Orthoacrylate Claisen Rearrangement. An Approach to Aliphatic α-Methylene Esters

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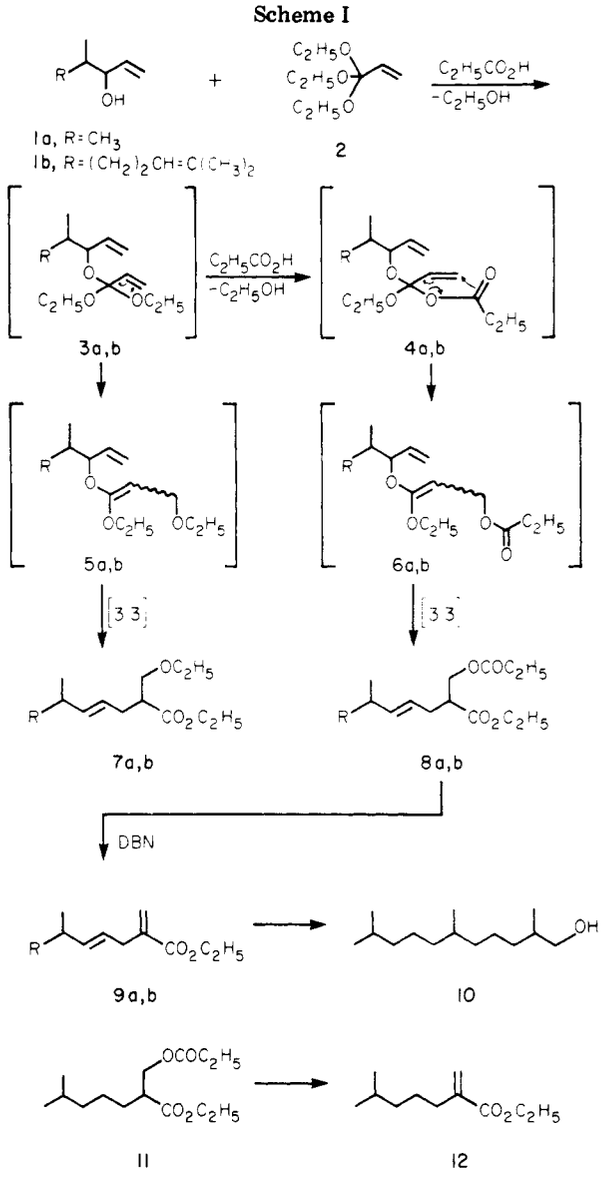
Treatment of vinyl carbinols **1a,b** with triethyl orthoacrylate (**2**) and excess propionic acid in refluxing toluene gives the α-propionoxymethyl esters **8a,b** as major products along with minor amounts of the α-ethoxymethyl esters **7a,b**. Similar treatment of ethynyl carbinol **13** affords allenic diester **14** (major) and ether ester **15** (minor). The diesters **8a,b** yielded the α-methylene esters **9a,b** upon exposure to 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in refluxing benzene. When **14** was treated with DBN, the Diels–Alder dimer **17** resulted. Mechanistic considerations involving the Claisen rearrangements are presented.

The Claisen rearrangement, in its many variations, has proven, historically, to be one of the most important and versatile classes of carbon–carbon bond-forming reactions.[1] As an outgrowth of a long-standing interest in these [3,3] sigmatropic processes,[2] we recently investigated their application to the preparation of acyclic α-methylene esters,[3] a class of compounds which we required in conjunction with certain ongoing synthetic studies involving isoprenoids. In particular, we were intrigued by a scheme in which an allylic alcohol such as **1** (Scheme I) was allowed to interact with triethyl orthoacrylate (**2**),[4] under the conditions of the ortho ester Claisen rearrangement.[5] We reasoned that the initially formed adduct **3** should undergo allylic rearrangement, as shown, affording the Claisen substrate ketene acetal **5** and, ultimately, the α-ethoxymethyl ester **7**.[6] β elimination of ethanol from the latter substance would then provide the desired α-methylene ester **9**. While this concept was found to be a viable one, the experimental conditions required in order to achieve practical yields of Claisen products were somewhat unexpected, and we present the details of our study herein.

