# Radical Additions of Alcohols to Esters of Fumaric and Maleic Acids

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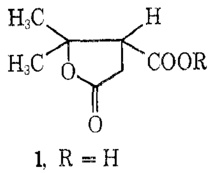
Peroxide-initiated radical additions of alcohols to esters of fumaric and maleic acids are described. By these radical additions γ-alkyl and γ-phenyl paraconic acid derivatives are produced in high yields, especially in the case of esters of maleic acid. The combination of some primary alcohols and diethyl fumarate (DEF) and diethyl maleate (DEM) yields two geometrical isomers with arbitrary isomer ratios, preferentially trans isomers from DEF and cis isomers from DEM. Relative ratios of two different attacks on DEF or DEM show straight lines in the Arrhenius plot and the compensating rule is applied for their activation parameters. A larger effect is observed in the radical additions to DEF. They are interpreted in terms of the steric effect in the transition states for the attacks of alcohol carbon radicals on DEF or DEM.

The α-hydrogen of alcohols is susceptible to abstraction, and the resulting radical is capable of reaction with olefins in a chain process.[1] The peroxide-[2] and photoinitiated[3] radical additions of alcohols to α,β-unsaturated carboxylic acids and their esters have produced a variety of γ-butyrolactone derivatives. Terebinic acid obtained by the photoinitiated addition resulted from the combination of 2-propanol and fumaric or maleic acid.[3] This investigation also provides several γ-substituted paraconic acid derivatives by the peroxide-initiated additions of several alcohols to esters of fumaric and maleic acids.

During the course of these reactions two adjacent asymmetric centers, generated in the addition step, give two geometrical isomers **a** and **b** as shown in Chart I. Accordingly, two isomers are determined by competition between two routes and the ratio of rate constants $k_a/k_b$ may be determined directly by measuring the isomer ratio **a/b.** Then we may expect the systematic change of the various isomer ratios from the different geometries of their transition states, which would probably be caused by combining several alcohols ($R_1 \neq R_2$) with DEF or DEM. On the basis of this consideration, to obtain any information on the behavior of the addition step was the second subject of this investigation.

