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Studies on the catalysis of the reaction of organotin phenoxides with diethyl acetylenedicarboxylate

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Different organotin phenoxides react at room temperature with diethyl acetylenedicarboxylate in diethyl ether, in the presence of lithium perchlorate to give a mixture of corresponding phenyl vinyl ethers and ring ethenylated phenols. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: organotin phenoxides; diethyl acetylenedicarboxylate; lithium perchlorate; catalysis

INTRODUCTION

In 1908, pure *o*-vinylphenol was synthetized for the first time by decarboxylation of *o*-hydroxycinnamic acid.[1] Since then, a number of methods have been developed for the synthesis of vinylphenols. Electrophilic acylation of phenol followed by reduction and dehydration was employed in the commercial production of *p*-vinylphenol by Maruzen Petrochemicals Co.[2,3] Another method which utilized benzylic oxidation of ethylphenol was reported.[4] Halophenol derivatives could be vinylated by the Heck reaction.[5] Yamaguchi[6–9] reported the ethenylation reaction of phenol using the $SnCl_4$–Bu_3N reagent system. Although this reaction can directly introduce the ethynyl group to the *o*-position of the phenol hydroxy group, it has the drawback of employing the $SnCl_4$–Bu_3N reagent mixture in the amount of 2 molar equivalent. Kobayashi and Yamaguchi[10] also described the catalytic version of the reaction using silylethyne. Butyllithium (50 mol%) and $SnCl_4$ (25 mol%) were added successively to phenol in chlorobenzene, and after addition of silylethyne, the mixture was heated at 105 °C for 3 h. β-Silylethenylation of phenol first took place at the *o*-position, which was followed by C–O migration of the trimethylsilyl group. The reaction was quenched by treatment with aqueous potassium fluoride in methanol, and the *o*-ethenylphenol was isolated after acetylation in 90% yield. 2-Phenoxy-fumaric acid diethyl ester as well as *ortho*- and *p*-tolyloxy-fumaric acid diethyl esters were obtained for the first time by Ruhemann and Beddow[11] using chloro-fumaric acid diethyl ester and the appropriate phenol sodium salt. Rosnati and Saba[12] observed that α-bromo Michael acceptors (e.g. ethyl 2-bromo-propionate) undergo ipso-substitution by phenol in the K_2CO_3–acetone system, leading to the derivative of the phenyl vinyl ether. The reaction generates the (*Z*) isomer. Recently, Strazisar and Wolczanski[13] studied the possibility of application of vinyl ethers (including phenyl vinyl ethers) for production of commercially important polymers generated using single-site Ziegler–Natta catalysts. For this purpose he studied the insertion of vinyl ethers into $(Bu_3SiO)_3TaH_2$ to afford the ethyl β-ether complexes which may undergo β-OR-elimination. Cleavage of the C–O bond of phenyl vinyl ethers by transition metal complexes is attracting much interest with regard to catalysis as well as organic and organometallic synthesis.[14] Also, recently, the authors have reported that organotin phenoxides react at room temperature with diethyl azodicarboxylate and bis(2,2,2-trichloroethyl) azodicarboxylate in diethyl ether, in the presence of lithium perchlorate to give the corresponding ring-aminated phenols in excellent yield.[15,16] Organotin phenoxides (Bu_3SnOAr) has been chosen for this work because it is easy to introduce or remove the organotin group and because of the pronounced polarity of the Sn–O bond.[17]

RESULTS AND DISCUSSION

The tributyltin phenoxides were prepared by azeotropic dehydration of a mixture of phenol and tributyltin oxide (TBTO) in toluene.[18] The tin phenoxide and diethyl acetylenedicarboxylate were added to 5 M solution of $LiClO_4$ in diethyl ether at 298 K. They were stored at room temperature for 2 days. The progress of the reaction was

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monitored by TLC (using petroleum–ethyl acetate mixture; 7 : 3 v/v as eluent). The yields of the reactions and products of studied additions of different tributyltinphenoxides with diethyl acetylenedicarboxylate carried in 5 M solutions of $LiClO_4$ in diethyl ether at 298 K are collected in Table 1.