Results

When vinyl carbinol **1a** was treated with triethyl orthoacrylate under conditions usually employed for the ortho ester Claisen rearrangement (catalytic amount of propionic acid[5]), only complex mixtures were formed.[6] We noted, however, that as increasing quantities of propionic acid were utilized, two products, **7a** and **8a**, became predominant. After considerable experimentation, it was found that **8a** and **7a** could be produced in yields of 66 and 16%, respectively, when **1a** was treated with 2 molar equiv of **2** and 1.5 molar equiv of propionic acid in refluxing toluene. These products were readily separated by column chromatography or GC, the diester **8a** being more polar than the ether ester **7a**. As expected,[5] the newly formed olefinic bond in these compounds was found to possess virtually entirely the *E* configuration.

Scheme I



While these initial results were somewhat surprising, they, nonetheless, provided us with a method for producing, in satisfactory yield, potential precursors for α-methylene ester synthesis (see below). A possible rationale for our observations is presented in Scheme I. Thus it is conceivable that, in the presence of excess propionic acid, the initial adduct **3** undergoes exchange, with loss of ethanol, forming an analogous acyl intermediate **4**. Rearrangement of the latter species as indicated produces the ketene acetal ester **6** which affords the observed, major product diester **8** after [3,3] sigmatropic reorganization.

(1) For excellent reviews of the Claisen rearrangement, see: (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1–252; (b) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227–32; (c) Bennett, G. B. *Synthesis* **1977**, 589–606.

(2) (a) Saucy, G.; Marbet, R. *Helv. Chim. Acta* **1967**, *50*, 2091–5. (b) Marbet, R.; Saucy, G. *Ibid.* **1967**, *50*, 2095–100. (c) Chan, K.-K.; Cohen, N.; DeNoble, J. P.; Specian, A. C., Jr.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 3497–505. (d) Cohen, N.; Eichel, W. F.; Lopresti, R. J.; Neukom, C.; Saucy, G. *Ibid.* **1976**, *41*, 3512–5. (e) Chan, K.-K.; Specian, A. C., Jr.; Saucy, G. *Ibid.* **1978**, *43*, 3435–40.

(3) For related studies, see: (a) Still, W. C.; Schneider, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 948–50; (b) Raucher, S.; Hwang, K.-J.; Macdonald, J. E. *Tetrahedron Lett.* **1979**, 3057–60.

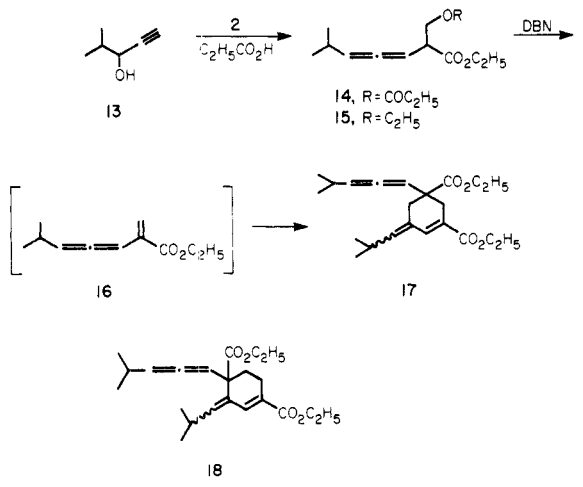
(4) Stetter, H.; Uerdingen, W. *Synthesis* **1973**, 207–208.

(5) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.-T.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741–3.

(6) Raucher and Macdonald were unable to effect Claisen ortho ester rearrangement when cinnamyl alcohol was treated with **2** (see ref 3b).

0022-3263/80/1945-2080$01.00/0

Scheme II



The minor product **7** presumably arises by the originally anticipated pathway (via **5**). Our results suggest that the transformation of **4** to **6** is substantially more facile than the corresponding conversion of **3** to **5**. Thus in the absence of sufficient propionic acid, alternative pathways intervene, leading to complex products.[7]

In order to eliminate the possibility that diester **8a** had arisen via β elimination of ethanol from **7a** (to **9a**) followed by conjugate addition of propionic acid, we heated the β-ethoxymethyl ester with excess acid under conditions simulating those of the rearrangement. This treatment led to recovery of **7a** in 89% yield, with no trace of **8a** being detectable by GC analysis.