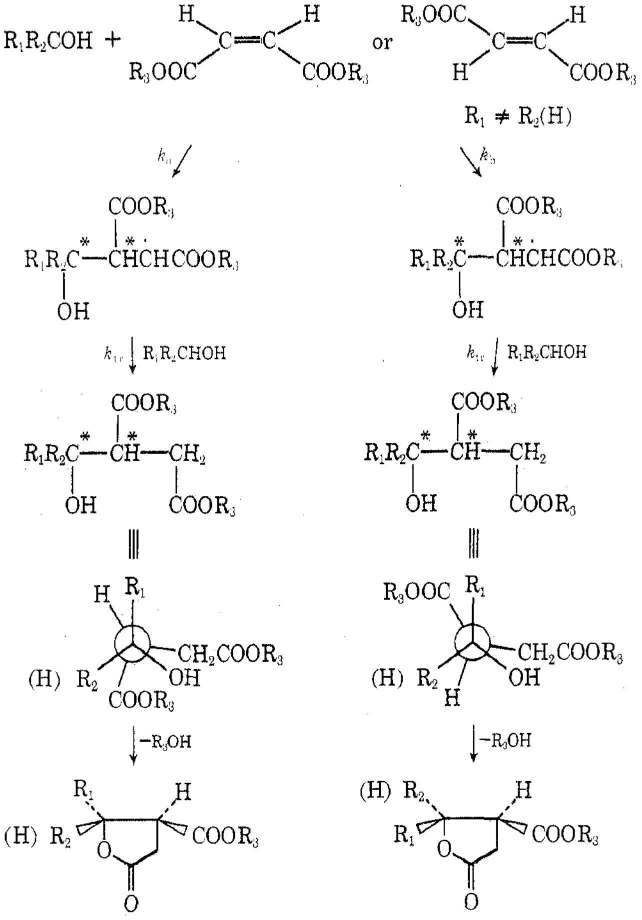
## Results and Discussion

The present reactions were accomplished by heating a reaction mixture in a sealed tube at an arbitrary temperature (70–150°). Upon continued heating a mixture of 2-propanol, maleic anhydride, and di-*tert*-butyl peroxide (DTBP), terebinic acid **1** and its ester **2** were obtained in 21 and 34% yields, respectively. In this reaction the 1:1 adduct of alcohol and maleic anhydride was not formed, because maleic anhydride in alcohol is esterified rapidly and quantitatively.[4] Furthermore, the reactions in monoisopropyl maleate, in diisopropyl fumarate, and in diisopropyl maleate yielded **2** in 49, 48, and 75% yields, respectively. In the case of the reaction in monoisopropyl maleate, **1** was also obtained in 37% yield in addition to **2.** It is obvious that **1**, derived from monoisopropyl maleate, is formed by an attack on the carbon adjacent to the carboxylic acid group, while **2** is formed by an attack on the carbon adjacent to the alkoxycarbonyl group.



**1**, R = H
**2**, R = $CH(CH_3)_2$

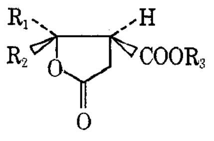
### Chart I
### Formation Routes of Two Isomers by Radical Addition to DEM or DEF



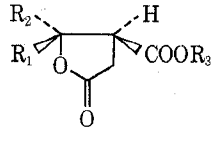
Similarly, reactions in a variety of alcohols and diesters of fumaric and maleic acids gave the various γ-substituted derivatives of paraconic acid. The survey of these products is shown in Tables I and II.

A good yield of a 1:1 adduct should be obtained by highly effective hydrogen abstraction before propagation. As is suggested by Mayo's equation,[5] a low molecular weight polymer or telomer containing a 1:1 adduct should be obtained under conditions of lower monomer concentration. The results for **7a** and **7b** listed in Table I apparently show the tendency expected from Mayo's equation. Generally, the chain transfer constant $C$ ($= k_{tr}/k_p$) increases with temperature because of higher activation energy for trans-

## Table I
## Products and Yields of γ-Substituted Paraconic Acid Derivatives



a



b

| Product[a] | $R_1$ | $R_2$ | $R_3$ | Mole ratio of alcohol to monomer | Temp, °C | Yield, %[b], for monomer used | |
|---|---|---|---|---|---|---|---|
| | | | | | | Fumarate | Maleate |
| 2 | $CH_3$ | $CH_3$ | $CH(CH_3)_2$ | 20 | 130 | | 75 |
| 3 | $CH_3$ | $CH_3$ | $CH_3$ | 20 | 130 | | 96 |
| 4 | H | H | $CH_3$ | 20 | 130 | | 20 |
| 5 | $(CH_2)_5$ | | $CH_3$ | 20 | 130 | | 50 |
| 6a,b | $CH_2CH_3$ | $CH_3$ | $CH_3$ | 20 | 130 | | 64 |
| 7a,b | $CH_3$ | H | $CH_2CH_3$ | 20 | 150 | 34 | 83 |
| | | | | 20 | 130 | 27 | 73 |
| | | | | 20 | 70 | 6 | 20 |
| | | | | 5 | 130 | 12 | 46 |
| | | | | 40 | 130 | 28 | 86 |
| 8a,b | $CH_2CH_3$ | H | $CH_2CH_3$ | 20 | 150 | 31 | 52 |
| | | | | 20 | 130 | 24 | 49 |
| 9a,b | $CH_2CH_2CH_3$ | H | $CH_2CH_3$ | 20 | 130 | | 35 |
| 10a,b | $C(CH_3)_3$ | H | $CH_2CH_3$ | 20 | 130 | | 30 |
| 11a,b | $C_6H_5$ | H | $CH_2CH_3$ | 20 | 130 | | 50 |

[a] Satisfactory elemental analyses for C, H (±0.35%) were obtained. [b] Yields were calculated, based on monomer employed and given as the sum of two isomers for the compounds 6–11 ([monomer]/[alcohol] = 0.05 mole ratio).

