
moles of acid/mol of **3** + **4**	38	46	45	36	41	49	50	35	34	31
concn, wt %	60	70	70	90	70	70	70	56	56	56
temp, °C										
olefin additn	2	2	3	3	32	50	50	50	50	88
first-stage oxidatn	60	29	29	30	30	50	50	50	50	88
second-stage oxidatn	71	50	70	70						
oxidation time, min[c]										
first stage	30	60	60	30	120	120	120	150	150	5
second stage[d]	30	120	60	120						
% **3** in feed	71	71	70	70	65	65	65	65	65	65
citric acid yield, %	54	63	50	19	42	64	56	45	8	29

[a] Recovered 4 mol of N_2O_4/mol of olefin feed at completion of reaction. [b] Air passed through reaction mixture at 2 volumes of air/volume of liquid/min. [c] Olefins added over a 20–40 min period. [d] Time for maximum yield. [e] Run number.

conditions were obtained by using an excess of 70 wt % of nitric acid, more than 2 mol of N_2O_4/mol of **3** plus **4**, and an oxidation temperature of 50 °C. The amount of nitric acid used was chosen to leave about 45 wt % of nitric acid in the final product solution.

The addition of the hydrophilic olefin to a N_2O_4–nitric acid solution at a temperature at which oxidation of the N_2O_4–olefin addition compound occurs is the preferred procedure, as it avoids the accumulation of large amounts of nitroso nitrate intermediate. Significant yields of citric acid from **3** were obtained at reaction temperatures up to 88 °C (run 10). At temperatures of 50 °C and above, the oxidation of the alcohol to the carboxylic acid proceeds rapidly.[9] Substantial amounts of N_2O_4 are formed from the nitric acid during this reaction. Only 0.5 mol of N_2O_4/mol of olefin was charged to the reaction in run 7, but 4 mol of N_2O_4/mol of olefin fed was recovered on completion of the olefin addition by stripping the reaction mixture with nitrogen and trapping the N_2O_4 at -78 °C. It appears likely that the high yields of citric acid at the conditions of run 6 are due in part to the high concentrations of N_2O_4 maintained by the formation of N_2O_4 during the addition of the hydrophilic olefins. The slightly lower yield in run 7 compared to that in run 6 is probably due to the low initial concentration of N_2O_4 in run 7. Removing N_2O_4 as it was formed during the addition of **3** by passing air through the reaction mixture in run 9 gave only an 8% yield of citric acid compared to a 45% yield in run 8, which was made at otherwise identical conditions. This result shows that addition of N_2O_4 to the double bond is a necessary step in the reaction.

Most known addition reactions of N_2O_4 to carbon–carbon double bonds[1a] result in the formation of substituted nitro compounds. These products result from free-radical reactions of NO_2. The liquid hydrophobic olefins and the solvents typically used for these reactions do not provide suitable conditions for the formation of NO^+ or NO_3^- ions. In some cases where aqueous nitric acid reactant has been used,[1c] the hydrophobic olefin has been almost totally insoluble in the aqueous solution. In these cases, the reaction probably occurs mainly between the olefin and N_2O_4 dissolved in the liquid olefin.

The phase relations are entirely different with the hydrophilic olefins used in the present work. These olefins readily dissolve in aqueous HNO_3–N_2O_4 solution. In nitric, sulfuric, or hydrofluoric acids, N_2O_4 is dissociated into NO^+ and NO_3^- ions.[10] Some ionization of this type also apparently occurs in liquid N_2O_4. The hydrophilic olefins used in this work apparently react with the NO^+ and NO_3^- ions to give nitrosonitrates, which can be converted into hydroxy acids. Most previous examples of the formation of nitroso nitrates and hydroxy acids from olefins and N_2O_4 have involved passing gaseous olefins into N_2O_4 or aqueous HNO_3–N_2O_4 solutions. In these cases, the olefins probably reacted at the gas–liquid interface, where ionic species of N_2O_4 are present.

From our results, we conclude the hydrophilic olefins which are reasonably soluble in N_2O_4 or aqueous HNO_3–N_2O_4 can be expected to react with N_2O_4 to give nitroso nitrates and their oxidation products when the olefins are added to N_2O_4 or the HNO_3–N_2O_4 solutions at such a rate that the solubility of the olefins in N_2O_4 or in a solution of N_2O_4 in aqueous HNO_3 is not exceeded. When the olefin or its solution is insoluble in N_2O_4 or the N_2O_4–HNO_3 reactants, the N_2O_4 dissolves in the olefin or in the solution of olefin in a nonionizing solvent. In these cases, the products of the reaction of the olefin with NO_2 should predominate. Further work with a variety of olefins is needed to verify this postulated generality of the ionic reactions of N_2O_4 with hydrophilic olefins.

Reaction conditions were adjusted in this work to oxidize the CH_2OH groups of **2** and **3** to carboxyl groups. The oxidation of primary alcohols, oximes, and aldehydes with nitric acid has received only limited coverage in the literature. Studies of the oxidation of cyclohexanol and cyclohexanone with nitric acid[11] and of 2-methoxyethanol with nitric acid in sulfuric acid solution[12] showed that oxidation rates are proportional to $-H_0$. A recent patent[13] shows that oxidation of 1-octanol with nitric acid should be carried out at a temperature below 60 °C and with at least 10 M (48 wt %) HNO_3 to obtain a carboxylic acid containing the same number of carbon atoms as the starting alcohol. Carboxylic acids with fewer carbon atoms than the starting alcohol were reportedly obtained at reaction temperatures above 80 °C or with reaction temperatures above 60 °C and nitric acid concentrations above 14 M (65 wt %). Our best yields of **6** and **7** were obtained at the conditions indicated in this reference as those which minimize degradation of the alcohol during oxidation by aqueous nitric acid.