In analogy to **1a**, the dienol **1b**[8] afforded esters **7b** and **8b** in 15 and 68% yields, respectively, when treated as described above. Unfortunately, attempts to further expand the scope of this rearrangement proved unrewarding. Thus, application of our optimized conditions to 1-vinyl-1-cyclohexanol, 2-cyclohexen-1-ol and 1-phenyl-2-propen-1-ol led, in all three examples, to complex mixtures containing, at best, traces of the desired products. The reasons for this lack of generality are not apparent. On a more positive note, it was found that allenic esters could be produced by our procedure. In this manner, the ethynyl carbinol **13** (Scheme II) furnished esters **14** (63%) and **15** (18%) (mixtures of diastereomers) when heated with **2** and excess propionic acid.

Elimination of propionic acid from diesters **8a,b** was effected by treatment with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in refluxing benzene. This procedure afforded diene esters **9a** and **9b** in 76 and 86% yields, respectively. Hydrogenation of **9b** over palladium followed by lithium aluminum hydride reduction gave, in 93% overall yield, racemic alcohol **10**, a useful α-tocopherol synthon.[9]

The α-ethoxymethyl esters **7a,b** were inert under the conditions employed for conversion of **8a,b** to **9a,b**. Since compounds **7a,b** were the minor products of the Claisen rearrangements, alternative methods for transforming these substances into α-methylene esters were not investigated.

Table I

wt, g	% 7a	% 8a	wt, g	% 7a	% 8a
1.11	76	19	1.19	3	93
7.16	12	84	0.37	3	94

Catalytic hydrogenation of **8a** (or **14**) provided the saturated diester **11**, which upon treatment with DBN yielded the α-methylene ester **12** (80% overall). This sequence demonstrates that, if desired, the α-methylene moiety can be introduced after removal of the in-chain olefinic function.

Elimination of propionic acid from allenic diester **14** by using the DBN procedure was extremely rapid and occurred even at −20 °C; however, the observed product was not the allenic α-methylene ester **16**, but rather a dimer thereof, isolated in 67% yield. On the basis of its spectral properties (see the Experimental Section), we have characterized this product as the Diels–Alder cycloadduct **17** (mixture of isomers). In particular, the ^1H NMR spectrum, while fully compatible with **17**, failed to exhibit a CH_2 resonance at relatively high field (i.e., in the nonallylic region). Although not definitive, this observation appears to rule out the regioisomeric structural possibility **18**.

In summary, these studies have demonstrated the synthetic utility of the orthoacrylate Claisen rearrangement, albeit in a limited number of examples. This approach provides a relatively straightforward route to aliphatic α-methylene esters and complements related synthetic methodology.[3]

Experimental Section

General Methods. All reactions except hydrogenations were carried out under an atmosphere of argon. The "usual workup" involves three extractions with the specified solvent. Organic solutions were then washed with saturated brine, dried over anhydrous $MgSO_4$, filtered, and concentrated on a rotary evaporator, under water aspirator pressure. Residues were dried to constant weight under high vacuum at 40–50 °C or water aspirator pressure in the case of volatile materials. Column chromatography was performed by using EM silica gel 60 (0.063–0.2 mm). Thin-layer chromatography was carried out by using EM silica gel 60 F-254 precoated plates with 4:1 hexane–ether as the mobile phase. Spots were detected with phosphomolybdic acid spray followed by heating. ^1H NMR spectra were obtained in $CDCl_3$ solution. Chemical shifts are reported relative to Me_4Si as an internal standard. GC analyses were carried out by using a Hewlett-Packard 5710A instrument with a 3 m × 4 mm (i.d.) column of 10% OV-101 on GCQ 100/120, a temperature program of 80–260 °C at 2 °C/min, and a carrier-gas flow rate of 30 mL/min. Alternatively, a 6 ft × 3 mm (i.d.) column of 10% XE 60 on Chromosorb W was employed, isothermally at 200 °C. The diesters **8a,b** and **14** exhibited greater GC retention times and smaller R_f values (TLC) than the corresponding ether esters **7a,b** and **15**, respectively. Carbinols **1a** and **13** are commercially available.