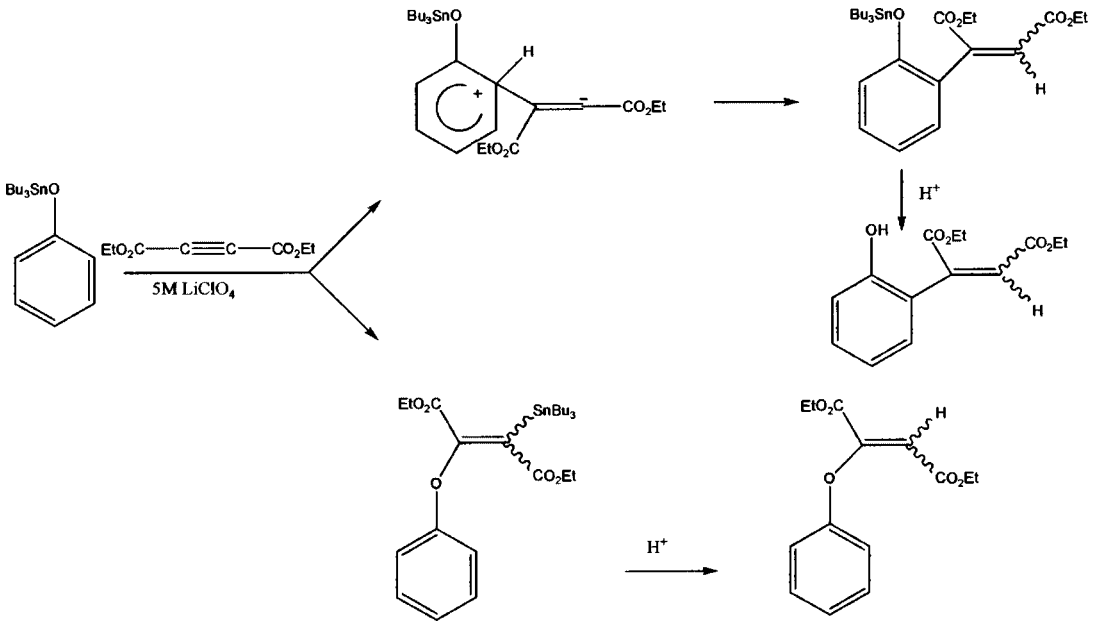
We believe that the reaction between studied organotin phenoxides and diethyl acetylenedicarboxylate proceeds according to two possible mechanisms, which may compete. As the result, a mixture of a pair of phenyl vinyl ethers and the analogous pair of *o*-vinylphenols can be obtained, as shown below.

The mechanism of reaction of vinylation in the *ortho*-position to the stannyloxy group of different organotin phenoxides must still be regarded as an open question, whether it is an ene reaction or the simple aromatic substitution. A detailed discussion of the possible mechanisms of the analogous reaction of organotin phenoxides with diethyl azodicarboxylate (DEAD) has been previously presented.[15] Lithium perchlorate is very soluble in ether and has been used to catalyse a wide variety of reactions,[19] and it strongly accelerates the rate of metalloene reaction between allyltin compounds and enophiles, including DEAD.[20,21] Isolation of products of studied reactions carried by column chromatography usually gave pairs of *ortho*-substituted vinylphenols and phenyl vinyl ethers (see Scheme 1). Exceptionally for the reaction of tributyl-(2,6-dimethoxyphenoxy)tin, only the formation of ethers was observed [equimolar mixture of 2-(2,6-dimethoxyphenoxy)fumaric acid diethyl ester and 2-(2,6-dimethoxyphenoxy)maleic acid diethyl ester]. All studied reactions were carried out in 5 M solutions of $LiClO_4$ in diethyl ether. No addition product could be detected for a reaction carried in pure diethyl ether. The elemental analysis as well as ^1H NMR and IR studies of obtained products confirmed their composition. For example 2,6-dimethoxyphenol exhibits two absorption bands at 3490 and 3456 cm^{-1}. IR spectra of other phenols also show analogous bands. They correspond to the stretching vibrations of the OH group. None of the obtained phenyl vinyl ethers exhibits the above-mentioned bands, whereas, vinylphenols (**5**, **6**, **9**, **10**, **13**, **14**, **17** and **18**) exhibit these bands. Additionally, to confirm the values of assigned chemical shifts for obtained phenyl vinyl ethers, we have compared their spectra with those synthesized by the reaction of sodium phenoxides with diethyl acetylenedicarboxylate carried out in benzene (see Table 2).

