B. To Prepare 2-Bromo-1,1,1,2-tetrafluoroethane (III).—Compound V (152 g, 0.5 mole) was added slowly (25 min) to a solution of 55 g (0.4 mole) of I in 75 ml of bromine. The reaction was cooled in an ice-water bath during the addition. (Reaction occurred so rapidly that some product passed through the Dry Ice cooled trap.) The temperature was then raised to about 60° with the condenser cooling water turned off. Product collection was stopped when bromine began to pass through the condenser. Glpc analysis showed the crude, scrubbed product (70.5 g) to consist of III (70 g, 77.1%) along with a trace of IV.

Fluorination of 2-Bromo-1,1,1-trifluoroethane (VII).—Compound VII (60 g, 0.378 mole) was added slowly to a solution of 55 g (0.4 mole) of I in bromine (75 ml). No heat of reaction was observed although product was given off, so the temperature was raised slowly to 50° and finally to 60°. The product that collected in the Dry Ice trap was scrubbed through caustic and analyzed by glpc. The crude product (35.2 g) consisted of 23.8 g (62%) of VIII (bp −26 to −24° (lit.[24] bp −26)) and 11.4 g of VII. The organic recovery was 80.5%. No higher brominated or fluorinated compounds were found.

Fluorination of 1,1,1,2-Tetrabromo-2,2-difluoroethane (IX).—Compound I (15 g, 0.105 mole) in 32 ml of bromine was added slowly (45 min) to a well-stirred solution of 120 g (0.314 mole) of IX in 65 ml of bromine. The reaction was cooled to keep the temperature below 50°. Stirring was continued for 30 min after the addition was complete to finish the reaction. The bromine in the mixture was then neutralized with 10% aqueous sodium hydroxide and the crude product (95 g) separated. The crude product was shown by glpc and mass spectral analysis to contain 2.2 g (2.7%) of 1,2-dibromo-1,1,2,2-tetrafluoroethane (X) (bp 45–47° (lit.[25] bp 46.4°)), 51.7 g (51.3%) of 1,1,2-tribromo-1,2,2-trifluoroethane XI (bp 115–117° (lit.[26] bp 117°)), and 41.5 g of IX.

Fluorination of 1,1,2-Tribromo-1,2-difluoroethane (XII).—Compound XII (61 g, 0.2 mole) was added slowly (20 min) to a solution of 34 g (0.25 mole) of I in 75 ml of bromine. The reaction was cooled in an ice-water bath during the addition. The low-boiling compounds which passed from the top of the reflux condenser were collected in a Dry Ice cooled trap. After all of the organic bromide had been added, the flask was heated slowly to about 60° to distill out as much product as possible. Glpc analysis showed the crude scrubbed product (25.0 g) to consist of III (23.5 g, 65.2%) and IV (1.4 g, 5.7%).

Registry No.—Bromine trifluoride I, 7787-71-5; II, 1894-81-1; III, 124-72-1; IV, 354-33-6; V, 677-34-9; VI, 354-04-1; VII, 421-06-7; VIII, 811-97-2; IX, 3470-67-5; X, 354-49-4; XI, 124-73-2; XII, 353-97-9.

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Evidence for Hyperconjugative Stabilization of Olefins from Tautomeric Equilibria[1a]

LLOYD J. DOLBY[1b] AND GARY N. RIDDLE

Department of Chemistry, University of Oregon, Eugene, Oregon

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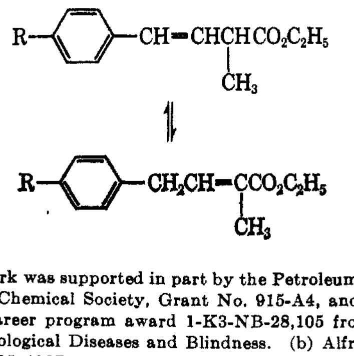
Equilibrium constants have been determined for the alkoxide-catalyzed isomerization of a series of ethyl 4-(*p*-alkylphenyl)-2-methyl-2- and -3-butenoates. The proportion of the β,γ-unsaturated isomer decreases with increasing branching in the *p*-alkyl group. These results are taken as evidence for CH hyperconjugative stabilization of the β,γ double bond in the ground state.