(*E*)-*rac*-Ethyl 6-Methyl-2-[(propionyloxy)methyl]-4-heptenoate (8a) and (*E*)-*rac*-Ethyl 6-Methyl-2-(ethoxymethyl)-4-heptenoate (7a). A solution of 5.01 g (50 mmol) of vinyl carbinol **1a**, 17.22 g (99 mmol) of triethyl orthoacrylate (**2**),[4] and 1.40 g (19 mmol) of propionic acid in 60 mL of toluene was stirred and heated at 110 °C for 19 h. Additional propionic acid was added as follows: 1.10 g after 80 min, 1.10 g after 2.67 h, 1.10 g after 3.75 h, 0.5 g after 5.5 h, and 0.5 g after 6.5 h (total of 5.70 g (77 mmol) of propionic acid employed). After cooling, the reaction mixture was diluted with ether and the ether solution was washed twice with saturated aqueous $NaHCO_3$ and once with brine, dried, filtered, and concentrated under reduced pressure. The residual yellow liquid (18.28 g) was chromatographed on 800 g of silica gel. Elution with 5–10% ether in hexane gave mixtures of **7a** and **8a** (Table I, analysis by GC). The percentages corre-

(7) It should be noted that, in contrast to standard ortho ester Claisen rearrangements,[5] the production of **8** *consumes* propionic acid, thus destroying the catalyst required for formation and rearrangement of the Claisen ketene acetal intermediates. This may explain why complex product mixtures were obtained when only catalytic amounts of propionic acid were utilized.

(8) *Chem. Abstr.* **1974**, *81*, 13119t; Givaudan Corp. Swiss Patent 547250.

(9) Alcohol **10** was produced as a mixture of racemates. The (2*R*,6*R*)-(+) isomer is a key intermediate in the total synthesis of (2*R*,4′*R*,8′*R*)-α-tocopherol. See: (a) Scott, J. W.; Bizzarro, F. T.; Parrish, D. R.; Saucy, G. *Helv. Chim. Acta* **1976**, *59*, 290–306; (b) Cohen, N.; Eichel, W. F.; Lopresti, R. J.; Neukom, C.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 3505–11.

Table II

wt, g	% 7b	% 8b	wt, g	% 7b	% 8b
0.263	60	34	0.494	0	98
0.413	7	91			

Table III

wt, g	% 14	% 15	wt, g	% 14	% 15
1.44	0	99	3.45	99	0
5.52	87	12			

spond to a total of 1.80 g of **7a** (15.8%) and 8.43 g of **8a** (65.9%). Pure **7a** was obtained by careful rechromatography of a sample of the material rich in this component, followed by evaporative distillation: colorless liquid; bp 85–90 °C (bath temperature) (12 mm); IR 1725 (ester C=O), 960 cm^{-1} (*E* olefin); NMR δ 5.38 (m, 2, *E* CH=CH), 4.13 (q, 2, J = 7 Hz, CH_3CH_2OCO), 3.50 (m, 4, OCH_2), 2.67 (m, 1, CHC=O), 2.25 (m, 3, allylic CH_2 and CH), 1.24, 1.16 (2 t, 6, J = 7 Hz, CH_3CH_2O), 0.95 (d, 6, J = 6.5 Hz, $(CH_3)_2CH$); mass spectrum, m/z 228 (M^+).

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.60. Found: C, 65.25; H, 10.91.

In a similar manner, pure **8a** was obtained by rechromatography and evaporative distillation of a sample to give a colorless liquid: bp 90–95 °C (bath temperature) (2 mm); IR 1730 (ester C=O), 970 cm^{-1} (*E* olefin); NMR δ 5.37 (m, 2, *E* CH=CH), 4.20, 4.14 (2 q, 4, OCH_2CH_3), 2.72 (quin, 1, J = 6.5 Hz, CHC=O), 2.28 (m, 5, allylic CH_2, CH, and CH_3CH_2C=O), 1.25, 1.12 (2 t, 6, J = 7 Hz, CH_3CH_2O, CH_3CH_2C=O), 0.95 (d, 6, J = 6.5 Hz, $(CH_3)_2CH$).

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.59; H, 9.44. Found: C, 65.55; H, 9.66.