The use of O-metallation of alcohols or enols to enhance their reactivity towards electrophiles such as aldehydes or alkyl or acyl halides has been reported by Davies.[17] He also reported the reaction of tin alkoxides with other polar multiply-bonded acceptors:

$$R_3SnOR + A{=}B \longrightarrow R_3Sn\text{-}A\text{-}B\text{-}OR$$

where A=B is RNC=O, RNC=S, O=CO, S=CS, RN=C=NR, $EtO_2C{-}C \equiv C{-}CO_2Et$ etc., but he did little or nothing on phenoxides. We believe that the tin phenoxides would react by introduction of A=B into the ring, perhaps by an ene process. The studied reaction of tin phenoxides with diethyl acetylenedicarboxylate gives a mixture of products which will require separation before it can be of interest to synthetic chemists, and further studies will be necessary to achieve better control. Additionally, we have found that the yield of vinylphenols obtained as products of the discussed reaction of studied tributyltin phenoxides increases in the following order: tributyl-(2-methoxyphenoxy)tin < trbutyl-(*o*-tolyloxy)tin ≈ tributylphenoxytin < tributyl-(*p*-tolyloxy)tin.



Scheme 1. Reaction of tributylphenoxytin with diethyl acetylenedicarboxylate catalysed by $LiClO_4$.