The importance of hyperconjugation has been controversial for a good many years. In particular, there is a lack of experimental observations which indicate that hyperconjugation is significant in the ground states of neutral molecules.[2,3] Over the years, many tautomeric equilibria have been examined in an effort to determine the extent of hyperconjugative stabilization at a given center. However, most of the systems studied were complicated by the fact that the equilibria were affected by both the electronic and steric effects of the substituent. In an effort to find a system insulated from steric effects in which hyperconjugative stabilization of olefins might be observable we have examined the equilibria between ethyl 4-(*p*-alkylphenyl)-2-methyl-2-butenoates and the corresponding β,γ-unsaturated isomers. This choice



was prompted by the extensive data available on similar equilibria for aliphatic and alicyclic unsaturated esters. Some pertinent data are presented in Table I.[4]

TABLE I

EQUILIBRIUM CONSTANTS AND FREE-ENERGY DIFFERENCES FOR ISOMERIC UNSATURATED ESTERS

$CH_2CH_2—C(R)\cdots CH \cdots C(CH_3)—CO_2C_2H_5$

R	Conjugated isomer, %	K_{obsd}[a]	K_{cor}[b]	$-\Delta F$,[c] kcal
CH_3	45	0.82	1.9–2.7	0.60–0.93
C_2H_5	68	2.1	4.2	1.33
i-C_3H_7	78	3.5	4.9–6.1	1.48–1.68
t-C_4H_9	86	6.1	6.1	1.68

[a] $K_{obsd} = (A_1 + A_2)/(B_1 + B_2)$, where A_1 and A_2 are *trans*- and *cis*-α,β-unsaturated isomers, respectively. B_1 and B_2 are *trans*- and *cis*-β,γ-unsaturated isomers, respectively. [b] $K_{cor} = A_1/B_1$. [c] $\Delta F = -RT \ln K_{cor}$; $T = 486°K$.

It is clear that hyperconjugative stabilization does not completely account for these observed equilibria. For example, the equilibrium mixture of 4-neopentyl-2,6-trimethyl-2-heptenoate and the Δ^3 isomer contained 84% of the conjugated isomer whereas the equilibrium mixture of ethyl 2-methyl-4-ethyl-2-hexenoate and the

(1) (a) This work was supported in part by the Petroleum Research Fund of the American Chemical Society, Grant No. 915-A4, and a U. S. Public Health Service career program award 1-K3-NB-28,105 from the National Institute of Neurological Diseases and Blindness. (b) Alfred P. Sloan Research Fellow, 1965–1967.

(2) (a) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962; (b) J. W. Baker, "Hyperconjugation," Oxford University Press, Fair Lawn, N. J., 1952.

(3) For a compilation of papers on hyperconjugation, see *Tetrahedron*, **5** 105 (1959).

(4) K. L. Rinehart and L. J. Dolby, *J. Org. Chem.*, **22**, 13 (1957).

Δ^3 isomer contains 74% of the conjugated isomer although the number of CH-hyperconjugative structures for the Δ^3 isomer is the same.[5,6]

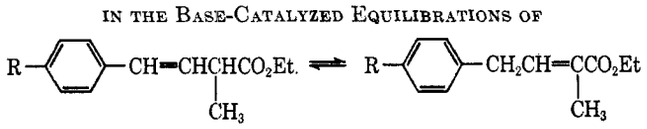
That steric interactions affect these equilibria cannot be doubted. Steric effects on olefinic stability have been recognized for many years. Moreover, steric interactions are the only reasonable explanation for the equilibria observed for unsaturated esters in which the δ carbon and its substituents are part of a carbocyclic ring.[6]

The ethyl 4-(*p*-alkylphenyl)-2-methyl-2- and -3-butenoates required for the present study were prepared in several steps from *p*-alkylacetophenones. The *p*-alkylacetophenones were converted to the corresponding N-(*p*-alkylphenylthioacetyl)morpholines by the Kindler modification of the Willgerodt reaction.[7] Hydrolysis of the thioamides afforded the corresponding *p*-alkylphenylacetic acids which were esterified and reduced with lithium aluminum hydride to yield β-(*p*-alkylphenyl)ethanols. Chromic acid oxidation of the β-(*p*-alkylphenyl)ethanols gave in poor yields *p*-alkyphenylacetaldehydes contaminated with the corresponding *p*-alkylbenzaldehydes. The benzaldehydes were not separated from the phenylacetaldehydes, but the aldehyde mixtures were converted to unsaturated esters by the method of Wadsworth and Emmons.[8] The condensation of the aldehyde mixtures with ethyl α-diethylphosphonopropionate afforded mixtures of ethyl *p*-alkyl-α-methylcinnamates and ethyl 4-(*p*-alkylphenyl)-2-methyl-2-butenoates which were separated by vapor phase chromatography. The β,γ-unsaturated esters were prepared from the α,β-unsaturated esters by preparative scale equilibration with ethoxide and separation by vapor phase chromatography.

The unsaturated esters were equilibrated using sodium ethoxide in dry ethanol. Equilibrium compositions were measured by vapor phase chromatography and equilibrium was approached starting with both pure isomeric unsaturated esters. These data and the derived free-energy changes are tabulated in Table II.