(*E*)-*rac*-Ethyl 6,10-Dimethyl-2-[(propionyloxy)methyl]-4,9-undecadienoate (8b) and (*E*)-*rac*-Ethyl 6,10-Dimethyl-2-(ethoxymethyl)-4,9-undecadienoate (7b). A 0.72-g (4.28 mmol) sample of vinyl carbinol **1b**[8] was treated with triethyl orthoacrylate (1.49 g, 8.56 mmol) and propionic acid (0.45 g total, 6.08 mmol) by using the procedure described in the preceding experiment. Chromatography of the crude product (1.85 g) on 100 g of silica gel, eluting with 5–7% ether in hexane, gave fractions of the compositions given in Table II (GC). These percentages correspond to a total of 0.187 g (14.8%) of **7b** and 0.949 g (68.4%) of **8b**. The last fraction was evaporatively distilled to give pure **8b** as a colorless oil: bp 110–115 °C (bath temperature) (0.05 mm); IR 1732 (ester C=O), 972 cm^{-1} (*E* olefin); NMR δ 5.30 (m, 2, *E* CH=CH), 5.02 (m, 1, CH=), 4.22, 4.15 (2 q, 4, OCH_2CH_3), 2.74 (quin, 1, J = 6.5 Hz, CHC=O), 2.30 (m, allylic CH_2, CH, CH_3CH_2C=O), 1.64, 1.54 (2 s, 6, $(CH_3)_2C$=), 1.23, 1.11 (2 t, CH_3CH_2O, CH_3CH_2C=O), 0.94 (d, J = 6.5 Hz, CH_3CH); mass spectrum, m/z 324 (M^+).

Anal. Calcd for $C_{19}H_{32}O_4$: C, 70.33; H, 9.94. Found: C, 70.53; H, 10.10.

A sample of purified **7b** from another experiment exhibited the following properties: bp 95–100 °C (bath temperature) (0.1 mm); IR 1730 (ester C=O), 970 cm^{-1} (*E* olefin); NMR δ 5.28 (m, 2, *E* CH=CH), 5.03 (m, 1, CH=), 4.15 (q, 2, J = 7 Hz, $CO_2CH_2CH_3$), 3.48 (m, 4, CH_2O, CH_3CH_2O), 2.70 (quin, 1, J = 6.5 Hz, CHC=O), 2.26 (m, 2, CH_2), 1.93 (m, 3, CH_2, CH), 1.67, 1.58 (2 s, 6, $(CH_3)_2C$=), 1.19, 1.10 (2 t, CH_3CH_2O), 0.93 (d, 3, J = 6.5 Hz, CH_3CH); mass spectrum, m/z 296 (M^+).

***rac*-Ethyl 6-Methyl-2-[(propionyloxy)methyl]-3,4-heptadienoate (14) and *rac*-Ethyl 6-Methyl-2-(ethoxymethyl)-3,4-heptadienoate (15).** A 5.0-g (51 mmol) sample of ethynyl carbinol **13** was treated with triethyl orthoacrylate (17.35 g, 99.7 mmol) and propionic acid (6.65 g total, 89.9 mmol; 5.15 g initially, 0.75 g after 1 h, and 0.75 g after 2.25 h) as described in the preceding experiments except that the reflux period was reduced to 4 h. The crude product (18.27 g) was chromatographed on 900 g of silica gel. Elution with 10–20% ether in hexane gave fractions of the compositions given in Table III (GC). These percentages correspond to a total of 2.08 g (18.0%) of **15** and 8.22 g (63.4%) of **14**. Evaporative distillation of the last fraction gave pure **14** as a colorless liquid: bp 90 °C (bath temperature) (0.3 mm); IR 1965 (allene), 1735 cm^{-1} (ester C=O); NMR δ 5.25 (m, 2, CH=C=CH), 4.27, 4.17 (d, q, 4, OCH_2CH, OCH_2CH_3), 3.32 (m, 1, CH), 2.30 (q, m, 3, CH_3CH_2C=O, $CH(CH_3)_2$), 1.25 (t, 3, OCH_2CH_3), 1.02, 0.98 (t, d, 9, CH_3CH_2C=O, $(CH_3)_2CH$).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.17; H, 8.84.

A sample of **15** from another experiment was purified by high-pressure LC and evaporative distillation to give a colorless liquid: IR 1965 (allene), 1728 cm^{-1} (ester C=O); NMR δ 5.25 (m, 2, CH=C=CH), 4.16 (q, 2, CH_3CH_2OC=O), 3.48 (m, 5, CH_3CH_2O, CH, CH_2O), 2.29 (m, 1, $CH(CH_3)_2$), 1.25, 1.15, 0.99 (2 t, d, 12, CH_3CH_2OC=O, CH_3CH_2O, $(CH_3)_2CH$).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.77; H, 9.58.

