ft, 115 °C) to determine the isomer ratio.

Recycle Experiments. For experiments in which the polymeric catalyst was reused, the bomb containing the previous reaction was brought into an argon-filled drybox prior to venting the pressure. The catalyst was then removed from the reaction mixture by filtration and was washed well with deoxygenated benzene. The catalyst was placed in a fresh glass liner, and fresh substrate and solvent were added. The reaction and workup were carried out as previously described.

^{31}P NMR. All ^{31}P experiments were performed on a highly modified[21] Bruker HFX-90 spectrometer interfaced to a Nicolet 1180B data system, operating at 36.4 MHz. Samples were run in 15-mm tubes (active volume only) at ambient temperature, about 35 °C, under conditions of proton-noise decoupling. Field/frequency lock was maintained via a capillary of C_4F_8 external to the ^{31}P insert.[22]

The ith chemical shift is $\delta_i = (\nu_i - \nu_r)/\nu_r$, where ν_i is the resonant frequency of the ith spin isochromat and ν_r is the resonant frequency of the reference, an external sample of 85% H_3PO_4. When this convention is used, an increase in chemical shift is an increase in resonant frequency and a decrease in shielding.

Spin–lattice relaxation time (T_1) measurements were performed by using a modified form of the inversion recovery (IRFT)[23] often referred to as fast inversion recovery Fourier transfer (FIRFT).[24] Radio-frequency phase alternation was used to eliminate rf pulse defect errors and coherent noise.[25] T_1 data were analyzed by a three-parameter fit.[26]

All samples were run in 15-mm tubes prepared under an inert atmosphere. Free ligands and soluble polymers were run as solutions in degassed benzene. Cross-linked polymers were run swollen in degassed benzene. Rhodium was introduced as $[Rh(CO)_2Cl]_2$ to avoid interferences in the region of interest.

Acknowledgment. The authors thank the National Science Foundation for support of this work (Grant DMR77-14447).

Registry No. 1, 61085-15-2; **2a**, 70703-27-4; **2b**, 70703-28-5; styrene, 100-42-5; divinylbenzene, 1321-74-0; sodium diphenylphosphide, 4376-01-6; lithium dibenzophosphole, 70703-24-1; *P*-phenyldibenzophosphole, 1088-00-2; dibenzophosphole sodium salt, 70703-25-2; hydridocarbonyltris(triphenylphosphine)rhodium(I), 64665-44-7; μ-dichloro-tetracarbonyldirhodium(I), 14523-22-9; vinylcyclohexane, 695-12-5; (*R*)-hydratropaldehyde, 38235-74-4; DIPHOL, 70703-26-3; (+)-DIOP, 37002-48-5; (*Z*)-2-butene, 590-18-1; (*E*)-2-butene, 624-64-6; 1-pentene, 109-67-1.

Supplementary Material Available: Data from electron-induced X-ray emission analysis (3 pages). Ordering information is given on any current masthead page.

(21) H. C. Dorn, L. Simeral, J. J. Matterstad, and G. E. Maciel, *J. Magn. Reson.*, 18, 1 (1975); J. J. H. Ackerman and G. E. Maciel, *ibid.*, 23, 67 (1976).
(22) J. L. Dallas, Ph.D. Thesis, Colorado State University, 1977.
(23) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, 48, 3831 (1968).
(24) G. C. Levy, I. R. Peat, and D. Canet, *J. Magn. Reson.*, 18, 199 (1975).
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(26) G. Levy and I. R. Peat, *J. Magn. Reson.*, 18, 500 (1975).

Reactions of Esters with Phosphorus Ylides. 3.[1,2] Direct Conversion into Branched Olefins

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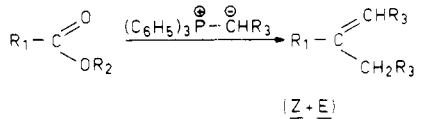
Aromatic and aliphatic esters can be directly converted into the corresponding isopropenyl compounds by reaction with methylenetriphenylphosphorane. In the case of aliphatic esters "salt-free" conditions are required to effect selective conversions. Reaction with other *n*-alkylidenetriphenylphosphoranes likewise affords the corresponding branched olefins as mixtures of *E* and *Z* isomers. α-Branched or stabilized phosphoranes do not react in this way. The reaction has also been extended to ylides containing (protected) functional groups. Examples are presented in which esters are reacted with ethoxycarbonyl-, carboxylate-, and ethylenedioxy-substituted phosphoranes and thereby converted into branched olefins containing these functional groups twice. The influence of ester structure and reaction conditions upon yield and product distribution is discussed.