TABLE II

EQUILIBRIUM CONCENTRATIONS AND FREE-ENERGY CHANGES IN THE BASE-CATALYZED EQUILIBRATIONS OF



R	% α,β isomer[a]	K_{obsd}[b]	ΔF ($= -RT \ln K$), kcal	$\Delta\Delta F$[b]
Hydrogen	59.2	1.45 ± 0.04	$-0.259 + 0.019$	
Methyl	39.8	0.66 ± 0.03	$+0.302 \pm 0.032$	
Ethyl	45.9	0.85 ± 0.03	$+0.112 \pm 0.023$	0.190
Isopropyl	50.0	1.00 ± 0.03	0.00 ± 0.024	0.112
t-Butyl	52.4	1.10 ± 0.04	-0.064 ± 0.030	0.064

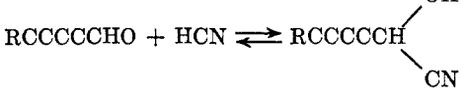
[a] Average of at least four runs for each R group; $77.3 \pm 0.5°$. [b] $K = [\alpha,\beta]/[\beta,\gamma]$.

The equilibria are complicated by the fact that *cis* and *trans* isomers are possible for both the α,β- and β,γ-unsaturated esters. The nuclear magnetic resonance spectra of the β,γ-unsaturated esters recovered from equilibration experiments and prepared by equilibration of the α,β-unsaturated isomers did not show any absorption which could be ascribed to the *cis* forms; however small amounts could have escaped detection. The situation is less clear with the α,β-unsaturated isomers, but the nmr spectra of these materials show coupling of about 1.5 cps between the α-methyl group and the vinyl proton which indicates that the α,β-unsaturated isomers are the *trans* isomers. In any event, the *cis–trans* equilibria should be determined primarily by the steric environment at the double bond and this would be the same for the entire series.

In the series presented in Table II, the largest difference is between the unsubstituted compound and any of the alkyl compounds. Thus, as might be anticipated the styrene double bond is stabilized by electron-donating groups. The stability of the β,γ-unsaturated esters follows the Baker–Nathan order of electron release, methyl > ethyl > isopropyl > *t*-butyl, which is taken as evidence for hyperconjugative stabilization. The possibility that an entropy or solvent effect is responsible for this result was examined. The *p*-methyl- and *p*-*t*-butyl-unsaturated esters were equilibrated at 35° in sodium ethoxide–ethanol to yield the entropy changes for these two systems. The effect of solvent was examined by carrying out the equilibration of the *p*-methyl and *p*-*t*-butyl compounds in *t*-butyl alcohol–potassium *t*-butoxide. These data are recorded in Table III.

It appears that the entropy effect is not decisive in these systems. The solvent effect is slight and raises the percentage of the α,β-unsaturated isomer by a few per cent in both cases. The fact that both equilibria were shifted in the same direction by the solvent change indicates that a solvent effect is not responsible for the observed Baker–Nathan order although the recovery of esters was only 70–75% in the runs carried out in *t*-butyl alcohol.

In the system examined in the present study, it is assumed that ponderal effects cannot explain the observed Baker–Nathan order. Ponderal effects were proposed by Scott[9] to account for the observed order of equilibrium constants for cyanohydrin formation.[10] However, the equilibrium constants were presented as reactants divided by products and Scott assumed they were products divided by reactants. In a further study of this question, Wolfsberg has concluded from his calculations that ponderal effects in the model system



are negligible at room temperature and above.[11] He further concludes that purely ponderal effects are negligible in assessing the effects of alkyl substituents on equilibria at room temperature and above.

It is of interest to compare the results of the present study of olefin stability with previous studies. The effect of changing the alkyl substituent in the unsatu-

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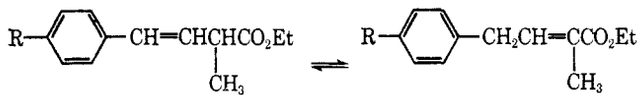
TABLE III

SOLVENT AND ENTROPY STUDIES ON THE EQUILIBRIUM



R	Temp, °C	Solvent–base[a]	% α,β[b]	K_{obsd}[c]	ΔF,[d] kcal/mole	Δs, eu
Methyl	35	C_2H_5OH–$NaOC_2H_5$	39	0.64 ± 0.03	+0.272 ± 0.028	0.75 ± 0.04
t-Butyl	35	C_2H_5OH–$NaOC_2H_5$	51	1.06 ± 0.03	−0.035 ± 0.018	0.73 ± 0.04
Methyl	77.3	*t*-C_4H_9OH–K-*t*-OC_4H_9	41	0.70 ± 0.03	+0.229 ± 0.026	...
t-Butyl	77.3	*t*-C_4H_9OH–K-*t*-OC_4H_9	54	1.19 ± 0.04	−0.107 ± 0.020	...