Table 1. Catalytic vinylation of different organotin phenoxides

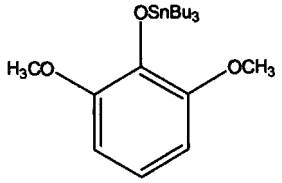
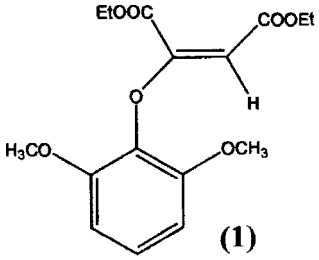
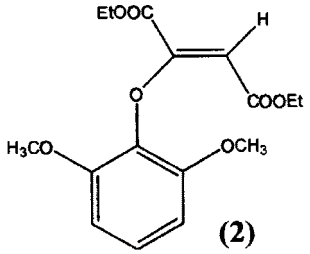
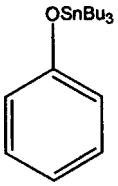
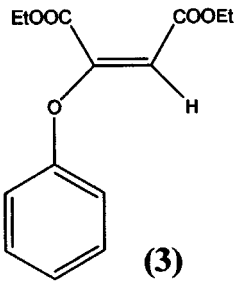
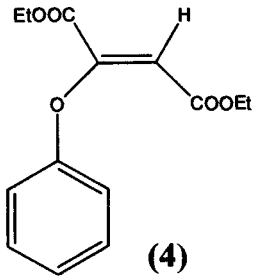
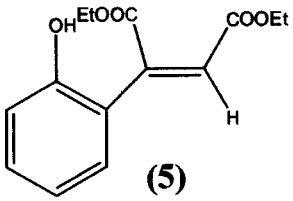
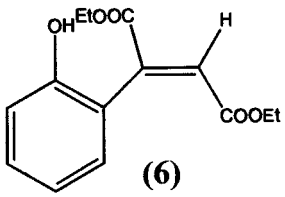
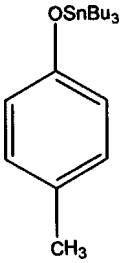
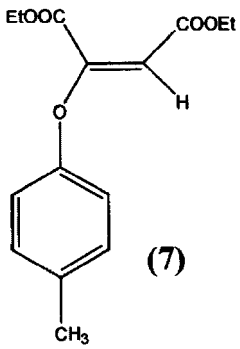
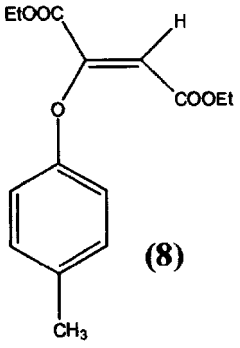
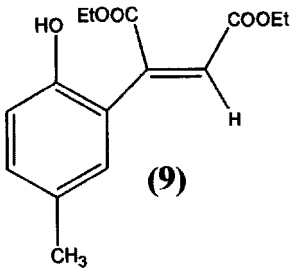
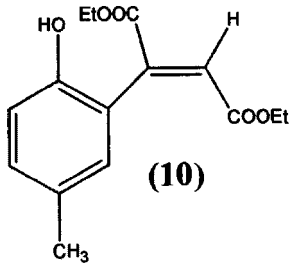
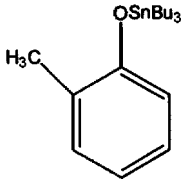
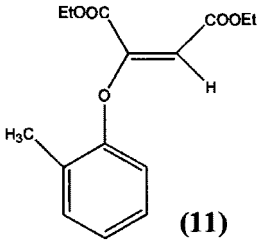
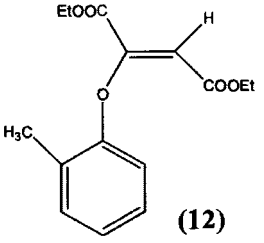
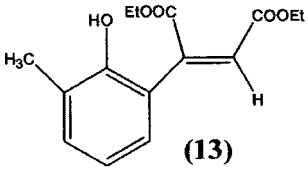
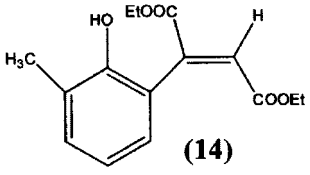
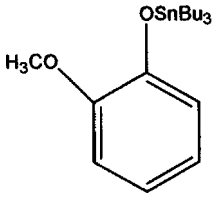
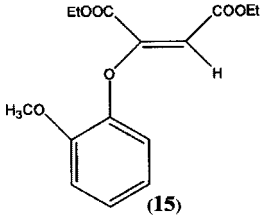
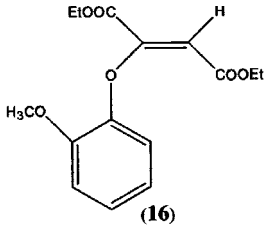
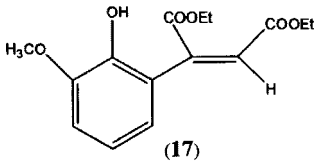
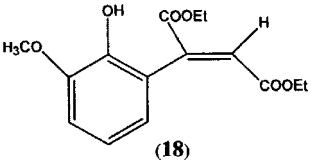
Organotin phenoxide	Product	Yield
	 (1)  (2) **1 : 2** = 1 : 1	80%
	 (3)  (4)  (5)  (6) **3 : 4 : 5 : 6** = 1 : 1 : 1 : 1	60%
	 (7)  (8)  (9)  (10) **7 : 8 : 9 : 10** = 1 : 1 : 1 : 1	100%

Table 1. (*Continued*).