Recently, the direct conversion of ester into isopropenyl groups by the action of methylenetriphenylphosphorane was described.[3] More generally this conversion can be depicted as the reaction in which an ester is allowed to react with an excess of alkylidenetriphenylphosphorane and thereby converted into a branched olefin in such a way that both oxygens in the original ester are replaced by the phosphorane alkyl moiety and that a double bond is introduced at the position of the original carbonyl group.



(Z + E)

Under the conditions originally employed [excess of phosphorane in dimethyl sulfoxide (Me_2SO)] several aromatic esters afforded good yields of olefins, but with aliphatic esters appreciable amounts of acylated phosphoranes 4 (Scheme I) were also formed.[3] Further study led to a proposal for the mechanism of this ester–ylide reaction.[1] Inspection of this mechanism (vide infra) indicated several possibilities to improve the yield and to affect the product distribution of the reaction. The influence of solvent, temperature, the presence of dissolved

(1) Part 2: A. P. Uijttewaal, F. L. Jonkers, and A. van der Gen, *J. Org. Chem.*, 43, 3306 (1978).
(2) Part of the Thesis of A. P. Uijttewaal, University of Leiden, 1978.
(3) A. P. Uijttewaal, F. L. Jonkers, and A. van der Gen, *Tetrahedron Lett.*, 1439 (1975).

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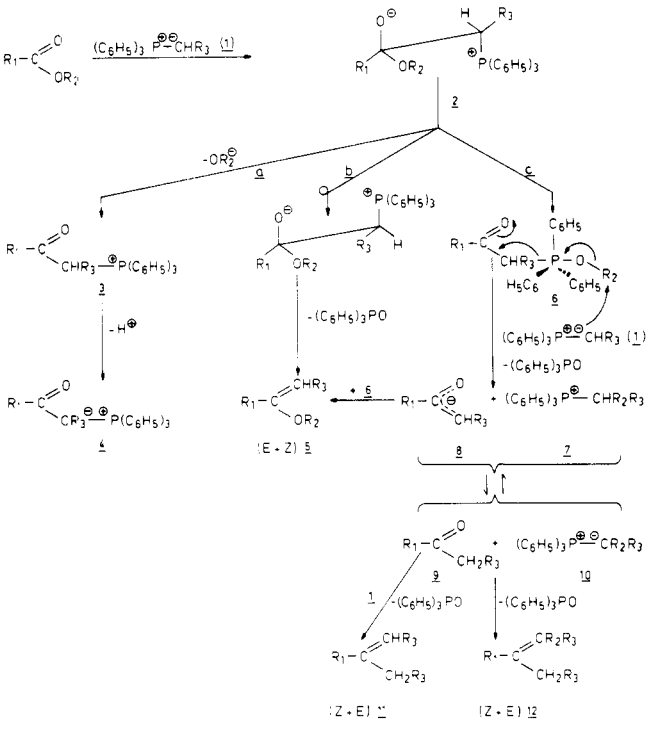
Scheme I



alkali halide, and the addition of extra phosphonium salt on the reaction of a variety of aromatic as well as aliphatic esters and some diesters with methylene-, other *n*-alkylidene-, and substituted alkylidenetriphenylphosphoranes is described in this paper. Reactions of esters with phosphoranes containing an α-hetero substituent, in particular methoxymethylenetriphenylphosphorane, are being investigated and will be reported separately.

Selectivity. Scheme I depicts the three major reactivities that esters can show toward phosphoranes. When lithium bases are used to prepare the ylide from its phosphonium salt, reaction path a, originally discovered by Wittig and Schöllkopf[4] and developed by Bestmann,[5] is followed exclusively. The intermediate alkoxybetaine **2** loses alkoxide ion to give the acylated phosphonium salt **3**, which is rapidly deprotonated by alkoxide ion or ylide to afford the stable acylated phosphorane **4**.

Reaction b, studied extensively by Le Corre,[6] occurs when activated esters (e.g. oxalic and cyanoacetic esters) are allowed to react with (semi)stabilized phosphoranes[7] in a solvent of low polarity. The alkoxybetaine **2** loses triphenylphosphine oxide to give an E/Z mixture of enol ethers **5**.