[a] Runs in ethanol were done for 36 hr; runs in *t*-butyl alcohol were carried out for 6 hr. [b] Average of two runs on each. [c] $K = [\alpha,\beta]/[\beta,\gamma]$. [d] $\Delta F = -RT \ln K$.

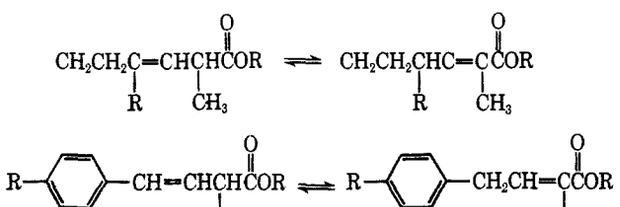
TABLE IV

p-ALKYLPHENYLTHIOACETYLMORPHOLINES

			Calcd, %				Found, %			
Alkyl group[a]	Mp, °C	Formula	C	H	N	S	C	H	N	S
Methyl	103.5–104.5	$C_{13}H_{17}NOS$	66.36	7.29	5.95	13.60	66.35	7.41	5.80	13.75
Ethyl	84.5–85	$C_{14}H_{19}NOS$	67.44	7.68	5.62	12.83	67.30	7.62	5.40	12.70
Isopropyl	61–62	$C_{15}H_{21}NOS$	68.41	8.04	5.32	12.16	67.96	7.93	4.84	11.57
t-Butyl	114–115	$C_{16}H_{23}NOS$	69.28	8.36	5.05	11.54	69.12	8.44	5.01	11.47

[a] Registry no.: methyl, 14182-63-9; ethyl, 14182-64-0; isopropyl, 14182-65-1; *t*-butyl, 14182-66-2.

rated aliphatic 2-methyl 4-alkyl esters[4] is more pronounced than a similar change in the 4-(*p*-alkylphenyl)-2-methyl-2-butenoates.



In the aliphatic series, the fraction of α,β-unsaturated ester changes from 45 to 86% in the series from methyl to *t*-butyl. A similar change of substituent in the 4-(*p*-alkylphenyl)-2-methylbutenoates causes the fraction of α,β-unsaturated isomer to change from 39 to 52%. Since it is difficult to estimate how much hyperconjugative effects are attenuated by a benzene ring it is not possible to decide the importance of hyperconjugative effects in the aliphatic series. However, it is reasonable to conclude that hyperconjugative effects are not negligible. In fact Bateman and Cuneen had some success quantitatively accounting for the equilibria between α,β and β,γ-unsaturated esters, acids, and nitriles in terms of hyperconjugation using stabilization factors derived from equilibrations of γ-alkylphenylpropenes.[12]

Experimental Section

General.—All boiling points and melting points are uncorrected. Infrared spectra were measured with a Beckman IR-5. Ultraviolet spectra were determined with a Perkin-Elmer 202 spectrometer. Nmr spectra were recorded with a Varian A-60 spectrometer using tetramethylsilane as internal standard. All distillations were carried out using a 4-ft Podbielniak column with a tantalum spiral. Refractive indices were corrected to 25° using a correction of 0.0004/deg. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill., and F. Pascher, Bonn, West Germany.

***p*-Alkylacetophenones** were prepared by the procedure of Heintzelman and Corson.[13]

N-(*p*-Alkylphenylthioacetyl)morpholines were prepared from *p*-alkylacetophenones by the Kindler modification of the Willgerodt reaction.[7] The morpholides were crystallized from ethanol–water. The melting points and analytical data are recorded in Table IV.

β-(*p*-Methylphenyl)ethanol.—N-(*p*-Methylphenylthioacetyl)-morpholine (150 g, 0.64 mole) was refluxed for 7 hr with 400 ml of 60% sodium hydroxide in 80% ethanol–water. The cooled reaction mixture was acidified to afford *p*-methylphenylacetic acid (70 g, 70%): mp 89.5–91° (lit.[14] mp 90–91°). Esterification with ethanol–sulfuric acid afforded ethyl *p*-methylphenylacetate (75 g, 90%): bp 107–110° (12 mm), $n^{25}D$ 1.4941 [lit.[15] bp 72–74° (0.9 mm), $n^{25}D$ 1.4930]. Ethyl *p*-methylphenylacetate (75 g, 0.42 mole) was added dropwise to a slurry of 11.5 g (0.30 mole) of lithium aluminum hydride in 200 ml of ether at 0°. The resulting mixture was stirred for 2 hr at room temperature and then cooled in an ice bath and hydrolyzed with 10% sulfuric acid. The ether layer was separated, dried over sodium sulfate, and distilled to yield 46 g (80%) of β-(*p*-methylphenyl)ethanol: bp 128° (22 mm), $n^{25}D$ 1.5220 [lit.[16] bp 120–125° (19 mm), $n^{26}D$ 1.5225].

