be ascribed exclusively to changes in rotational entropy in going from reactants to products. For a reaction leading to the formation of benzyl cation, $\Delta S°$ is nearly zero within the framework of the model.[23]

$$\Delta S° \approx \Delta S°_{\mathrm{ROT}} = R \ln \left\{ \left[\frac{(I_xI_yI_z)_{\mathrm{benzyl}^+}(I_xI_yI_z)_{t\text{-}\mathrm{BuCl}}}{(I_xI_yI_z)_{\mathrm{benzyl\text{-}Cl}}(I_xI_yI_z)_{t\text{-}\mathrm{Bu}^+}} \right]^{1/2} \times \left[\frac{\sigma_{\mathrm{benzyl\text{-}Cl}}\sigma_{t\text{-}\mathrm{Bu}^+}}{\sigma_{\mathrm{benzyl}^+}\sigma_{t\text{-}\mathrm{BuCl}}} \right] \right\} = R \ln \left(0.9 \times \frac{2 \times 81}{2 \times 81} \right) = -0.2 \text{ eu}$$

For the process leading to tropylium, however, the entropy change is sizable.

$$\Delta S° \approx \Delta S°_{\mathrm{ROT}} = R \ln \left\{ \left[\frac{(I_xI_yI_z)_{\mathrm{tropylium}^+}(I_xI_yI_z)_{t\text{-}\mathrm{BuCl}}}{(I_xI_yI_z)_{\mathrm{benzyl\text{-}Cl}}(I_xI_yI_z)_{t\text{-}\mathrm{Bu}^+}} \right]^{1/2} \times \left[\frac{\sigma_{\mathrm{benzyl\text{-}Cl}}\sigma_{t\text{-}\mathrm{Bu}^+}}{\sigma_{\mathrm{tropylium}}\sigma_{t\text{-}\mathrm{BuCl}}} \right] \right\} = R \ln \left(0.9 \times \frac{2 \times 81}{14 \times 81} \right) = -4.1 \text{ eu}$$

The temperature of the ICR cell may be varied from 303 to 408 K. Thus, while the free energy for reaction 3 leading to benzyl cation would be nearly independent of temperature over this range, the change in $\Delta G°$ for the corresponding process resulting in tropylium would be 0.43 kcal/mol. The energy changes associated with the formation of the benzyl and tropylium cations are different enough so as to be readily distinguishable at the level of precision with which the equilibrium constant measurements are performed. Experimentally, ΔG for eq 2 at 408 K is 0.23 ± 0.10 kcal/mol. Thus, our measured value for the free energy change over the stated temperature range, $\Delta\Delta G° = 0.05 \pm 0.15$ kcal/mol, is, within experimental error, in accord with the estimate based on rotational entropy changes alone for reaction leading to the generation of benzyl cation.[25] It is not readily interpretable in terms of the process forming tropylium.

In conclusion, both $\Delta H°$ (0.03 ± 0.24 kcal/mol) and $\Delta S°$ (-0.5 ± 1.5 eu), measured by ICR spectroscopy for the halide transfer equilibrium between benzyl and *tert*-butyl chlorides, are consistent with the notion that the $C_7H_7^+$ cation formed is the benzylic system and not the thermodynamically favored tropylium ion.[26] We feel that our results, taken together with those recently obtained by McLafferty and Dunbar and their respective co-workers, provide strong evidence for the stable existence of the benzyl cation in the gas phase.

References and Notes

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(4) Error quoted corresponds to 3 standard deviations.

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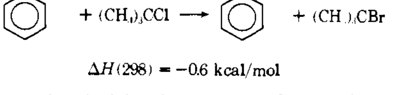

$\Delta H(298) = -0.6$ kcal/mol

mental thermochemical data from: (b) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.

(6) Such a value has been arrived at by combining the ionization potential of the *tert*-butyl free radical, as determined by Lossing and Semeluk,[7] with its heat of formation recently reported by Tsang.[8] It is in excellent agreement with a value of 169.2 kcal/mol, recently determined by pulsed ion cyclotron resonance spectroscopy.[9]

(7) F. P. Lossing and G. P. Semeluck, *Can. J. Chem.*, **48**, 955 (1970).