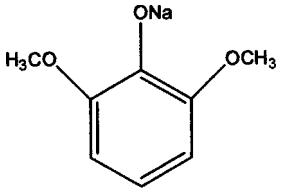
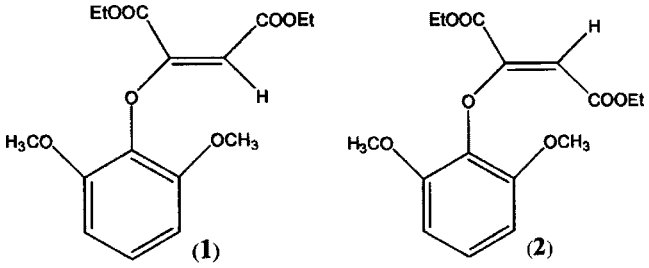
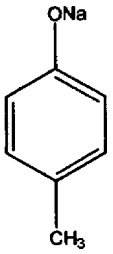
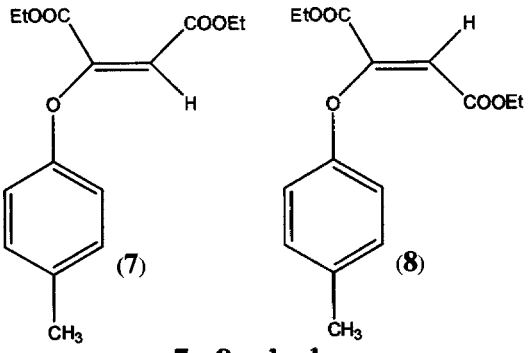
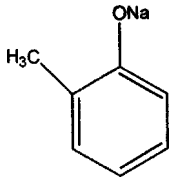
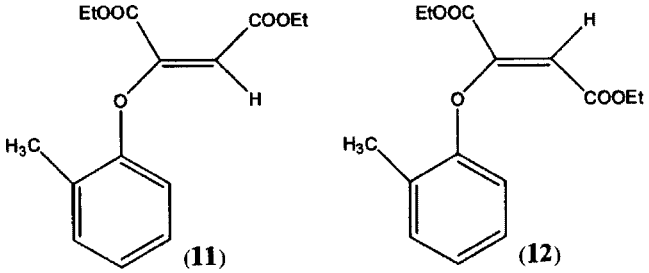
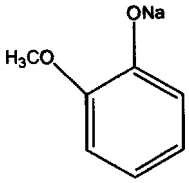
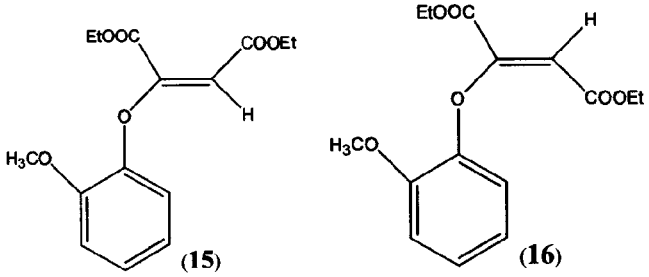
Organotin phenoxide	Product	Yield
	    **11 : 12 : 13 : 14** = 1.5 : 1.5 : 1 : 1	80%
	    **15 : 16 : 17 : 18** = 2 : 2 : 1 : 1	80%

Although the kinetic studies have not been carried out for the studied reactions, the comparison of their yields seems to indicate that tributyl-(*p*-tolyloxy)tin is the most reactive out of other organotin phenoxides.

