& -CH=) 47.1 (s, C of α-CH to CO) 25.6 (s, C of CH_3 in =C-CH_3) 18 (s, C of CH_3 in =C-CH_3) 16.8 (s, C of CH_3 in CO-CH-CH_3); IR (neat) 3040, 2970, 2930, 2870, 1690, 1570, 1492, 1450, 1375, 1260, 1170, 1065, 955, 825, 795 cm^{-1}; mass spectra, m/e; 239 (M^+), 224 (M^+-CH_3), 211 (M^+-CO), 156, 128; TLC R_f=0.55, hexane; ethylacetate=2;5, SiO_2. The reaction mechanism is similar to that of vinylcyclopropane. Hydrogen addition to the terminal olefinic methylene group of α-methyl vinylcyclopropane in **5b** gave **8b**, a sterically much more congested cyclopropylcarbinyl complex than **6b**. Ring-opening of cyclopropyl group of 8b and subsequent isomerization of the resulting **9b** gave **10b**. Above hydride insertion reaction, **5** to **8**, follows the Markovnikov's rule which is the unusual cases for the hydrometallation due to the steric hindrance. All these results confirm the radical involvement in hydrogen atom insertion in **5** to generate secondary or tertiary alkyl complexes of **8**. More detailed mechanistic investigation is under study.

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Characteristic Oxidative Aromatization Pattern of Isophorone, 4-Hydroxyisophorone, and Rearrangement of 4-Oxoisophorone Under a Strong Acidic Condition

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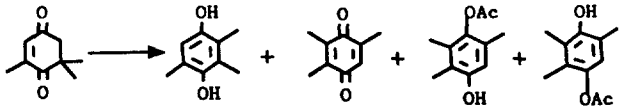
2,3,5-Trimethyl-1,4-hydroquinone (**2**), an intermediate for the production of vitamin E[1], is being prepared by rearrangement of 4-oxoisophorone[1], or by oxidation of trimethylphenols[2], isophorone[3a], or 2,5,6-trimethyl-2-cyclohexen-1-one[3b]. Thus, much attention has been paid to the preparation of 4-oxoisophorone[4], or trimethylphenols[5a]. During our investigation on the method for the production of 2,3,5-trimethyl-1,4-hydroquinone (**2**)[6], we found that 4-oxoisophorone (**1**) was converted to the 2,3,5-trimethyl-1,4-hydroquinone under an acidic condition[1b]. Thus, we examined the products formed from isophorone and 4-hydroxyisophorone when treated similarly with sulfuric acid, and isolated many products which seemed to be formed by multiple oxidations and rearrangements. The results are summarized in Table 1.

Table 1. Products (yields, %) Formed on Treatment of Isophorone (**6**), 4-hydroxyisophorone (**7**) and 4-oxoisophorone (**1**) with Sulfuric Acid

Starting material	Products, yields (%)						
	3	**4**	**5**	**11**	**12**	**13**	**14**
isophorone (**6**)	–	–	–	46	1	9	1
4-hydroxyisophorone(**7**)	–	–	–	11	36	23	2
4-oxoisophorone (**1**)	37	24	7	–	–	–	–



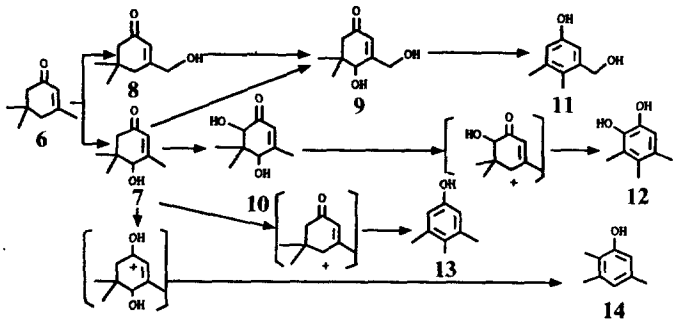
1 **2** **3** **4** **5**

Scheme 1.

As shown in Table 1, when 4-oxoisophorone (**1**) was dissolved in acetic anhydrde to give a 5% solution and added with concentrated sulfuric acid (5 eq) portion by portion at room temperature, 2,3,5-trimethyl-1,4-benzoquinone (**3**), 2,3,5-trimethyl-4-acetoxyphenol (**4**), and 2,3,6-trimethyl-4-acetoxyphenol (**5**) were isolated in 37%, 24% and 7% yields, respectively[7]. However, 4-hydroxyisophorone (**7**) was converted to completely unexpected products under a similar treatment of sulfuric acid; 3,4,5-trimethylphenol (**13**)[5b], 2,3,5-trimethylphenol (**14**), 3,4,5-trimethyl-1,2-hydroquinone (**12**)[7], and 4,5-dimethyl-3-hydroxymethylphenol (**11**)[7] were isolated in 23%, 2%, 36%, and 11% yields, respectively. Treatment of isophorone (**6**) with sulfuric acid gave similar products as in the case of 4-hydroxyisophorone (**7**); 3,4,5-trimethylphenol (**13**), 2,3,5-trimethylphenol (**14**), 4,5-dimethyl-3-hydroxymethylphenol (**11**) and 3,4,5-trimethyl-1,2-hydroquinone (**12**) were isolated in 9%, 1%, 46%, and 1% yields, respectively. The reaction proceeded at room temperature in 3-4 hrs.