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(10) Heats of formation for the neutral molecules taken from ref 5b. Because of the uncertainty in the experimental $\Delta H_f°(298)$ for benzyl chloride, our value for the heat of formation of $C_7H_7^+$ could be in error by as much as 2 kcal/mol.

(11) We have actually used the experimental $\Delta H°$ for reaction 2 in the calculation of the heat of formation of $C_7H_7^+$. See subsequent discussion.

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(14) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

(15) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1972); all calculations were carried out using the Gaussian 70 series of computer programs.[16] Standard model geometries[17] have been used for neutral molecules. Structures for the benzyl[3f] and allyl[18] cations have been optimized using the minimal basis set STO-3G method.[19]

(16) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

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(21) Previous experience indicates that energetic comparisons such as those dealt with here (i.e., between species of markedly similar electronic structure) are generally well described using even simple levels of ab initio molecular orbital theory (cf. ref 3e and 3f). Although the absolute heats of formation reported may be somewhat in error (due to the uncertainty in $\Delta H_f°$ for the allyl cation) we strongly suspect that the calculated difference in energies between the benzyl and tropylium cations (9.2 kcal/mol) is correct to within 2 or 8 kcal/mol. Our theoretical results, although seemingly internally consistent, are, therefore, not in good accord with Lossing's estimate for this quantity[12] (1 or 4 kcal/mol) or for that arrived at by Dunbar[2b] (3 kcal/mol).

(22) Lossing[12] has already raised the possibility that, because of rearrangement to tropylium, the heat of formation he reports for the benzyl cation is in fact too low. The theoretical results presented here, in particular with regard to the *difference* in stabilities of the benzyl and tropylium cations, lends support to such a notion.

(23) For discussions, see: (a) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968, p 37; (b) J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley-Interscience, New York, N.Y., 1975, p 1; (c) N. Davidson, "Statistical Mechanics", McGraw-Hill, New York, N.Y., 1962, p 125.

(24) This reference deleted in proof.

(25) Consult ref 9 for comparisons of $\Delta S°$ measured experimentally and calculated on the basis of symmetry number entropy changes alone for simple ion–molecule reactions involving species of known geometrical structure. In all cases agreement is within 10–20%.

(26) Although our measured value of $\Delta\Delta G°$ does not rule out the possibility of $C_7H_7^+$ having a geometrical structure such as V, unpublished ab initio calculations by Dill, Schleyer, and Pople[27] show that such a species is very unstable relative to benzyl and tropylium cations and would result in an energy of eq 3 far different from the experimental value.

(27) J. A. Pople, private communication.

(28) Alfred P. Sloan Fellow, 1974–1976.

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Received March 29, 1976

Novel Carbon–Hydrogen Bond Cleavage by Bis(dimethylphosphino)ethane Complexes of Iron, Ruthenium, and Osmium

Sir:

We wish to report the first transition metal complex capable of rapidly cleaving a variety of C–H bonds (activated sp^3, aromatic sp^2, and sp) under mild conditions, resulting in adducts which can be fully characterized. The new complex $Fe(dmpe)_2H(C_{10}H_7)$ (**1**) ($C_{10}H_7$ = 2-naphthyl, dmpe = $Me_2PCH_2CH_2PMe_2$) prepared by the reaction of Fe-