## Table II
## Indices of Refraction and Ir and Nmr Spectra

| Product | Nmr, δ | | | | | | |
|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | α-$CH_2$ and β-CH | $n^{20}D$ | Ir, $\nu_{C=O}$, $cm^{-1}$ | |
| 2[a] | 1.56 (s) | 1.28 (s) | 4.8–5.2 (m), 1.27 (d) | 2.4–3.4 (m) | 1.4500 | 1735 | 1785 |
| 3[a] | 1.61 (s) | 1.31 (s) | 3.68 (s) | 2.4–3.4 (m) | 1.4502 | 1746 | 1785 |
| 4[a] | 4.39 (d) | 4.31 (d) | 3.69 (s) | 2.4–3.6 (m) | 1.4618 | 1745 | 1792 |
| 5[a] | 1.0–1.9 (m) | | 3.72 (s) | 2.4–3.4 (m) | c | 1748 | 1787 |
| 6a[b] | 1.83 (q), 0.97 (t) | 1.20 (s) | 3.69 (s) | 2.4–3.4 (m) | | 1748 | 1794 |
| 6b[b] | 1.49 (q), 0.72 (t) | 1.48 (s) | 3.69 (s) | 2.4–3.4 (m) | | | |
| 7a | 1.49 (d) | 4.65 (m) | 4.17 (q), 1.27 (t) | 2.5–3.2 (m) | 1.4443 | 1744 | 1793 |
| 7b | 1.27 (d) | 4.85 (m) | 4.21 (q), 1.28 (t) | 2.4–3.6 (m) | 1.4462 | 1743 | 1794 |
| 8a | 1.81 (m), 1.05 (t) | 4.50 (m) | 4.24 (q), 1.30 (t) | 2.5–3.3 (m) | 1.4539 | 1725 | 1780 |
| 8b | 1.50 (m), 1.07 (t) | 4.57 (m) | 4.27 (q), 1.32 (t) | 2.4–3.6 (m) | 1.4547 | 1734 | 1792 |
| 9a | 1.5–1.9 (m), 0.98 (t) | 4.0–4.7 (m) | 4.18 (q), 1.28 (t) | 2.4–3.2 (m) | 1.4480 | 1740 | 1780 |
| 9b | 1.1–1.9 (m), 0.98 (t) | 4.2–4.8 (m) | 4.19 (q), 1.30 (t) | 2.4–3.6 (m) | 1.4514 | 1740 | 1780 |
| 10a | 0.99 (s) | 4.11 (d) | 4.24 (q), 1.27 (t) | 2.4–3.3 (m) | 1.4498 | 1739 | 1786 |
| 10b | 1.00 (s) | 4.18 (d) | 4.17 (q), 1.30 (t) | 2.4–3.4 (m) | 1.4568 | 1738 | 1791 |
| 11a[b] | 7.33 (s) | 5.52 (d) | 4.16 (q), 1.21 (t) | 2.2–2.9 (m) | | 1725 | 1770 |
| 11b[b] | 7.26 (s) | 5.65 (d) | 3.63 (q), 0.77 (t) | 2.6–3.8 (m) | | | |

[a] $R_1$ and $R_2$ groups of 2, 3, 4, and 5 are situated in the trans and cis positions to the alkoxycarbonyl group, respectively, *i.e.*, in the configuration of **a**. [b] Separation of two isomers was unsuccessful. [c] Mp 67–69°.

fer reaction than for propagation. Furthermore, the chain transfer constant for DEM becomes inevitably larger, compared with that for DEF, because the rate of propagation of DEM is considerably smaller. Reactions of DEM at higher temperatures may therefore give lactones in higher yields.

Reactions of DEF and DEM with some primary alcohols (except methanol) produced the respective sets of two geometrical isomers (**7a** and **7b**; **11a** and **11b**) with arbitrary ratios as evidenced by elemental analyses and nmr and ir spectra.

Evidence for the configurational assignment of two isomers was obtained by the comparison of nmr spectra between γ-substituted paraconic acid derivative(s) and the corresponding itaconic acid derivative(s),[6] which is derived by the treatment of γ-substituted paraconic acid derivative(s) with potassium *tert*-butoxide.[7] It was concluded in our earlier results that the resonance of the cis methyl protons (1.53 and 1.31 ppm) to the carboxyl group of 1 and to the alkoxycarbonyl group of 3 is shifted to a higher field than that of the trans methyl protons (1.73 and 1.61 ppm) as identified from the results of nmr spectra for terebinic acid 1 and its ester 3 reported by Savostianoff, *et al.*[8] Similar results for the assignment of **7a** and **7b** were also obtained between any signals for a cis hydrogen atom (4.65 ppm) and cis methyl protons (1.27 ppm) to the alkoxycarbonyl group and those for the corresponding trans protons (4.85 and 1.49 ppm). Also, in the case of γ-phenyl paraconic