As described above, reaction path c allows the direct conversion of esters into branched olefins **11**. According to the proposed mechanism,[1] alkoxybetaine **2** now undergoes an intramolecular rearrangement in which the ester alkoxy group is picked up by the positively charged phosphorus atom to give, after transformation of the ligand bonds around phosphorus ("pseudorotation"), the pentacoordinate phosphorus intermediate **6**. The apical alkoxy group in **6** undergoes nucleophilic attack (usually by another molecule of phosphorane) to give triphenylphosphine oxide, alkylated phosphonium salt **7**, and enolate ion **8**. Equilibration between **7** and **8** gives ketone **9** and alkylated phosphorane **10**. Reaction of **9** with a third molecule of phosphorane **1** then affords the branched olefin **11** as the final product.

Apart from the desired olefins **11**, a number of side products can be expected. Not only acylated phosphoranes **4** and enol ether mixtures **5** (E + Z) can be formed by reaction paths a and b respectively, there is also the possibility of formation of homologous olefins **12** from reaction of ketones **9** with alkylated phosphoranes **10**. In addition it has been shown[1] that enol ethers **5** can be formed by an alternative route, namely by nucleophilic attack of enolate **8** on the alkoxy group in intermediate **6**.

An excellent way to improve the yields of **11** and suppress the formation of side products **12** and **5** was found in the addition of 1 equiv of the phosphonium salt corresponding to **1** to the reaction mixture (in practice this is done by using 3 equiv of base and 4 equiv of phosphonium salt). This results in a rapid conversion of enolate **8** into ketone **9** with concomitant formation of phosphorane **1** rather than alkylated phosphorane **10**. Consequently the formation of enol ethers **5** from **8** and of homologous olefins **12** from **10** will be avoided.

For the reaction to proceed along path c the conformation of alkoxybetaine **2** is of crucial importance. Stabilization of betaines by complex formation with alkali halides, in particular lithium salts, in not strongly solvating solvents is well documented.[8] Under such conditions a twisted boat form of the complexed betaine prevails, in which the alkoxy group is far removed from the phosphorus atom[1] and reaction paths a and b are promoted. In a polar, aprotic solvent, however, solvation will stimulate intermediate **2** to retain the staggered conformation, necessary for the intramolecular rearrangement in path c. A more efficient way to exclude the influence of alkali halide can be found in the application of "salt-free" conditions.[9] It was therefore expected that in the case of aliphatic esters, where originally mixtures of olefins **11** and acylated phosphoranes **4** were obtained,[3] reaction with salt-free ylides would result in improved selectivity.

Results and Discussion

Methylenetriphenylphosphorane. Most aromatic esters afford high yields of isopropenyl compounds when 4 equiv of methyltriphenylphosphonium iodide and 3 equiv of dimethyl sulfoxide anion are used in Me_2SO at room temperature (method A). Aliphatic esters (and aromatic esters possessing electron-donating substituents) necessitate the use of 4 equiv of salt-free phosphorane[9] at room temperature (method B).[10] Only when aromatic esters with strongly electron-donating substituents are used are elevated temperatures needed to suppress the formation

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(5) H. J. Bestmann and B. Arnason, *Chem. Ber.*, **95**, 1513 (1962); *Tetrahedron Lett.*, 455 (1961); H. J. Bestmann, N. Sommer, and H. A. Staab, *Angew. Chem.*, **74**, 293 (1962); H. A. Staab and N. Sommer, *ibid.*, **74**, 294 (1962).
(6) M. Le Corre, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **276**, 963 (1973); *Bull. Soc. Chim. Fr.*, **9–10**, 2005 (1974).
(7) A. W. Johnson, "Ylid Chemistry", Academic Press, New York, 1966.
(8) M. Schlosser, *Top. Stereochem.*, **5**, 1 (1970).
(9) Methylenetriphenylphosphorane was prepared salt-free in three different ways. (a) The "sodium amide/liquid ammonia" method.[5] (b) The "sodium amide in refluxing THF" method: R. Köster, D. Sinič, and M. A. Grassberger, *Justus Liebigs Ann. Chem.*, **739**, 211 (1970). The "sodium hydride in THF" method, which in our hands seemed only successful in the case of methyltriphenylphosphonium bromide: H. Schmidbaur, H. Stühler, and W. Vornberger, *Chem. Ber.*, **105**, 1084 (1972). The salt-free nature of the ylide was for each method confirmed by ^{13}C NMR. The values found for $J(^{13}C–^{31}P)$ were completely in accordance with literature data [see: T. A. Albright and E. E. Schweitzer, *J. Org. Chem.*, 41, 1168 (1976)]. The other alkylidenetriphenylphosphoranes were prepared salt-free according to method a. Another convenient method was recently published by Bestmann et al., *Chem. Ber.*, **109**, 1694 (1976).
(10) After the results shown in Table I had been obtained, it was found that methods B and C give better results when 3 equiv of salt-free ylide and 1 equiv of the corresponding phosphonium salt are used.