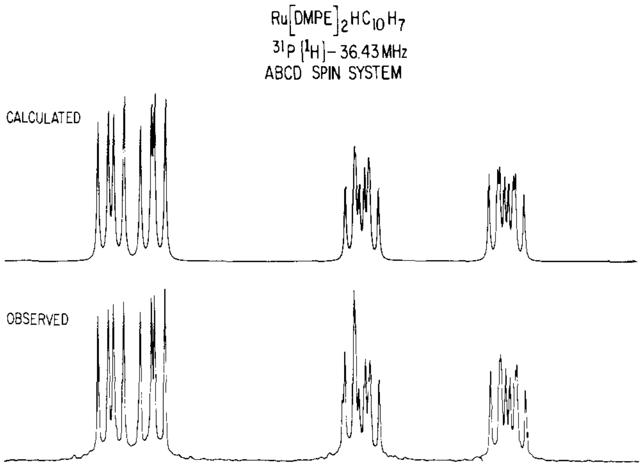


Figure 1. The observed and calculated $^{31}P\{^1H\}$ −36.43 MHz spectrum of *cis*-Ru(dmpe)$_2$H(C$_{10}$H$_7$) in THF-d_8 at 25 °C. The calculated spectrum is constructed using δ_A −43.7, δ_B −41.9, δ_C −33.3, δ_D −27.4, J_{AB} = O, J_{AC} = 15.5, J_{AD} = 23.5, J_{BC} = 21, J_{BD} = 16.5, J_{CD} = 13 Hz.

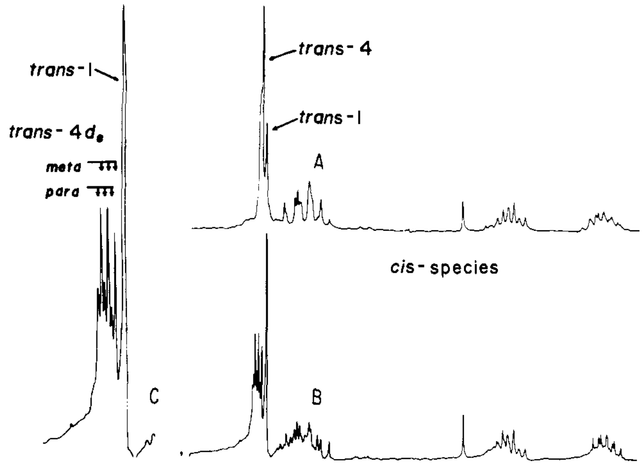
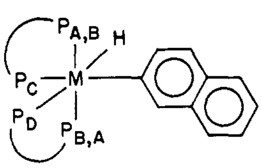


Figure 2. The $^{31}P\{^1H\}$ −36.43 MHz spectra of Fe(dmpe)$_2$H(C$_{10}$H$_7$) in toluene (A) and toluene-d_8 (B). C is an expansion of the trans region of B, displaying the singlet of **1** and 1:1:1 triplets of para and meta **4**-d_8. See text for explanation. The $^{31}P\{^1H\}$ NMR spectrum of **1** has been completely simulated.

(dmpe)$_2$Cl$_2$ with sodium naphthalenide[1] can also be used to prepare a number of new five-coordinate, zero-valent iron complexes,



1

The golden orange powder **1** has an ir spectrum (Nujol) similar to those of Ru(dmpe)$_2$*H*(C$_{10}$*H*$_7$)(**2**)[2] and Os(dmpe)$_2$H(C$_{10}$H$_7$) (**3**),[3] which we have prepared for comparison; the only substantial difference in the spectra is ν_{MH} (1725 cm^{-1} for Fe, 1780 cm^{-1} for Ru, and 1875 cm^{-1} for Os). $^{31}P\{^1H\}$ and ^1H NMR spectra of THF-d_8 solutions of all three complexes indicate a mixture of cis and trans isomers at equilibrium, though only the iron complex reaches equilibrium quickly. Figure 1 shows observed and calculated $^{31}P\{^1H\}$ spectra of *cis*-**2**. Selcetive $^1H\{^{31}P\}$ decoupling experiments establish that P$_C$ is trans to naphthyl and P$_D$ is trans to H. The NMR data for the cis molecules are consistent with the x-ray crystal structures of *cis*-**2** and -**3** [3]

1 reacts within a few minutes at 25 °C with a variety of aromatic compounds by the equation

$$\mathrm{M(dmpe)_2H(C_{10}H_7) + ArH} \overset{K_1}{\rightleftharpoons} \mathrm{M(dmpe)_2H(Ar) + C_{10}H_8} \quad (1)$$