Clearly, the products obtained from 4-oxoisophorone (**1**) should occur by an acid catalyzed rearrangement to give 2,3,6-trimethyl-1,4-hydroquinone (**2**), which was further oxidized or acetylated to the final products. However, formation of the prducts obtained from 4-hydroxyisophorone (**7**) and from isophorone (**6**) was not mechanistically quite clear. The phenols (**11-14**) obtained from isophorone (**6**) seemed to be produced by multiple oxidations of the carbonium ions formed by protonation on the oxygen atom of the carbonyl group followed by rearrangements (Scheme 2).

To prove the multiple oxidative rearrangement mecha-



Scheme 2.

nism, probably by oxygen molecules under a strong acidic condition, we examined products formed in the reaction mixture at certain time intervals after treatment of sulfuric acid. The reaction was stopped by diluting the reaction mixture with water followed by extraction with ethyl acetate to give phenolic compounds. The aqueous layer was neutralized with $Ba(OH)_2$, filtered and evaporated to give compound **9**[7] as a major intermediate. From this experiment, we found that isophorone was oxidized very fast to **7** and **8**, and further to **9**. Phenols and intermediate **9** were isolated by column chromatography in 40% and 56% yields, respectively after the reaction was stopped in 1 min and in this reaction mixture no isophorone was left at all. Also, all the aromatization processes were found to occur almost spontaneously under the strong acidic condition except the rearrangement of **9** to **11**, which might be slowed down due to the formation of an intramolecular hydrogen bond of the hydroxyl groups. This transformation was proceeded slowly but terminated completely by addition of water. Also, oxidative rearrangement of 4-hydroxyisophorone (**7**) was very fast to produce **10**, or **13** and **14**. Product **10** was rearranged immediately to **12**. Oxidation of silyl enol ether of isophorone to 6-hydroxyisophorone was reported[4c]. The multiple oxidation of **6** or **7** under a strong acidic condition has not been reported to our knowledge and it is interesting to observe the oxidative aromatization of isophorone and 4-hydroxyisophorone.

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7. Phenols **2, 3, 4, 5, 13** and **14** were identified by comparison with authentic samples; **12**: mp. 110-114℃, ^{1}H-NMR ($CDCl_3$), δ, 2.09 (s, 3H), 2.21 (s, 6H), 6.51 (s, 1H); **11**: mp. 210℃ (dec.), ^{1}H-NMR ($CDCl_3$): δ, 2.21 (s, 3H), 2.23(s, 3H), 4.08(s, 2H), 6.55 (d, J=3.2 Hz), 6.71 (d, J=3.2 Hz); M^+: m/z 152; **9**: mp. 258℃ (dec.), ^{1}H-NMR, δ, 1.05 (s, 3H), 1.37 (s, 3H), 2.35 (d, 1H, J=17 Hz), 3.26 (dd, 1H, J=17 & 2 Hz), 3.30 (s, 1H), 3.68 (s, 2H), 6.89 (d, 1H, J=2 Hz).

Formation of Deoxybenzoins and β-Keto Sulfides by the Reaction of α-Stabilized Anion of Phosphonates with Nitriles

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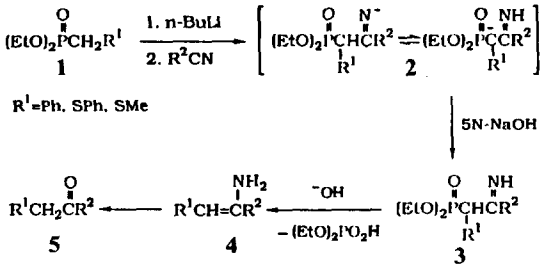
In the course of our research program toward the preparation of various β-keto phosphonates using nitriles as an acyl cation equivalent[1], we have partly found that the reaction of α-lithio anion of phosphonate bearing a phenyl or thiophenyl substituent on a carbon to the phosphorus function with nitriles gives deoxybenzoins or β-keto sulfides as byproducts during hydrolysis. From this observation, we report here the nucleophilic addition of an α-stabilized anion of phosphonates to nitriles and subsequent basic hydrolysis to afford deoxybenzoins[2] or β-keto sulfides in good yield.

A general reaction procedure is as follows: To a stirred solution of phosphonate (1 mmol) in dry THF (5 m*l*) is added *n*-butyllithium (1.1 mmol, 1.6 M in hexane) at −78℃ under nitrogen atmosphere. After being stirred for 1 h at same temperature, nitrile (1 mmol) is added and the reaction mixture is warmed to room temperature. After being stirred for additional 2 h, the mixture is added 5 N-NaOH solution (1 m*l*) and stirred for 2 h at room temperature. Normal work up gives the deoxybenzoin or β-keto sulfide, which is purified by Kugelrohr distillation or recrystallization (ethyl acetate).



Scheme 1.