EXPERIMENTAL

IR spectra were recorded using a FT-IR Nexus spectrometer (Thermo Nicolet). NMR spectra were recorded using an AVANCE DRX 500 Bruker and a Varian Gemini 200 BP spectrometer. Studied tributyltin phenoxides were prepared by the azeotropic dehydration of a mixture of the appropriate phenol and bis(tributyltin) oxide in toluene.[18] Typical examples of studied reactions are as follows: tributyl-(*o*-tolyloxy)tin (199 mg, 0.5 mmol) and diethyl acetylenedicarboxylate (85 mg, 0.5 mmol) were added to 5 mol dm^{-3} solutions of $LiClO_4$ in diethyl ether (1 cm^3). The progress of the reaction was monitored by TLC (using light petroleum–ethyl acetate mixture (4 : 1, v/v) as eluent) and by NMR spectroscopy which showed that a mixture of 2-(*o*-tolyloxy)maleic acid diethyl ester (**11**), 2-(*o*-tolyloxy)fumaric acid diethyl ester (**12**), 2-(2-hydroxy-3-methylphenyl)maleic acid diethyl ester (**13**) and 2-(2-hydroxy-3-methylphenyl)fumaric acid diethyl ester (**14**) was formed with 80% yield. The ratio of obtained products **11 : 12 : 13 : 14** was equal to 1.5 : 1.5 : 1 : 1. Products of all studied reactions were separated in the same way. First, lithium perchlorate was removed from the reaction mixture by washing it with water. Next, to hydrolyse the remaining unreacted tributyltin phenoxides, the reaction mixture was stored over aqueous 0.1 M solution of HCl for 24 h. After removing the water, the organic materials were dissolved in diethyl ether and dried over Na_2SO_4. Preliminary isolation of the products of the studied reactions was carried by column chromatography using petroleum–ethyl acetate mixture (7 : 3, v/v as eluent). Further isolation of separate isomers from the mixture of products was performed using the petroleum–ethyl acetate mixture (1 : 10, v/v as eluent). Products of the reactions of sodium phenoxides with diethyl acetylenedicarboxylate were purified by column chromatography using petroleum-ethyl acetate mixture (7 : 3, v/v as eluent). Although the compounds **1, 2, 7, 8, 11, 12, 15** and **16** were obtained previously,[11] their NMR data were not available. The reaction products were

Table 2. Reation of sodium phenoxides with diethylacetylenedicarboxylate carried out in benzene

Sodium Pheoxide	Product
	 (1) (2) **1 : 2 = 1 : 1**
	 (7) (8) **7 : 8 = 1 : 1**
	 (11) (12) **11 : 12 = 1 : 3**
	 (15) (16) **15 : 16 = 1 : 2**

The yield of all collected above reactions was approximately equal to 80%. Formation of product was not observed for sodium phenoxide under studied conditions.

characterized by the following values of chemical shifts:

(1) 2-(2,6-Dimethoxyphenoxy)maleic acid diethyl ester oil. δ_H ($CDCl_3$): 1.14 (6H, dt, $J = 7.1$ and 4.2 Hz), 3.74 (3H, s), 4.09 (2H, q, $J = 7.1$ Hz), 4.30 (2H, q, $J = 7.1$ Hz), 4.99 (1H, s), 6.54 (2H, d, $J = 8.4$ Hz), 6.99 (1H, m).

(2) 2-(2,6-Dimethoxyphenoxy)fumaric acid diethyl ester oil. δ_H ($CDCl_3$): 1.08 (2H, t, $J = 7.1$ Hz), 1.30 (2H, t, $J = 7.1$ Hz), 3.72 (3H, s), 4.03 (4H, dt, $J = 7.1$ and 3.5 Hz), 6.06 (1H, s), 6.49 (2H, d, $J = 8.4$ Hz), 6.90 (1H, m).

(3) 2-(Phenoxy)maleic acid diethyl ester oil. δ_H ($CDCl_3$): 1.12 (3H, t, $J = 7.2$ Hz), 1.26 (3H, t, $J = 7.2$ Hz), 4.05 (2H, q, $J = 7.2$ Hz), 4.30 (2H, q, $J = 7.2$ Hz), 5.01 (1H, s), 7.01 (2H, dd, $J = 8.2$ and 1.0 Hz), 7.16 (1H, m), 7.30 (2H, d, $J = 8.2$ Hz).