**Table III**
**Isomer Ratios and Activation Parameters for the Additions to DEF and DEM**

| Product | Isomer ratios a/b($k_a/k_b$)[a] at temp, °C 150 | 130 | 110 | 70 | Activation parameters $\Delta H_a^* - \Delta H_b^*$, kcal/mol | $\Delta S_a^* - \Delta S_b^*$, cal/deg |
|---|---|---|---|---|---|---|
| | | | DEF | | | |
| **7a,b** | 1.16 | 1.23 | 1.21 | 1.30 | −0.6 | −1.1 |
| **8a,b** | 1.13 | 1.26 | 1.40 | 1.59 | −1.3 | −2.7 |
| **9a,b** | 1.52 | 1.96 | 2.68 | 4.24 | −3.8 | −8.1 |
| **10a,b** | 1.43 | 1.93 | 2.74 | 6.30 | −5.6 | −12.4 |
| **11a,b** | 1.32 | 1.77 | 1.98 | 2.89 | −2.8 | −6.1 |
| | | | DEM | | | |
| **7a,b** | 0.92 | 0.84 | 0.80 | 0.74 | 0.9 | 2.0 |
| **8a,b** | 0.91 | 0.88 | 0.82 | 0.79 | 0.5 | 1.3 |
| **9a,b** | 0.87 | 0.83 | 0.75 | 0.72 | 0.9 | 1.9 |
| **10a,b** | (0.85)[b] | (1.12) | (1.59) | (2.04) | | |
| **11a,b** | (1.16)[b] | (1.67) | | | | |

[a] The $k_a/k_b$ ratios were determined by extrapolating the isomer ratios to infinite dilution. [b] The reversible addition to DEM ([DEM]/[alcohol] = 0.05 mole ratio) is designated in parentheses.

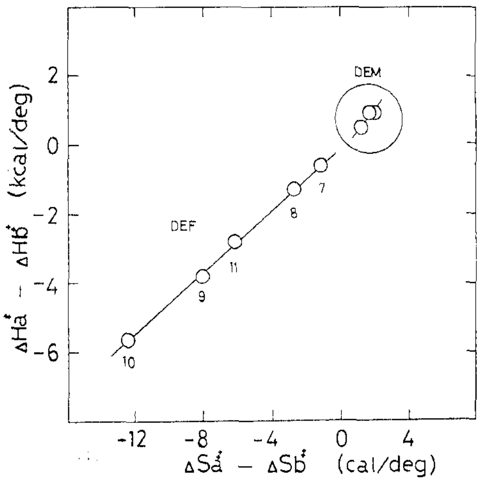


**Figure 1.** Isokinetic relationship in the effect of alcohols ($RCH_2OH$) on **a**/**b** ratios in the radical additions of alcohols to DEF and DEM. R: 7, $CH_3$; 8, $CH_3CH_2$; 9, $CH_3CH_2CH_2$; 10, $(CH_3)_3C$; 11, $C_6H_5$.

acid esters (**11a,b**), cis alkoxy protons (3.63 and 0.77 ppm) to the phenyl group resonate upfield, compared with trans alkoxy protons (4.16 and 1.21 ppm). In conclusion, the results presented in Table II show that the resonances of cis methyl protons, a cis hydrogen atom, and even cis phenyl protons are shifted to the higher field by 0.3–0.2, 0.2–0.1, and 0.07 ppm, respectively, when they are in the cis position to the alkoxycarbonyl group. Also cis alkoxy protons to the phenyl group resonate upfield by *ca.* 0.5 ppm. These upfield shifts can be attributed to the diamagnetic anisotropy and the long-range shielding effects in the carbonyl and phenyl groups.