For example, the $^{31}P\{^1H\}$ and ^1H NMR spectra of **1** in toluene show both *cis*- and *trans*-**1** and two *cis*- and two *trans*-Fe(dmpe)$_2$H(C$_6$H$_4$CH$_3$) (**4**) (Figure 2A). In C$_6$D$_5$CD$_3$, the two *trans*-Fe(dmpe)$_2$(C$_6$D$_4$CD$_3$) (**4**-d_8) resonances are 1:1:1 triplets (Figure 2B[4]) in the relative intensities of 1 to 1.6. Observation of phosphorus–deuterium coupling in the $^{31}P\{^1H\}$ NMR spectra of selectively deuterated para and meta toluene-d_1 complexes allows assignment of the smaller downfield triplet (δ −74.7) (Figure 2C) to *trans*-Fe(dmpe)$_2$H(*p*-tolyl) and the upfield triplet (δ −74.6) to the *m*-tolyl isomer. No *o*-tolyl isomer was observed, indicating a significant steric effect on the isomer distribution. Electron-withdrawing groups stabilize the Ar–M bonds as shown by increasing K_1 in the order:

$$\mathrm{C_6H_5NH_2 < C_6H_5CH_3 < C_6H_6 < C_{10}H_8 < C_6H_5CN <} \ o\text{-}\mathrm{C_6H_4(CF_3)_2}$$

Compound **2** also reacts by eq 1, but requires more forcing conditions; 8 h at 60 °C; the reaction product invariably contains more cis isomer than that of Fe. Compound **3** is much less reactive; no reaction with C$_6$D$_6$ was observed after 60 h at 75 °C.

1 and **2** also react within hours with activated sp^3 C–H bonds (acetonitrile, acetone, ethyl acetate, and methyl α-cyanoacetate).[5] For instance, acetonitrile and **1** give *trans*-Fe(dmpe)$_2$H(CH$_2$CN), as identified by the infrared spectrum [ν_{CN} = 2165 cm^{-1} (C$_6$D$_6$)] and 220-MHz ^1H NMR [FeH appears as a quintet at δ −23.20 ($^2J_{PH}$ = 48 Hz) and (NCCH$_2$)Fe as a quintet twice as intense at δ −0.59 ($^3J_{PH}$ = 5.5 Hz)]. **1** reacts with monosubstituted acetylenes to form trans hydrido acetylide complexes and with cyclopentadiene to yield *trans*-Fe(dmpe)$_2$H(h$_1$-Cp).

1 and **2** react with Lewis base ligands (L = CO, disubstituted acetylenes, olefins, and phosphorus ligands) to give zero-valent complexes by the equation

$$\mathrm{M(dmpe)_2H(C_{10}H_7) + L \rightarrow M(dmpe)_2L + C_{10}H_8} \quad (2)$$

Carbon monoxide adducts show very low stretching frequencies (ν_{CO} 1810 cm^{-1} for Fe and 1830 cm^{-1} for Ru), indicating a high electron density on the metals; for comparison, ν_{CO} in Ni(CO)(PEt$_3$)$_3$ is 1908 cm^{-1}.[6] A high metal electron density is also indicated by the high field shift of ethylene hydrogens in the ^1H spectrum of Fe(C$_2$H$_4$)(dmpe)$_2$ (δ 0.60, quintet, $^3J_{PH}$ = 4 Hz, toluene-d_8, 80 °C).[7] Olefin complexes, Fe(CH$_2$=CHR)(dmpe)$_2$, are fluxional on the NMR time scale and the barrier to intramolecular exchange increases with increasing metal-olefin bond strength (R = Me < H ~ CH=CH$_2$ < COOMe < CN).[8] The acrylonitrile complex is rigid on the NMR time scale at room temperature, as is a complex of diphenylacetylene.