(4) 2-(Phenoxy)fumaric acid diethyl ester oil. δ_H ($CDCl_3$): 1.14 (6H, t, $J = 7.2$ Hz), 4.11 (4H, q, $J = 7.2$ Hz), 6.51 (1H, s), 6.99 (2H, d, $J = 8.2$ Hz), 7.18 (1H, m), 7.31 (2H, d, $J = 8.2$ Hz).

(5) 2-(2-Hydroxy-1-phenyl)maleic acid diethyl ester oil. δ_H ($CDCl_3$): 1.14 (3H, t, $J = 7.2$ Hz), 1.30 (3H, t, $J = 7.2$ Hz), 4.11 (2H, q, $J = 7.2$ Hz), 4.30 (2H, q, $J = 7.2$ Hz), 5.01 (1H, s), 7.05 (1H, d, $J = 7.1$ Hz), 7.20 (2H, m), 7.32 (1H, dd, $J = 7.1$ and 2.4 Hz).

(6) 2-(2-Hydroxy-1-phenyl)fumaric acid diethyl ester oil. δ_H ($CDCl_3$): 1.14 (6H, t, $J = 7.2$ Hz), 4.11 (4H, q, $J = 7.2$ Hz), 6.51 (1H, s), 6.90 (1H, dd, $J = 8.2$ and 1.4 Hz), 7.03 (1H, m), 7.21 (2H, d, $J = 8.2$ Hz).

(7) 2-(*p*-Tolyloxy)maleic acid diethyl ester oil. δ_H ($CDCl_3$): 1.16 (3H, t, $J = 7.1$ Hz), 1.38 (3H, t, $J = 7.1$ Hz), 2.35 (3H, s), 4.16 (2H, q, $J = 7.1$ Hz), 4.30 (2H, q, $J = 7.1$ Hz), 5.09 (1H, s), 7.00 (2H, d, $J = 8.3$ Hz), 7.19 (2H, d, $J = 8.3$ Hz).

(8) 2-(*p*-Tolyloxy)fumaric acid diethyl ester oil. δ_H ($CDCl_3$): 1.22 (3H, t, $J = 7.1$ Hz), 1.33 (3H, t, $J = 7.1$ Hz), 2.29 (3H, s), 4.16 (2H, q, $J = 7.1$ Hz), 4.29 (2H, q, $J = 7.1$ Hz), 6.52 (1H, s), 6.85 (2H, d, $J = 8.3$ Hz), 7.08 (2H, d, $J = 8.3$ Hz).

(9) 2-(2-Hydroxy-5-methyl-1-phenyl)maleic acid diethyl ester oil. δ_H ($CDCl_3$): 1.22 (3H, t, $J = 7.2$ Hz), 1.37 (3H, t, $J = 7.2$ Hz), 2.27 (3H, s), 4.12 (2H, q, $J = 7.2$ Hz), 4.39 (2H, q, $J = 7.2$ Hz), 5.10 (1H,s), 6.73 (1H, d, $J = 8.3$ Hz), 6.99 (1H, d, $J = 8.3$ Hz), 7.19 (1H, d, $J = 8.3$ Hz).

(10) 2-(2-Hydroxy-5-methyl-1-phenyl)fumaric acid diethyl ester oil. δ_H ($CDCl_3$): 1.35 (6H, t, $J = 7.2$ Hz), 2.35 (3H, s), 4.28 (2H, q, $J = 7.1$ Hz), 4.39 (2H, q, $J = 7.1$ Hz), 6.53 (1H, s), 6.85 (1H, d, $J = 8.3$ Hz), 7.08 (1H, d, $J = 8.3$ Hz), 7.20 (1H,m).

(11) 2-(*o*-Tolyloxy)maleic acid diethyl ester oil. δ_H ($CDCl_3$): 1.22 (3H, t, $J = 7.1$ Hz), 1.39 (3H, t, $J = 7.1$ Hz), 2.25 (3H,s), 4.14 (2H, t, $J = 7.1$ Hz), 4.40 (2H, t, $J = 7.1$ Hz), 4.94 (1H, s), 7.05 (1H, dd, $J = 7.5$ and 2.0 Hz), 7.18 (1H, dd, $J = 8.0$ and 2.0 Hz), 7.25 (2H, m).