Further evidence for the isomer assignment was indirectly obtained by predicting the predominant isomer **7b** or **11b** on the basis of Cram's rule[9] from the reaction of the ethyl ester of acetylsuccinic acid or benzoylsuccinic acid with sodium borohydride. This selective reduction, in which a new asymmetric center is created on a carbon adjacent to the asymmetric center already present in a molecule, gave two isomers **7a** and **7b** or **11a** and **11b**. Cram's model predicts that the threo isomer should predominate over the erythro isomer because of the order of decreasing effective size of three groups on the adjacent carbon to the carbonyl group: COOR > $CH_3$ = $CH_2COOR$[10] > H. The spectral data for **7a** and **7b** or **11a** and **11b** obtained by this reduction were completely identical with those for the corresponding products in Table II.

Consequently, the faster eluting component (Apiezon Grease L) of two isomers is confirmed to be a trans isomer, *i.e.*, the **a** type, and its refractive index shows a slightly smaller value.

The two geometrical isomers formed in the addition of the alcohol carbon radicals in the presence of DEF or DEM are governed by the competing reactions. Accepting the premise that the rate-determining step of this process is the addition step, the isomer ratio should give the ratio of the rate constants, $k_a/k_b$, directly. Although it has been said that the reversible radical addition of the carbon radical species under usual experimental conditions does not occur,[11] the cis–trans isomerization of DEM in the cases of neopentanol and phenylmethanol was observed to occur frequently. However, such a reversible reaction of DEM in each solution of ethanol, 1-propanol, and 1-butanol was negligibly small, as well as that of DEF in any alcohol solution. All of our data in some five alcohols and the two monomers DEF and DEM are shown in Table III. *A trans isomer* **a** *from DEF and a cis isomer* **b** *from DEM are predominantly produced, respectively, and furthermore, the isomer ratios from both monomers become closer to unity with an increase in temperature.*

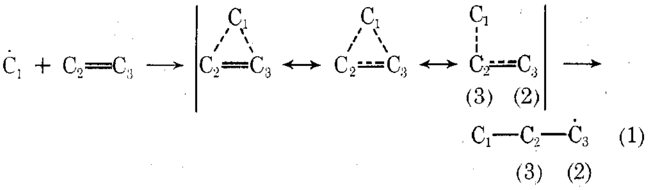
From the transition state theory, we express the rate constant in terms of the corresponding free energy of activation. As all the required data are given as the ratios of rate constants, this expression is given as the difference of the corresponding energies. From the isomer ratios, the activation parameters may be calculated in the usual manner by plotting log $k_a/k_b$ *vs.* $1/T$. The results for the differences in the enthalpy and entropy of activation are given on the right side of Table III. The interchange of DEF and DEM is effective in reversing reactivity and, also, a variety of alcohols are efficient in altering reactivity, especially in the reactions of DEF.

Such an effect caused by a change in alcohol resembles seemingly very closely the solvent effects in many radical reactions. Changes in the reaction rates caused by solvents have been discussed as the effects of solvents on the transition states involved and the compensating law applies to the changes in enthalpy and entropy of activation.[12] This research provides also an example of such a compensating trend as can be seen from Table III or by examination of the isokinetic plot (Figure 1), introduced by Leffer.[13] This excellent linear relationship in a negative region suggests a certain steric influence of a substituent in alcohol in the order of methyl, ethyl, phenyl, propyl, and *tert*-butyl. This is about the order expected on the basis of the steric effect, which appears to be that of increasing effective size of the substituent.[14] The small clump of encircled points includes the reactions of DEM in ethanol, 1-propanol, and 1-butanol, implying an undiscernible dependence of such an effect on the substituent.

The two different types of the effect permit us to conclude that both additions to DEF and DEM proceed through the respective different transition states and give trans and cis isomers with arbitrary ratios. The difference in the reactivity between DEF and DEM means that the transition state is rigid in respect to the central C–C bond. The contribution of a considerable resonance energy to the transition state is reflected in the higher reactivity of DEF, which is approximately planar, and manifested by the lower activation energy of the addition reaction to DEF.[15]

Since the transition state is rigid and no internal rotation takes place along the C–C bond, the configuration of the transition state should resemble somewhat that of the starting material, especially in the case of DEF.[15,16]

Next we turn our attention to an important problem, namely, how to account for the dependence of the isomer ratios on monomers used. Since the radical addition reactions are of the three-center type, *via* the transition states such as shown in eq 1,[17] where $C_1$ and $C_2{=}C_3$ are R$\dot{C}$HOH



(1)

and DEF or DEM, respectively, we can speculate on selectivity in the formation of trans and cis isomers from the tentative models of the transition states.