of acylated phosphoranes (method c).[10] The results are summarized in Table I. The presence of strongly electron-withdrawing substituents (2-benzo[*b*]furyl-, 4-pyridyl-[11]) leads to a sharp decrease in olefin formation. In these cases loss of alkoxide ion from betaine **2** (as occurs in routes a and c) is retarded and enol ethers (path b) become major reaction products.[12]

The ester–ylide reaction described here is expected to show the same pattern of compatibility with the presence of other functional groups as the Wittig reaction when run under salt-free conditions or in aprotic polar solvents. An aldehyde or ketone function, if not protected, will be rapidly converted into a methylene group (entry **34**). On the other hand, selective reaction of a ketone or aldehyde group in the presence of an ester function can usually be achieved by avoiding an excess of ylide.[13]

Carbonyl and alcohol functions can be protected by a range of protecting groups, as illustrated by entries **35–37**. It should be noted however that interference with protecting groups has been observed when the distance between ester and protecting group was small, e.g. in the case of methyl 2-ketocyclohexanecarboxylate ethylene acetal or trimethylene dithioacetal. Isolated double bonds do not interfere (entries **31** and **32**). In the case of ethyl cinnamate, the desired 1,2-addition product is formed exclusively and no 1,4 addition is observed (entry **27**).[14]

Special mention should be made of entry **38**, where a 55% yield of 4-isopropenylcyclohexanone is obtained. Apparently the *p*-tosylhydrazone group reacts with the ylide in such a way that upon quenching with water a carbonyl group is formed.

Table II contains the results obtained with diesters ($R_2O_2C(CH_2)_nCO_2R_2$). When the distance between the ester groups is small ($n \leq 3$) appreciable interaction between the two functional groups occurs as evidenced by the low yields of olefins. When the ester groups are separated by four carbon atoms or more, reaction with 8 equiv of salt-free ylide proceeds satisfactorily and good yields of the corresponding bis(isopropenyl) compounds are obtained.[10]

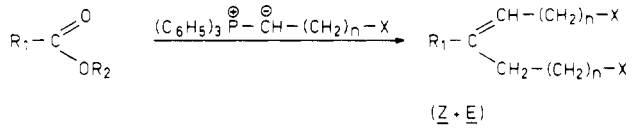
Application of salt-free conditions allows the use of a wide range of aprotic solvents. The influence of the nature of the solvent upon yield and product distribution was studied for one aromatic and one aliphatic ester. The results are presented in Table III (ethyl 2-naphthoate) and Table IV (methyl *n*-nonanoate). As can be seen from Table III, Me_2SO is the solvent of choice for this aromatic ester. The use of hexamethylphosphoric triamide (HMPA) gives rise to substantial enol ether formation, most likely as a result of O-alkylation of the intermediate enolate **8**. With aliphatic esters (Table IV) the use of either benzene, tetrahydrofuran (THF), or HMPA affords high yields of the desired isopropenyl compounds.

Table V shows the influence of the nature of the ester alkoxy group upon rate and product composition as studied with a number of *o*-methoxybenzoates. *tert*-Butyl esters do not react, no doubt because of the steric encumberment on the ester carbonyl group. The other esters react at widely differing rates, which is in line with the suggestion that nucleophilic attack of the phosphorane on the ester carbonyl group is the rate-determining step.[1] No side products are observed in these cases. (N.B. this is different when higher phosphoranes are used, vide infra.)

***n*-Alkylidenetriphenylphosphoranes.** The results of the reactions of several methyl and ethyl esters with ethylidenetriphenylphosphorane are presented in Table VI. The *E*/*Z* ratios of the 3-substituted 2-pentenes agree well with the values expected for the reaction of an intermediate ketone[1] with ethylidenetriphenylphosphorane under these conditions. Although both ethyl and methyl esters afford high yields of products, the use of methyl esters has the advantage of giving a faster reaction and less side products.[16] Table VII shows the influence of solvent upon the reaction of ethyl benzoate with ethylidenetriphenylphosphorane.[17] As before, HMPA turns out to be less suitable because of the formation of large amounts of enol ethers. The results of the reactions of aromatic and aliphatic esters with *n*-butylidene- and *n*-hexylidenetriphenylphosphorane are presented in Tables VIII and IX. As expected, reaction with these two phosphoranes gives rise to the formation of 5-substituted 4-nonenes and 7-substituted 6-tridecenes, respectively. The same general tendencies as observed before persist. Me_2SO appears to be the solvent of choice and the use of methyl esters suppresses the formation of side products. In most of the products obtained from aliphatic esters with these higher phosphoranes neither GC nor NMR analysis allowed determination of the *E* to *Z* ratio.