(12) 2-(*o*-Tolyloxy)fumaric acid diethyl ester oil. δ_H ($CDCl_3$): 1.14 (3H, t, $J = 7.1$ Hz), 1.22 (3H, t, $J = 7.1$ Hz), 2.36 (3H, s), 4.16 (4H, dq, $J = 7.1$ and 1.2 Hz), 6.53 (1H, s), 6.68 (1H, d, $J = 8.0$ Hz), 6.99 (1H, dd, $J = 7.4$ and 1.5 Hz), 7.06 (1H, dd, $J = 7.9$ and 1.5 Hz), 7.19 (1H, d, $J = 7.4$ Hz).

(13) 2-(2-Hydroxy-3-methyl-1-phenyl)maleic acid diethyl ester oil. δ_H ($CDCl_3$): 1.22 (3H, t, $J = 7.1$ Hz), 1.39 (3H, t, $J = 7.2$ Hz), 2.24 (3H, s), 4.14 (2H, q, $J = 7.1$ Hz), 4.41 (2H, q, $J = 7.2$ Hz), 4.93 (1H, s), 7.04 (1H, d, $J = 8.0$ Hz), 7.25 (2H,m).

(14) 2-(2-Hydroxy-3-methyl-1-phenyl)fumaric acid diethyl ester oil. δ_H ($CDCl_3$): 1.25 (6H, t, $J = 7.2$ Hz), 2.36 (3H, s), 4.14 (2H, q, $J = 7.2$ Hz), 4.23 (2H, q, $J = 7.2$ Hz), 6.52 (1H, s), 6.74 (1H, d, $J = 8.0$ Hz), 7.15 (2H, m).

(15) 2-(2-Methoxyphenoxy)maleic acid diethyl ester oil. δ_H ($CDCl_3$): 1.23 (3H, t, $J = 7.1$ Hz), 1.38 (3H, t, $J = 7.1$ Hz), 3.86 (3H, s), 4.16 (2H, q, $J = 7.1$ Hz), 4.39 (2H, q, $J = 7.1$ Hz), 5.01 (1H,s), 6.92 (1H, d, $J = 8.0$ Hz), 7.01 (1H, m), 7.10 (1H, d, $J = 8.0$ Hz), 7.23 (1H, m).

(16) 2-(2-Methoxyphenoxy)fumaric acid diethyl ester oil. δ_H ($CDCl_3$): 1.16 (3H, t, $J = 7.1$ Hz), 1.22 (3H, t, $J = 7.1$ Hz), 3.86 (3H, s), 4.14 (4H, q, $J = 7.1$ Hz), 6.46 (1H, s), 6.86 (2H, m), 6.92 (1H, d, $J = 8.0$ Hz), 7.01 (1H, m).

(17) 2-(2-Hydroxy-3-methoxy-1-phenyl)maleic acid diethyl ester oil. δ_H ($CDCl_3$): 1.23 (3H, t, $J = 7.1$ Hz), 1.38 (3H, t, $J = 7.1$ Hz), 3.86 (3H, s), 4.16 (2H, q, $J = 7.1$ Hz), 4.39 (2H, q, $J = 7.1$ Hz), 5.01 (1H, s), 6.86 (2H, m), 6.89 (1H, m).

(18) 2-(2-Hydroxy-3-methoxy-1-phenyl)fumaric acid diethyl ester oil. δ_H ($CDCl_3$): 1.16 (3H, t, $J = 7.1$ Hz), 1.22 (3H, t, $J = 7.1$ Hz), 3.86 (3H, s), 4.14 (4H, q, $J = 7.1$ Hz), 6.46 (1H, s), 6.79 (2H, m), 6.84 (1H, m).

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