An attack of C-1 on C-2 of DEM leads to a trans isomer and the other attack of C-1 on C-3 gives a cis isomer, as expected from the geometry of transition state models (see Chart II). Since the bridging model of the C=C double bond presents exactly a common geometry to the formation of trans and cis isomers, the effect of a substituent R on both routes does not appear. However, when the energy localized on the C=C double bond migrates onto the C—C single bond (quasi-single $C_1$—$C_2$ and $C_1$—$C_3$ bonds), the difference in the potential energies between two routes first develops. As it can be assumed that models of these two states resemble approximately the final states ($C_1$—$C_2$—$\dot{C}_3$ and $C_1$—$C_3$—$\dot{C}_2$ radicals), the radical species leading to a threo isomer proves to be more stable, judged from the effective size of substituents around two carbons ($C_1$—$C_2$ and $C_1$—$C_3$) in Newman's projection diagram of the resulting radicals. This means that the addition reaction with alcohol and DEM demonstrates the predominance of a cis isomer **b**.

**Chart II**

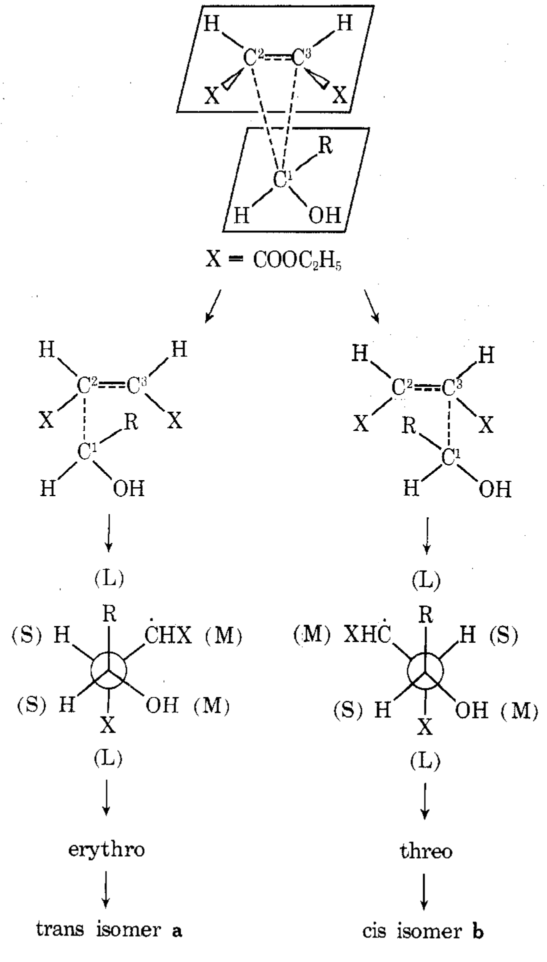
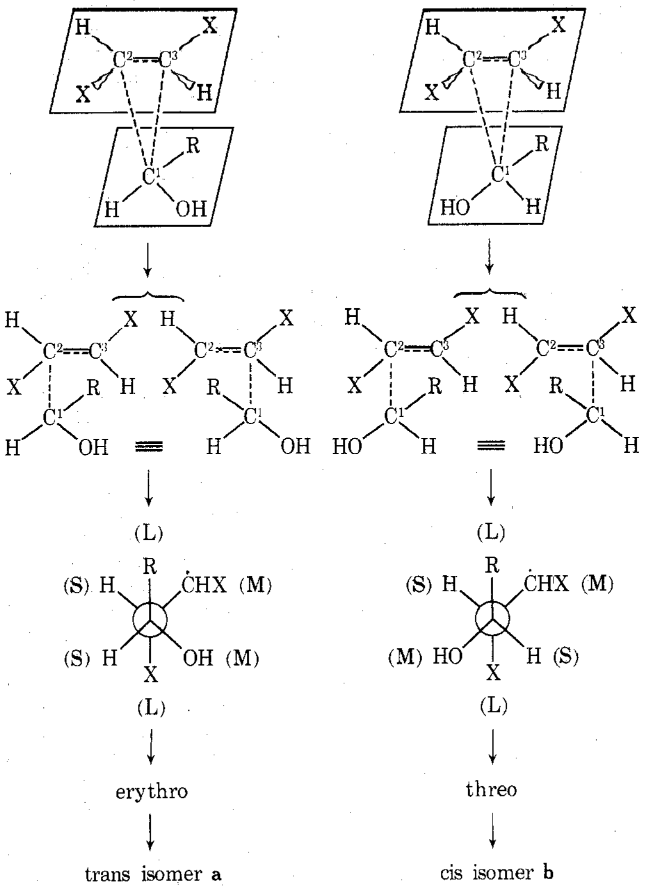