β-(*p*-Ethylphenyl)ethanol.—By the same sequence of reactions, N-(*p*-ethylphenylthioacetyl)morpholine was converted to *p*-ethylphenylacetic acid [mp 90–91° (lit.[16,17] mp 93 and 88–90°)] and thence to ethyl *p*-ethylphenylacetate: bp 141° (19 mm) [lit.[18] bp 151–154° (35 mm)]. Lithium aluminum hydride reduction of the ester afforded β-(*p*-ethylphenyl)ethanol: bp 120–122° (21 mm) [lit.[19] bp 90–95° (10 mm)]. The yield from N-(*p*-ethylphenylthioacetyl)morpholine was 52%.

β-(*p*-Isopropylphenyl)ethanol.—By the same sequence of reactions, N-(*p*-isopropylphenylthioacetyl)morpholine was converted to *p*-isopropylphenyl acetic acid [mp 42–44° (lit.[18,20] mp 51–52 and 53.5°)] which was esterified to give ethyl *p*-isopropylphenylacetate: bp 138–142° (15 mm) [lit. bp 139–141° (15 mm)]. Lithium aluminum hydride reduction of ethyl *p*-isopropylphenylacetate afforded β-(*p*-isopropylphenyl)ethanol: bp 140–141° (17 mm) [lit.[18] bp 132–133° (11 mm)]. The yield from N-(*p*-isopropylthioacetyl)morpholine was 40%.

β-(*p*-*t*-Butylphenyl)ethanol was prepared from N-(*p*-*t*-butylphenylthioacetyl)morpholine by the sequence described above.

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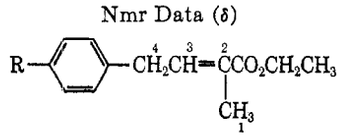
TABLE V

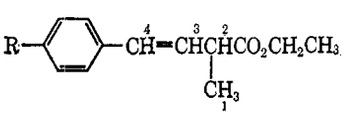
Analyses

p-Alkyl[b]	Double bond position	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
Methyl	2	$C_{14}H_{18}O_2$	77.03	8.31	76.95	8.01
Methyl	3		77.03	8.31	76.91	8.17
Ethyl	2	$C_{15}H_{20}O_2$	77.58	8.68	77.68	9.03
Ethyl	3		77.58	8.58	77.57	8.49
Isopropyl	2	$C_{16}H_{22}O_2$	78.01	9.00	78.05	8.65
Isopropyl	3		78.01	9.00	78.61	8.81
t-Butyl	2	$C_{17}H_{24}O_2$	78.42	9.29	78.78	9.59
t-Butyl	3		78.42	9.29	78.61	9.64

Nmr Data (δ)



	1	3	4	R	$J_{1,3}$, cps	$n^{25}D$
Methyl	1.88	6.75	3.38	2.28	1.5	1.5072
Ethyl	1.88	6.85	3.37	2.54, 1.24	1.5	1.5100
Isopropyl	1.86	6.74	3.37	2.77, 1.12	1.5	1.5076
t-Butyl	1.90	6.86	3.39	1.34	1.5	1.5010



R	1	2	3	4[a]	R	$J_{3,4}$, cps	$n^{25}D$
Methyl	1.31	3.31	6.27	~7.2	2.33	7.2	1.5162
Ethyl	1.32	3.33	6.25	~7.2	2.59, 1.25	7.3	1.5095
Isopropyl	1.30	3.32	6.24	~7.2	2.79, 1.14	7.3	1.5088
t-Butyl	1.32	3.30	6.25	~7.2	1.31	7.4	1.5078

[a] Hidden in aromatic region. [b] Registry no.: methyl (Δ^2), 14182-69-5; methyl (Δ^3), 14182-70-8; ethyl (Δ^2), 14182-71-9; ethyl (Δ^3), 14182-72-0; isopropyl (Δ^2), 1418-2-73-1; isopropyl (Δ^3), 14182-74-2; *t*-butyl (Δ^2), 14182-75-3; *t*-butyl (Δ^3), 14182-76-4.