Phosphorus ligands usually give Fe(dmpe)$_2$L complexes with AB$_4$ $^{31}P\{^1H\}$ spectra at 25 °C. Ability to coordinate depends strongly on the size of L. Thus, reaction 2 goes to completion for L = PF$_3$, P(OCH$_2$)$_3$CEt, P(OMe)$_3$, or PEt$_3$, but not with P(*i*-Pr)$_3$. The large cone angle (145°)[9] of PPh$_3$ hinders formation of a Fe(dmpe)$_2$L complex; instead attack on a phenyl C–H bond gives Fe(dmpe)$_2$H(Ph$_2$PC$_6$H$_4$). Formation of Fe(PEt$_3$)(dmpe)$_2$ is in contrast to recent attempts to prepare Fe(PMe$_3$)$_5$, where the five-coordinate species apparently does not form for steric reasons; intramolecular oxidative addition instead gives Fe(PMe$_3$)$_3$H(Me$_2$PCH$_2$).[10-12]

Acknowledgment. We gratefully acknowledge M. A.

Cushing, G. Watunya, and D. W. Reutter for skilled technical assistance.

References and Notes

(1) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 2545 (1962) used a similar reaction to prepare a red-brown complex reported to be Fe(dmpe)$_2$. We have been able to isolate a second product from our reaction which fits the description of Chatt's compound, but is actually $[\{Fe(dmpe)_2\}_2(\mu\text{-}dmpe)]$. Both products, separated by selective crystallization from pentane, are isolated in about 40% yield. This complex is also isolated from the reaction of Fe(dmpe)$_2$H(C$_{10}$H$_7$) with ½ dmpe. To date, four-coordinate zero-valent iron complexes have been postulated,[10,11] but not observed.

(2) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965) reported the preparation of (C$_{10}$H$_7$)RuH(dmpe)$_2$ and (C$_6$H$_5$)RuH(dmpe)$_2$ by Na reduction in the presence of C$_{10}$H$_8$ or C$_6$H$_6$.

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(5) T. Herskovitz of this department has made similar observations in a different system.

(6) C. A. Tolman, unpublished results in cyclohexane.

(7) This is the highest field shift reported for a transition metal ethylene complex: see C. A. Tolman, A. D. English, and L. E. Manzer, *Inorg. Chem.*, **14,** 2353 (1975).

(8) C. A. Tolman, *J. Am. Chem. Soc.*, **96,** 2780 (1974); S. D. Ittel, *ibid.*, submitted for publication.

(9) C. A. Tolman, *J. Am. Chem. Soc.*, **92,** 2956 (1970).

(10) E. L. Muetterties and J. W. Rathke, *J. Chem. Soc., Chem. Commun.*, 850 (1974).

(11) H. H. Karsch, H.-F. Klein, and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, **14,** 637 (1975).

(12) Independently prepared in this laboratory; identified by an assignment of the ^{31}P {^{1}H} NMR.

(13) Contribution No. 2390 from E. I. du Pont de Nemours and Company.

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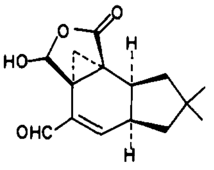
Total Synthesis of Marasmic Acid

Sir:

Marasmic acid (**1**),[1] one of the many fungal metabolites isolated from the *Basidiomycetes*, has been the target of recent synthetic attempts. In their work, de Mayo and his colleagues synthesized methyl isomarasmate (**2**), which differs from the natural product in the stereochemistry of the polycyclic ring system.[2] During the course of our work, Wilson and Turner reported studies in which a Diels–Alder reaction was utilized for construction of the hydrindane ring system, and described an intermediate which was regarded as possessing the skeleton of marasmic acid.[3] We now wish to report the results of our own, independently conceived work on the Diels–Alder approach to marasmic acid, which has led to the first total synthesis of the molecule, and further, places the stereochemical assignments of Wilson and Turner in serious jeopardy.[4]