(*E*)-Ethyl 6-Methyl-2-methylene-4-heptenoate (9a). A solution of 0.3 g (1.09 mmol) of diester **8a** (93% pure by GC), 0.17 g (1.37 mmol) of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, Aldrich), and 4 mL of benzene was stirred and refluxed for 45 h. The resulting red solution was cooled and absorbed on a column of 15 g of silica gel. Elution with 5 and 10% ether in hexane gave 151 mg (76.1%) of α-methylene ester **9a** as a colorless liquid. In another experiment, a chromatographed sample was evaporatively distilled, affording an analytical specimen as a colorless liquid: bp 75–80 °C (bath temperature) (12 mm); IR 1710 (ester C=O), 1631 (CH_2=C), 971 cm^{-1} (*E* olefin); NMR δ 6.02 (br s, 1, CH_2=), 5.39 (br s, 1, CH_2=), 5.28 (m, 2, *E* CH=CH), 4.19 (q, 2, J = 6.5 Hz, OCH_2CH_3), 2.96 (br d, 2, allylic CH_2), 2.25 (m, 1, $CH(CH_3)_2$), 1.25 (t, 3, J = 6.5 Hz, OCH_2CH_3), 0.93 (d, 6, J = 6.5 Hz, $(CH_3)_2CH$); mass spectrum, m/z 182 (M^+).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.33; H, 10.09.

(*E*)-*rac*-Ethyl 6,10-Dimethyl-2-methylene-4,9-undecadienoate (9b). A solution of 1.51 g (4.66 mmol) of diester **8b**, 0.69 g (5.56 mmol) of DBN, and 17 mL of benzene was stirred and refluxed for 66 h. An additional 0.5 g (4.03 mmol) of DBN was added and refluxing was continued for 3 h. After cooling, the solution was poured into water and worked up with ether in the usual manner (the organic extracts were additionally washed with 1 N HCl), giving 1.17 g of oily product. This material was evaporatively distilled, affording 1.0 g (85.8%) of pure **9b** as a colorless oil: bp 100–105 °C (bath temperature) (2.5 mm); IR 1710 (ester C=O), 1633 cm^{-1} (CH_2=); NMR δ 6.10 (br s, 1, CH_2=), 5.47 (br s, 1, CH_2=), 5.34 (m, 2, *E* CH=CH), 5.04 (m, 1, CH=$C(CH_3)_2$), 4.17 (q, 2, J = 6.5 Hz, OCH_2CH_3), 2.96 (br d, 2, allylic CH_2), 1.91 (m, 3, allylic CH, CH_2), 1.64, 1.54 (2 s, 6, $(CH_3)_2C$=), 1.35 (t, 3, J = 6.5 Hz, OCH_2CH_3, and m, 2, CH_2), 0.93 (d, 3, J = 6.5 Hz, CH_3CH); mass spectrum, m/z 250 (M^+).

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.76; H, 10.47. Found: C, 76.80; H, 10.75.

***rac*-2,6,10-Trimethylundecan-1-ol (10).** A 0.818-g (3.27 mmol) sample of ester **9b** was hydrogenated in ethanol, over 5% palladium on carbon, at room temperature and 1 atm. After 3 h, approximately the theoretical volume of H_2 had been taken up, and gas absorbtion ceased. The catalyst was filtered, and the filtrate was concentrated in vacuo. The residue was evaporatively distilled under high vacuum, giving 0.833 g (99.5%) of *rac*-ethyl 2,6,10-trimethylundecanoate. A 0.62-g (2.42 mmol) sample of this ester was reduced, in ether, at 0 °C, with 0.094 g (2.47 mmol) of lithium aluminum hydride. After being stirred at room temperature for 1 h, the mixture was decomposed with wet ether and poured into 1 N aqueous HCl. Workup with ether in the usual manner gave an oily product. Evaporative distillation furnished 0.487 g (94%) of pure alcohol **10** as a colorless liquid, bp 105–110 °C (bath temperature) (3 mm). This material was identical with authentic (2*R*,6*R*)-**10**[9] by TLC, GC, and IR and NMR spectral comparison.