The *p*-*t*-butylphenylacetic acid exhibited mp 76–79° (lit.[21] mp 78–79°) and the derived ethyl ester had bp 147–149° (20 mm) [lit.[18] bp 134–137° (8 mm)]. The β-(*p*-*t*-butylphenyl)ethanol had bp 157–159° (23 mm), $n^{25}D$ 1.5240 [lit.[22] bp 141–143° (14 mm), $n^{17}D$ 1.5209].

***p*-Alkylphenylacetaldehydes** were prepared by adding a twofold excess of standard oxidant[23] (35 ml of oxidant/0.1 mole of phenethanol) to a solution of the alcohol in ether at 0°. The mixture was allowed to stir for 10–30 min after addition was completed. The reaction mixture was then poured into ice water. The ether layer was dried and the solvent was removed. The crude reaction mixture was then distilled to yield an aldehyde mixture which contained variable proportions of *p*-phenylacetaldehydes and *p*-alkylbenzaldehydes. These were not separated at this point but were carried together into the condensation step. The yields of mixed aldehydes varied between 5 and 15% from run to run.

Ethyl α-Diethylphosphonopropionate.[24]—Ethyl α-bromopropionate (18.1 g, 0.10 mole) was placed in a 100-ml round-bottom flask fitted with a pressure-equilibrating dropping funnel and a condenser. Triethylphosphite (17.4 g, 0.1 mole) was placed in the dropping funnel. Approximately one-fourth of the triethylphosphite was added to the bromo ester and this mixture was heated with a Bunsen burner until an exothermic reaction started. The remaining triethylphosphite was then added at such a rate as to maintain reflux. The reaction mixture was then heated for 18 hr at reflux. After distilling the resultant ethyl bromide and excess starting materials, the residue was distilled and the fraction boiling at 93–95° (0.85 mm) was taken to yield 14.6 g (0.06 mole, 59.4%) of ethyl α-diethylphosphonopropionate [lit.[24] bp 138.5–138.75° (10 mm)]. The spectrum (neat) showed the following patterns: δ 4.00 (quintet, OCH_2, six protons), 2.91 (octet, α-methine, one proton), and 1.25 (complex multiplet, methyls, 12 protons). The coupling constant between phosphorus and the α-methine proton was 24.0 cps.

TABLE VI

EQUILIBRATIONS OF 4-(*p*-ALKYLPHENYL) BUTENOATES

p-Alkyl group	Isomer	Temp, °C	Time, hr	*K*
H	α,β	77.3	12	1.45, 1.49
H	α,β	77.3	12	1.42, 1.52
H	α,β	77.3	12	1.47, 1.41
H	α,β	77.3	12	1.41, 1.49
H	α,β	77.3	12	1.52, 1.37
H	α,β	77.3	12	1.40, 1.48
H	β,γ	77.3	12	1.41, 1.50
H	β,γ	77.3	12	1.41, 1.48
H	β,γ	77.3	12	1.40, 1.48
H	β,γ	77.3	12	1.40, 1.48
Methyl	α,β	77.3	12	0.62, 0.70
Methyl	α,β	77.3	12	0.61, 0.68
Methyl	α,β	77.3	12	0.65, 0.69
Methyl	α,β	77.3	12	0.66, 0.60
Methyl	α,β	77.3	12	0.61, 0.69
Methyl	α,β	77.3	12	0.61, 0.69
Methyl	β,γ	77.3	12	0.63, 0.68
Methyl	β,γ	77.3	12	0.67, 0.65
Methyl	β,γ	77.3	12	0.64, 0.67
Methyl	β,γ	77.3	12	0.63, 0.68
Methyl	α,β	35	36	0.60, 0.64
Methyl	α,β	35	36	0.65, 0.69
Ethyl	$\alpha,\$$	77.3	12	0.94, 0.80
Ethyl	α,β	77.3	12	0.88, 0.81
Ethyl	α,β	77.3	12	0.82, 0.88
Ethyl	α,β	77.3	12	0.80, 0.88
Ethyl	β,γ	77.3	12	0.82, 0.89
Ethyl	β,γ	77.3	12	0.81, 0.86
Ethyl	β,γ	77.3	12	0.84, 0.90
Isopropyl	α,β	77.3	12	0.92, 0.98
Isopropyl	α,β	77.3	12	0.99, 0.98
Isopropyl	α,β	77.3	12	0.92, 1.03
Isopropyl	α,β	77.3	12	1.04, 1.06
Isopropyl	α,β	77.3	12	1.06, 0.99
Isopropyl	β,γ	77.3	12	1.03, 0.96
Isopropyl	β,γ	77.3	12	1.00, 1.01
t-Butyl	α,β	77.3	12	1.10, 1.16
t-Butyl	α,β	77.3	12	1.11, 1.10
t-Butyl	α,β	77.3	12	1.14, 1.05
t-Butyl	α,β	77.3	12	1.06, 1.13
t-Butyl	β,γ	77.3	12	1.07, 1.12
t-Butyl	β,γ	77.3	12	1.14, 1.06
t-Butyl	β,γ	77.3	12	1.07, 1.04
t-Butyl	β,γ	77.3	12	1.14, 1.13
t-Butyl	α,β	35	36	1.04, 1.09
t-Butyl	α,β	35	36	1.03, 1.07
Methyl[a]	α,β	77.3	6	0.72, 0.74
Methyl[a]	α,β	77.3	6	0.69, 0.66
t-Butyl[a]	α,β	77.3	6	1.22, 1.24
t-Butyl[a]	α,β	77.3	6	1.15, 1.18