Our initial approach to marasmic acid involved Diels–Alder addition of an acetylenic dienophile to diene acetal **6**, which was synthesized in the following manner. Aldehyde **3**, available by the ring contraction method of Magnusson and Thoren,[5] was transformed to the diethyl acetal **4**,[6] bp 74.5–75.5 °C (4.5 mm), in 95% yield by treatment with triethyl orthoformate and a catalytic amount of *p*-toluenesulfonic acid in ethanol (24 h at room temperature). The acetal **4** was allowed to react with ethyl vinyl ether and anhydrous zinc chloride in ethyl acetate (24 h at room temperature) and the resulting ethoxy acetal, without isolation, was subjected to the action of sodium acetate in aqueous acetic acid[7] (4 h at 90 °C), affording the diene aldehyde **5**,[6] bp 68–69 °C (1 mm), in 93% yield. Treatment of **5** with trimethyl orthoformate in methanol containing a catalytic amount of ammonium nitrate gave the dimethyl acetal **6**,[6] bp 82–85 °C (2 mm), in 86% yield.



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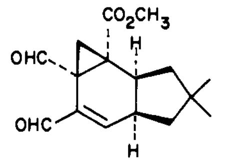

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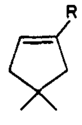
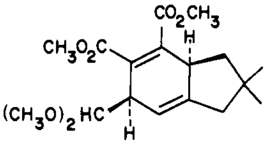


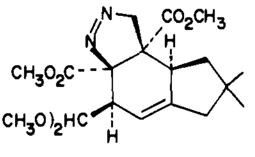
	R
3	–CHO
4	–CH(OCH$_2$CH$_3$)$_2$
5	–CH$\overset{t}{=}$CHCHO
6	–CH$\overset{t}{=}$CHCH(OCH$_3$)$_2$
18	–CH$\overset{t}{=}$CHCH$_2$OH



7

Diels–Alder reaction of **6** with dimethyl acetylenedicarboxylate was quite slow, requiring 8 days at 110 °C, but the adduct **7** was formed in high yield. When **7** was allowed to contact a sixfold excess of ethereal diazomethane, a 4:1 mixture of pyrazolines **8**[6] and **9**,[6] mp 117–118 °C (hexane-acetone), was formed over a period of 14 days. Irradiation of the mixture of pyrazolines in ether solution (Pyrex filter) gave, after column chromatography on silica gel, a single cyclopropane, **10**,[6] mp 79–79.5 °C (hexane), in 60% overall yield from **6**.

Saponification of **10** with sodium hydroxide in aqueous methanol (48 h, 90 °C) provided diacid **11** as a white foam in 97% yield. The diacid, without purification, was warmed with acetic anhydride (30 min, 55 °C), affording the anhydride **12**,[6] mp 106.5–107.5 °C (hexane), in 96% yield. Reduction of **12** with disodium tetracarbonylferrate in tetrahydrofuran[8] gave a 1:1 mixture of the lactols **13** and **14.** Treatment of this lactol mixture with acetic anhydride (2 h, 90 °C), followed by column chromatography on silica gel, gave lactol acetates **15**,[6] mp 115–116.5 °C (hexane), and **16**,[6] mp 125–128.5 °C (hexane), in 31% combined yield from **12.** Saponification of **15** with potassium carbonate in wet methanol gave pure **13**, mp 96–99 °C (hexane-methyl acetate), in 95% yield. Hydrolysis of the acetal moiety of **13** with tetrahydrofuran–10% aqueous HCl (1:1) afforded (to our surprise![4]) isomarasmic acid (**17**),[6] mp



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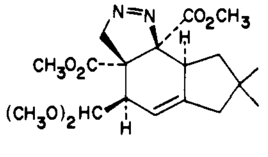

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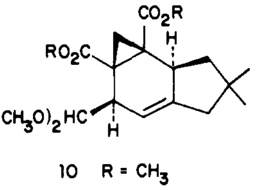
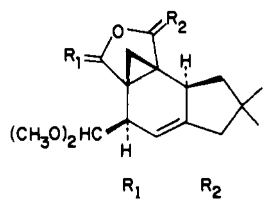


10 R = CH$_3$
11 R = H



	R$_1$	R$_2$
12	=O	=O
13	H,OH	=O
14	=O	H,OH
15	H,OAc	=O
16	=O	H,OAc