**Chart III**



On the other hand, in the case of DEF, models of the respective transition states between two routes are geometrically different from each other (see Chart III). A bridging model gives a trans isomer by an attack of C-1 on either C-2 or C-3, and also a cis isomer is obtained by a similar attack on another bridging model. From the steric grounds between both models the former is apparently more operative, because nonbonded repulsion between the attacking radical and DEF is more significant in the latter model, while the model having a quasi-single bond ($C_1$---$C_2$==$C_3$ and $C_1$---$C_3$==$C_2$) is operative for the cis isomer in a case similar to DEM. However, since the transition state of the addition to DEF resembles the structure of the starting material very closely, the state of the bridging model may be considered to function more largely. The conclusion is, therefore, obvious: the trans isomer is obtained by the addition to DEF in preference to the cis isomer.

## Experimental Section

All alcohols, dimethyl maleate, DEM, DEF, and di-*tert*-butyl peroxide (DTBP), are of commercial origin and these reagents were purified by fractional distillation. Maleic anhydride and benzoyl peroxide (BPO) were recrystallized from benzene and carbon tetrachloride, respectively. Diisopropyl maleate was prepared from maleic anhydride and 2-propanol and diisopropyl fumarate was formed from the inversion of the maleate.[18]

Nmr spectra were obtained on a Japan Electron Optics Laboratory 4H 100 spectrometer and taken in a $CCl_4$ solution. Chemical shifts are reported as δ (parts per million) relative to tetramethylsilane as standard. According to our requirements, the spin decoupling procedure was used. Infrared spectra were obtained with a Japan Spectroscopic Co. DS-402G spectrometer and taken in a $CCl_4$ solution. Glc analyses were performed with a Yanagimoto MFG Co. GCG-550T gas chromatograph with a 3 mm × 2.5 m 10% Apiezon GL column on 60–80 mesh Neopack 1A.

**Reactions of 2-Propanol with Maleic Anhydride and Its Esters.** A solution of 2-propanol (120.2 g, 2.00 mol), maleic anhydride (9.81 g, 0.10 mol), and DTBP (1.46 g, 0.01 mol) was sealed under nitrogen in a glass tube and heated for 10 hr at 130°. Unreacted 2-propanol was evaporated. The residue was gas chromatographed and yields of terebinic acid **1** and its isopropyl ester **2** were determined to be 21 and 34%, respectively. On standing or cooling **1** was isolated from the residue: mp 172–173° (lit.[3] 174–175°); ir (KBr) 1740; nmr ($CCl_4$) 1.73 (s, $CH_3$), 1.53 (s, $CH_3$) (lit.[8] 1.75 and 1.56, respectively), 2.8–3.9 (m, $\alpha$-$CH_2$ and $\beta$-CH). *Anal.* Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 52.98; H, 6.37.

Also the preparative glpc or the vacuum distillation of the residue gave **2**, bp 115–116° (5 mm). Physical data for **2** are shown in Table II.

A similar procedure for the reaction of 2-propanol with monoisopropyl maleate (half ester) yielded **1** and **2** in 37 and 49% yields, respectively. Also, the similar reactions of diisopropyl maleate and diisopropyl fumarate gave **2** in 75 and 48% yields, respectively.