[a] Carried out in *t*-butyl alcohol with potassium *t*-butoxide as catalyst. All other runs were performed with ethanol–sodium ethoxide.

Ethyl 2-Methyl-4-phenyl-2-buteneoate and Ethyl 2-Methyl-4-phenyl-3-buteneoate.—Ethyl diethylphosphonopropionate (11.9 g, 0.05 mole) was added dropwise at 20° to a slurry of 50% sodium hydride in mineral oil (2.4 g, 0.05 mole) in 100 ml of 1,2-dimethoxyethane (distilled from potassium and stored over molecular sieves). The addition was controlled so that the temperature would not exceed 20°. During the addition, hydrogen was given off. After the addition was complete, the solution was stirred at room temperature for 1 hr and then cooled in an ice bath. Phenylacetaldehyde (6.0 g, 0.05 mole) was then added dropwise at such a rate as to maintain the temperature at less

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(23) C. Djerassi, R. P. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).
(24) A. E. Arbuzov and A. A. Durin, *J. Russ. Phys. Chem. Soc.*, **46**, 295 (1914); *Chem. Abstr.*, **8**, 2551 (1914).

than 30°. During the addition of the aldehyde, the solution turned deep lemon yellow. After the addition was complete, the solution was stirred at room temperature for 20 min after which 100 ml of water was added. The resultant mixture was extracted with ether, the ether solution was dried, and the solvent was evaporated. The crude esters were distilled to yield 6.84 g (67%) of material [bp 88–92° (0.55 mm)] which was mainly a 1:1 mixture of the two title compounds.

The isomers were separated by gas–liquid partition chromatography (glpc) using an Autoprep A-700 chromatograph equipped with a 20 ft × 3/8 in. aluminum column charged with 30% SE-30-coated firebrick. The temperature of separation was 175° at *ca.* 200-cc/min helium flow rate. The nmr spectrum of the Δ^2 ester shows a singlet at δ 7.13 (aromatics), a complex multiplet at δ 6.91 (vinyl proton), a quartet at δ 4.08 (OCH_2CH_3), a multiplet at δ 3.38 ($ArCH_2CH=$), a multiplet at δ 1.88 ($-HC=C(CH_3)CO_2Et$), and a triplet at δ 1.12 (OCH_2CH_3). The coupling constant between the vinyl hydrogen and the allylic methyl was 1.4 cps. The coupling constant between the benzylic methylene and the allylic methyl was 1.6 cps. These data, along with the value of the coupling constant between the benzylic methylene and vinyl proton (7.8 cps), indicate that the double bond is *trans* with relation to the vinyl hydrogen and allylic methyl.[25]

Anal. Calcd for $C_{13}H_{16}O_2$; C, 76.44; H, 7.90. Found: C, 76.17; H, 8.02.

The nmr spectrum of the Δ^3 ester had a multiplet at δ 7.25 (aromatics), a multiplet at δ 6.30 (vinyl proton), a multiplet centered at δ 3.31 (methine proton), and a doublet at δ 1.31 [$CH—CH_3)CO_2Et$]. The ester ethyl group gave normal patterns. The infrared spectrum showed a medium absorption at 965 cm^{-1} (*trans* –HC=CH–) and the ultraviolet spectrum shows λ_{max} 246 mμ (ϵ 11,460).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.17; H, 8.02.

Ethyl 4-(*p*-Alkylphenyl)-2-methyl-2- and -3-butenoates.—The title compounds were prepared in the same manner as described for ethyl 4-phenyl-2-methyl-2- and -3-butenoates. The mixture of *p*-alkylphenylacetaldehyde and *p*-alkylbenzaldehyde were added to equimolar amounts of the anion generated from sodium hydride and ethyl α-diethylphosphonopropionate in glyme. After working-up in the normal manner, mixtures of the title compounds and ethyl *p*-alkyl-2-methylcinnamates were isolated. These were separated *via* glpc. The ethyl 4-(*p*-alkylphenyl)-2-methyl-2-butenoates were then treated with sodium ethoxide in ethanol and the products were again separated by glpc to give finally pure ethyl 4-(*p*-alkylphenyl)-2-methyl-2-butenoates and ethyl 4-(*p*-alkylphenyl)-2-methyl-3-butenoates.