***rac*-Ethyl 6-Methyl-2-[(propionyloxy)methyl]heptanoate (11).** A 1.0-g (3.90 mmol) sample of diester **8a** was hydrogenated in 15 mL of ethanol, over 0.103 g of 5% palladium on carbon, at room temperature and 1 atm. After 1 h, the theoretical amount of H_2 had been absorbed, and no further gas uptake was noted. The catalyst was filtered, and the filtrate was concentrated in vacuo. Evaporative distillation of the oily residue afforded 0.97 g (97%) of pure diester **11** as a colorless liquid, bp 80–85 °C (bath temperature) (1.5 mm). Identical material was obtained by hydrogenation of allenic diester **14**. A sample of this material was redistilled to give an analytical specimen: IR 1733 cm^{-1} (ester C=O); NMR δ 4.21 (m, 4, CH_2O, CH_3CH_2O), 2.71 (m, 1, CHC=O), 2.32 (q, 2, J = 7 Hz, CH_3CH_2C=O), 1.26, 1.12 (2 t,

J = 7 Hz, CH_3CH_2O, $CH_3CH_2C{=}O$), 0.86 (d, 6, J = 6.5 Hz, $(CH_3)_2CH$).

Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.09; H, 10.14. Found: C, 64.95; H, 10.27.

Ethyl 6-Methyl-2-methyleneheptanoate (12). A mixture of 0.411 g (1.59 mmol) of diester 11, 0.409 g (3.30 mmol) of DBN, and 10 mL of benzene was stirred and refluxed for 95 h. At the end of this time, GC analysis indicated ca. 15% starting diester still present. An additional 0.2 mL of DBN was added, and refluxing was continued for 23 h. The mixture was cooled, treated with 1 N aqueous HCl and worked up with ether in the usual manner. The oily residue was chromatographed on 50 g of silica gel. Elution with 19:1 hexane–ether gave pure α-methylene ester **12** which was evaporatively distilled. There was obtained 0.241 g (82.4%) of a colorless liquid: bp 80–88 °C (bath temperature) (13 mm); IR 1710 (ester C=O), 1640 cm^{-1} ($CH_2{=}$); NMR δ 6.07 (br s, 1, $CH_2{=}$), 5.43 (br s, 1, $CH_2{=}$), 4.22 (q, 2, J = 7 Hz, OCH_2CH_3), 2.29 (br t, 2, allylic CH_2), 1.29 (t, J = 7 Hz, OCH_2CH_3), 0.86 (d, 6, J = 6.5 Hz, $(CH_3)_2CH$).

***rac*-Diethyl 3-(4-Methyl-1,2-pentadien-1-yl)-5-(2-methylpropylidene)-1(6)-cyclohexen-1,3-dicarboxylate (17).** To a stirred solution of 0.324 g (1.28 mmol) of allenic diester 14 in 5 mL of anhydrous ether, at −20 °C, was added a solution of 0.25 g (2.02 mmol) of DBN in 1 mL of dry ether. The mixture was stirred at −20 °C for 2 h and was then allowed to warm to 0 °C over 0.5 h whereupon it was treated with 1 N aqueous HCl. Workup with ether in the usual manner gave a pale yellow oil which was chromatographed on 20 g of silica gel. Elution with 9:1 hexane–ether afforded 0.155 g (67.3%) of diester **17** as a pale yellow oil. A sample was evaporatively distilled to give an analytical specimen: bp 100–108 °C (bath temperature) (0.2 mm); IR 1960 (allene), 1722 (ester C=O), 1700 (conj ester C=O), 1630 (C=C), 1610 cm^{-1} (C=C); UV max (95% C_2H_5OH) 275 nm (ϵ 17 125); NMR δ 7.50 (br s, 1, CH=), 5.57 (minor isomer), 5.52 (major isomer, 2 d, 1, J = 9 Hz, =CHCH of two isomers), 5.20 (m, 2, CH=C=CH), 4.18 (m, 4, OCH_2CH_3), 2.90 (m, 1, $CH(CH_3)_2$), 2.60–1.45 (br m, 5, allylic CH_2, CH), 1.29, 1.21 (2 t, J = 6.5 Hz, OCH_2CH_3), 1.01, 0.95 (2 d, 12, J = 6.5 Hz, $(CH_3)_2CH$) (nonallylic CH_2 not discernible); mass spectrum, m/z 360 (M^+).