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(11) (a) W. J. van Asselt and D. W. van Krevelen, *Recl. Trav. Chim. Pays-Bas*, **82**, 51 (1963); (b) *ibid.*, **82**, 429 (1963).

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(13) P. H. Washecheck, Belgian Patent 775729 (1971).

Vanadium salts are commonly used to catalyze the oxidation of alkanols to carboxylic acids with nitric acid. The use of vanadium catalyst can greatly influence the oxidation of cyclohexanol and cyclohexanone with nitric acid.[11] Vanadium appears to have little effect on the oxidation[14] of 1 by N_2O_4 and HNO_3 to 12. In our work, it was found that traces of vanadium cause the destruction of citric acid (7) by nitric acid.[15]

The yields of 6 and 7 were surprisingly high when the oxidation was carried out with aqueous nitric acid in the absence of vanadium. Several model diols and triols were oxidized with aqueous nitric acid. It was found that the yield of polycarboxylic acids decreased with increasing number of hydroxyl groups. The oxidation of 3-(hydroxymethyl)-1,3,5-pentanetriol[16] with nitric acid gave yields of only 3–12% citric acid. Oxidation of 3-methyl-1,5-pentanediol at 50 and 60 °C with 70 wt % of nitric acid containing 1.4 wt % of N_2O_4 gave 33 and 23% yields of 3-methylpentanedioic acid and 45 and 62% yields of 2-methylbutanedioic acid, respectively. The yields of **6** and **7** from **2** and **3** were much higher than would be predicted from the results of the oxidation of these model polyols. Very little degradation occurs during the oxidation of the monohydric alcohol **2**. The yield of citric acid (**7**) from the diol **3** was about 65 mol %, compared to a maximum yield of 33% in the apparently analogous oxidation of 3-methyl-1,5-pentanediol to 3-methylpentanedioic acid. It is possible that the terminal carbon of the double bonds in **2** and **3** is rapidly oxidized to a carboxyl group, and this forms a lactone such as **5**, which may oxidize to the polycarboxylic acid in a higher yield than the free alcohol. This is speculative at present, as no evidence is available on the factors influencing yields for oxidation of this type in nitric acid.

Registry No. 2, 763-32-6; **3**, 40760-35-8; (*E*)-**4**, 16933-29-2; (*Z*)-**4**, 39149-97-8; **6**, 597-44-4; **7**, 77-92-9; N_2O_4, 10544-72-6; 3-methyl-2,5-furandione, 616-02-4.

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Synthesis and Nuclear Magnetic Resonance Spectra of Some Substituted Vinyldiphenylphosphines

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Some substituted vinyl tertiary phosphines have been synthesized by the reaction of the substituted vinyl Grignard reagents with $(C_6H_5)_2PCl$ and $C_6H_5PCl_2$. The compounds include $(C_6H_5)_2PC(CH_3){=}CH_2$, (*Z*)- and (*E*)-$(C_6H_5)_2PCH{=}CHCH_3$, $(C_6H_5)_2PCH{=}C(CH_3)_2$, (*Z*)- and (*E*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$, and the compound mixture (*Z,E*)-, (*Z,Z*)-, and (*E,E*)-$(C_6H_5)P(CH{=}CHCH_3)_2$. ^{31}P and ^1H NMR data are reported. Those phosphines which have a methyl group cis to phosphorus in the ethylene group have unusually large upfield (highly shielded) ^{31}P chemical shifts.

The utility of vinyl tertiary phosphines for the synthesis of unsymmetrical bis(tertiary phosphines),[1-3] poly(tertiary phosphines),[4-6] and some other novel tertiary phosphines[7] via addition of an alkali metal diorganophosphide or a phosphorus–hydrogen bond to the vinyl group has been clearly demonstrated. In the pursuit of some unsymmetrical bis(tertiary phosphines) with two carbons bridging the phosphorus atoms, we have prepared several substituted vinyldiphenylphosphines and substituted divinylphenylphosphines, which have some unusual ^{31}P NMR chemical shifts. The synthesis, ^{31}P NMR, and ^1H NMR results are presented here.

Results and Discussion

The reaction of chlorodiphenylphosphine with the Grignard reagent of a mixture of (*Z*)- and (*E*)-2-bromo-2-butene produces a crude reaction mixture of (*Z*)- and (*E*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$, which have ^{31}P chemical shifts of −18.5 and 5.9 ppm, respectively (Table I lists the ^{31}P NMR data). Since the corresponding saturated alkyldiphenylphosphine has a chemical shift of −3.2 ppm,[8] the highly shielded resonance at −18.5 ppm was quite

Table I. Phosphorus-31 Chemical Shifts of Substituted Vinyl Tertiary Phosphines

compd	δ_P[a]
$(C_6H_5)_2PCH{=}CH_2$	−11.7,[b] −13.8[c]
$(C_6H_5)_2PC(CH_3){=}CH_2$	−0.9
$(C_6H_5)_2PCH{=}C(CH_3)_2$	−28.3
(*E*)-$(C_6H_5)_2PCH{=}CHCH_3$	−14.2
(*Z*)-$(C_6H_5)_2PCH{=}CHCH_3$	−32.7
(*E*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$	+5.9
(*Z*)-$(C_6H_5)_2PC(CH_3){=}CHCH_3$	−18.5
(*E,E*)-$(C_6H_5)P(CH{=}CHCH_3)_2$	−21.4
(*E,Z*)-$(C_6H_5)P(CH{=}CHCH_3)_2$	−39.8
(*Z,Z*)-$(C_6H_5)P(CH{=}CHCH_3)_2$	−57.9

[a] Positive values are downfield from 85% H_3PO_4. [b] Reference 8. [c] Reference 22.

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