Analyses and major nmr absorptions for the compounds are listed in Table V.

Equilibrations of Unsaturated Esters (Table VI).—Sodium (sufficient to make a 3 *M* sodium ethoxide) was added to dried ethanol in a 10-ml flask which was protected from carbon dioxide and moisture with a Drierite–Ascarite drying tube. After the sodium had disappeared, the unsaturated ester was added (~20 mg for each 5 ml of 3 *M* sodium ethoxide). The equilibration mixture was then placed in a constant temperature bath (77.3 ± 0.5) for 12 hr. After that time, the mixture was treated with 10% solution of sodium carbonate solution and finally with water. The ether layer was dried and the solvent was removed. The residual ester mixture was then weighed and analyzed using a Wilkins Autoprep A-700 gas chromatograph fitted with a 20 ft × 3/8 in. aluminum column filled with 30% SE-30 on firebrick. The yields were determined by comparing the ester peaks to an internal standard. The glpc traces corresponding to the esters were then cut-out and weighed. The ratio of the weights of α–β to β–γ isomers was taken as the K_{obsd} which are tabulated herein. The relative thermal conductivity response was found to be 1.01 ± 0.01 for known mixtures of the isomeric *p*-hydrogen, *p*-methyl, and *p*-*t*-butyl compounds. The yield of isomeric esters for all tabulated runs was >85%. Each run was chromatographed twice and equilibrium constants were calculated for each glpc trace.

The runs in *t*-butyl alcohol were treated in the same way but the recoveries of esters were somewhat lower (70–75%).

Registry No.—Ethyl 2-methyl-4-phenyl-2-butenoate, 14182-67-3; ethyl 2-methyl-4-phenyl-3-butenoate, 14182-68-4; ethyl α-diethylphosphonopropionate, 3699-66-9.

(25) M. S. Newman, G. Fraenkel, and W. N. Kirn, *J. Org. Chem.*, **28**, 1851 (1963).

Mass Spectrometry in Structural and Stereochemical Problems. CXL.[1] Competitive McLafferty Rearrangements in Bifunctional Compounds[2]

J. K. MACLEOD AND CARL DJERASSI

Department of Chemistry, Stanford University, Stanford, California

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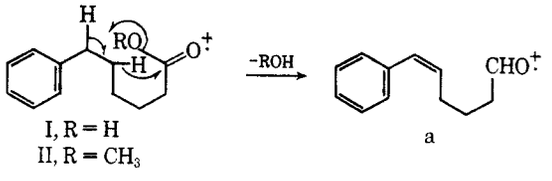
An investigation of the competition between different functional groups in the same molecule for electron impact induced γ-hydrogen transfer indicates that rearrangement takes place preferentially to the carbonyl moiety in both the phenylalkyl methyl ketones and the keto esters studied. However, the dominant fragmentation process in some of these compounds is a 1:6 elimination analogous to that observed in an earlier publication[4] with 6-phenylhexanoic acid.

Although a considerable amount of recent work in organic mass spectrometry has been devoted to the study of the site-specific hydrogen-transfer process known as the McLafferty rearrangement,[3] scant attention has been paid to the competitive aspect of this electron impact induced fragmentation. The analysis by Meyerson and Leitch[4] of the competition for the common γ-hydrogens between the carboxyl group and the aromatic nucleus in the mass spectra of 6-phenylhexanoic acid (I) and its methyl ester (II) was hindered by the presence of a dominant alternative fragmentation which involved initial expulsion of the elements of water (from I) or methanol (from II) *via* a 1:4, 1:5, or preferentially a 1:6 elimination (I or II → a).



I, R = H
II, R = CH_3

a

By replacing the carboxylate function by a methyl ketone group as in 7-phenyl-2-heptanone (III) it was thought that the interference of such elimination

(1) For paper CXXXIX, see G. Schroll, S.-O. Lawesson, A. M. Duffield, and C. Djerassi, *Arkiv Kemi*, in press.

(2) We are grateful to the National Institutes of Health for financial assistance (grants No. AM-04257 and CA-07195). The purchase of the Atlas CH-4 mass spectrometer was made possible by NASA grant NsG 81-60.

(3) For a recent review and leading references see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, section 3-7.

(4) S. Meyerson and L. C. Leitch, *J. Am. Chem. Soc.*, **88**, 56 (1966).