Anal. Calcd for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95. Found: C, 73.12; H, 9.16.

Attempted Conversion of 7a to 8a. A solution of 0.339 g (1.49 mmol) of ether ester **7a** and 0.17 mL (2.27 mmol) of propionic acid in 7 mL of toluene was stirred and refluxed for 21 h, cooled, diluted with ether, and treated with saturated aqueous $NaHCO_3$ solution. Workup with ether in the usual manner gave 0.301 g (88.8%) of a pale yellow liquid. Analysis by TLC and GC revealed that this material consisted of only recovered ether ester **7a** with none of the diester **8a** being detectable.

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Registry No. (±)-**1a**, 73262-52-9; **1b**, 52093-38-6; **2**, 42216-96-6; (*E*)-(±)-**7a**, 73262-53-0; (*E*)-(±)-**7b**, 73262-54-1; (*E*)-(±)-**8a**, 73262-55-2; **8b**, 73262-56-3; (*E*)-**9a**, 73262-57-4; (*E*)-(±)-**9b**, 73262-58-5; (±)-**10** (isomer 1), 63568-64-9; (±)-**10** (isomer 2), 73306-83-9; (±)-**11**, 73262-59-6; **12**, 73262-60-9; (±)-**13**, 73262-61-0; (±)-**14** (isomer 1), 73262-62-1; (±)-**14** (isomer 2), 73306-84-0; (±)-**15** (isomer 1), 73262-63-2; (±)-**15** (isomer 2), 73306-85-1; **16** dimer, 73262-71-2; **17**, 73262-64-3; propionic acid, 79-09-4.

Trifluoroacetic Acid Quenching of Naphthalene Fluorescence: Implications for the Mechanism of Photoelectrophilic Hydrogen Exchange

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The quenching of naphthalene fluorescence by trifluoroacetic acid involves the dimer of the acid. In isooctane, the activation energy for quenching is essentially zero. The previously observed decrease in quenching efficiency in more polar solvents results from their lower dimer content. Hydrogen isotope exchange in the system naphthalene–trifluoroacetic acid–alkane solvent also involves the dimer of trifluoroacetic acid.

Photochemical hydrogen isotope exchange in aromatic compounds is of interest as a rare example of a photochemical electrophilic substitution. In the case of naphthalene, which is the subject of this paper, exchange was first observed by Kuz'min et al.,[1] who used acetic acid/sulfuric acid as the exchange medium. Exchange has been observed also in acetic acid,[2] sulfuric acid,[3] and in alkane solutions of trifluoroacetic acid[4,5] but not in aqueous perchloric acid.[6] These results were reviewed recently.[7]

Hydrogen isotope exchange is a singlet-state reaction, as evidenced by kinetic arguments[1] and a failure to sensitize.[5] In alkane solvents, the fluorescence of naphthalene is quenched by trifluoroacetic acid (TFA), but the efficiency of quenching exceeds the effect of TFA on the quantum yield of hydrogen exchange by a large factor.[5] It was therefore concluded that the initial reaction of TFA with singlet excited naphthalene affords an intermediate in which the incoming and outgoing hydrogen atoms are not equivalent.

The quenching efficiency of TFA is strongly solvent dependent.[5] It is most efficient in alkanes and increasingly less so in benzene, 1-octene, and acetonitrile. In ether and in ethanol no quenching is observed. Since Mataga et al.[8]

(1) M. G. Kuz'min, B. M. Uzhinov, G. S. Gyorgy, and I. V. Berezin, *Russ. J. Phys. Chem. (Engl. Transl.)*, **41**, 400 (1967).
(2) E. Vander Donckt, D. Lietaer, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **79**, 283 (1970).
(3) C. G. Stevens and S. J. Strickler, *J. Am. Chem. Soc.*, **95**, 3922 (1973).
(4) G. Lodder and E. Havinga, *Tetrahedron*, **28**, 5583 (1972).
(5) N. J. Bunce, Y. Kumar, and L. Ravanal, *J. Org. Chem.*, **44**, 2612 (1979).
(6) S. F. Mason and B. E. Smith, *J. Chem. Soc. A*, 325 (1969).
(7) W. J. Spillane, "Isotopes in Organic Chemistry", Vol. 4, Elsevier, Amsterdam, 1978, p 51.

0022-3263/80/1945-2083$01.00/0