**Reactions of Alcohols with Esters of Fumaric and Maleic Acids.** A solution of DTBP or BPO (10 mol % of monomer used), the diester of fumaric or maleic acid (0.05–0.40 equiv), and each of several alcohols (2.0 equiv) was packed into a glass tube under nitrogen and heated at an arbitrary temperature for 5 (DTBP, 130 and 150°) or 10 (DTBP, 110°, and BPO 70°) hr. After evaporation of unreacted materials, the residue was gas chromatographed to determine the yields and the isomer ratio, and thereafter distilled *in vacuo*. Subsequently, two geometrical isomers were separated by preparative glpc. The faster eluting component of isomers was assigned as an **a** type lactone (trans isomer), as a result of this work. The isomer ratios of **6a** and **6b** and **11a** and **11b** were determined by the intensity ratios on nmr spectra because of the unsuccessful separation by means of glpc. Experimental results and physical and spectral data for the products are summarized in Tables I, II, and III.

**Reaction of Diethyl Ester of Acetylsuccinic Acid[19] with Sodium Borohydride.** A cold aqueous solution (4 ml) of sodium borohydride (0.95 g, 0.025 mol) was added dropwise while stirring a cold solution of the ethyl ester (10.8 g, 0.05 mol) dissolved in alcohol (35 ml). The mixture was stirred for 1 hour at room temperature, hydrolyzed with aqueous ammonia, and then extracted with ether. The ether solution was washed with diluted hydrochloric acid and with a saturated sodium chloride solution, then dried with sodium sulfate, and finally evaporated. Glpc analysis of the crude product mixture yielded two compounds and the ratio of the faster eluting component to the second was calculated to be 1:4.3. Glpc and nmr analyses of the respective components showed identical results with those of **7a** and **7b**: nmr ($CCl_4$) for the faster eluting component 1.47 (d, $\gamma$-$CH_3$), 4.57 (m, $\gamma$-H), 2.5–3.2 (m, $\alpha$-$CH_2$ and $\beta$-CH), 4.17 (q, $COOCH_2CH_3$), 1.27 (t, $COOCH_2CH_3$), $J_{\beta,\gamma\text{-H}}$ = 5.6 Hz; for the second component 1.27 (d, $\gamma$-$CH_3$), 4.79 (m, $\gamma$-H), 2.4–3.6 (m, $\alpha$-$CH_2$ and $\beta$-CH), 4.21 (q, $COOCH_2CH_3$), 1.28 (t, $COOCH_2CH_3$), $J_{\beta,\gamma\text{-H}}$ = 7.0 Hz.

**Reaction of Diethyl Ester of Benzoylsuccinic Acid[20] with Sodium Borohydride.** The ester was reduced in a manner similar to that described above. Nmr analysis of the crude product mixture yielded two products **11a** and **11b** with a ratio of 1:2.5: nmr ($CCl_4$) for **11a** 7.28 (s, 5 aromatic H), 5.49 (d, $\gamma$-CH), 2.2–2.9 (m, $\alpha$-$CH_2$ and $\beta$-CH), 4.14 (q, $COOCH_2CH_3$), 1.21 (t, $COOCH_2CH_3$), $J_{\beta,\gamma\text{-H}}$ = 7.4 Hz; for **11b** 7.21 (s, 5 aromatic H), 5.61 (d, $\gamma$-H), 2.6–3.8 (m, $\alpha$-$CH_2$ and $\beta$-CH), 3.61 (q, $COOCH_2CH_3$), 0.77 (t, $COOCH_2CH_3$), $J_{\beta,\gamma\text{-H}}$ = 7.5 Hz.

**Registry No.**—**1,** 79-91-4; **2,** 34341-66-7; **3,** 6934-77-6; **4,** 5204-91-1; **5,** 18363-04-7; **6a,** 53684-24-5; **6b,** 53684-25-6; **7a,** 34310-48-0; **7b,** 34310-47-9; **8a,** 34310-49-1; **8b,** 34310-50-4; **9a,** 53684-26-7; **9b,** 53684-27-8; **10a,** 53684-28-9; **10b,** 53684-29-0; **11a,** 53684-30-3; **11b,** 53684-31-4; DEF, 623-91-6; DEM, 141-05-9; 2-propanol, 67-63-0; methanol, 67-56-1; ethanol, 64-17-5; maleic anhydride, 108-31-6; monoisopropyl maleate, 924-83-4; diisopropyl maleate, 10099-70-4; diisopropyl fumarate, 7283-70-7; diethyl acetylsuccinate, 1115-30-6; sodium borohydride, 16940-66-2; diethyl benzoylsuccinate, 10539-50-1.

## References and Notes

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