The α-branched ylide isopropylidenetriphenylphosphorane, prepared under salt-free conditions, reacted neither with esters nor even with acid chlorides. Semistabilized ylides such as allylene- and benzylidenetriphenylphosphorane, either salt-free or in polar aprotic solvents, did not react with normal aliphatic or aromatic esters.

Functionalized Alkylidenetriphenylphosphoranes. The synthetic utility of the ester–ylide reaction could be significantly extended by reacting esters with ylides containing an additional functional group.



(Z + E)

This allowed conversion into branched olefins containing the additional functional group in each side chain. A prerequisite for such a functional group is of course its stability under the reaction conditions. Successful reactions of this kind were carried out with ylides containing as a second functionality: ω-ethoxycarbonyl (n = 8), ω-carboxylate (n = 3), and ω-(2-methyl-1,3-dioxolan-2-yl) (n = 2). The requisite phosphonium salts were synthesized from the corresponding iodides.[18-20] Table X shows the

(11) The fact that no 4-isopropenylpyridine was obtained is probably due to polymerization of this reactive olefin. Note that upon reaction with ethylidenetriphenylphosphorane a good yield of 3-(4′-pyridyl)-2-pentene is obtained (Table VI).

(12) The positive effect of electron-withdrawing substituents on enol ether formation has been observed by H. J. Bestmann, K. Rostock, and H. Dornauer, *Angew. Chem.*, 78, 335 (1966). See also H. J. Bestmann, H. Dornauer, and K. Rostock. *Chem. Ber.*, **103**, 2011 (1970).

(13) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 692.

(14) Several aliphatic α,β-unsaturated esters failed to react under these conditions.

(15) M. Schlosser and K. F. Christmann, *Justus Liebigs Ann. Chem.*, **708**, 1 (1967).

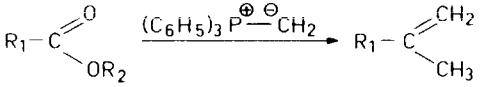
(16) The use of ethyl esters, e.g. in Table VII, was prompted by the desire to induce a clear effect upon the product composition. For preparative purposes the use of methyl esters is advisable.

(17) Dimethylformamide (DMF) seemed not to be a suitable solvent for the ester–ylide reaction under salt-free conditions, e.g. reaction with ethylidenetriphenylphosphorane in DMF gave rise to formation of appreciable quantities of 2-methylpenten-2-al, probably via an aldol-type condensation reaction.

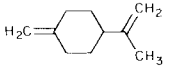
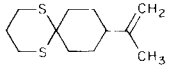
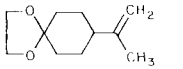
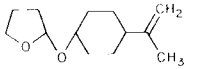
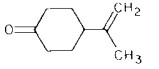
(18) E. J. Corey, N. M. Weinshenker, T. K. Schaaf, and W. Huber, *J. Am. Chem. Soc.*, **91**, 5675 (1969).

(19) L. Crombie, P. Hemesley, and G. Pattenden, *J. Chem. Soc.*, 1016 (1969).

Table I. Reaction of Esters with Methylenetriphenylphosphorane

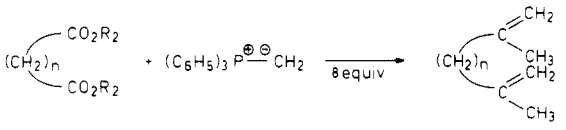


compd	R_1	R_2	method	solvent	product	% yield	NMR δ ($CDCl_3$)
13	phenyl	ethyl	A	Me_2SO	isopropenylbenzene	56	7.48–7.17 (m, 5, arom), 5.32 (s, 1, =CH), 5.03 (s, 1, =CH), 2.13 (s, 3, $-CH_3$)
14	*p*-chlorophenyl	ethyl	A	Me_2SO	*p*-chloroisopropenylbenzene	68	7.20 (m, 4, arom), 5.24 (s, 1, =CH), 5.00 (s, 1, =CH), 2.05 (s, 3, $-CH_3$)
15	*p*-bromophenyl	ethyl	A	Me_2SO	*p*-bromoisopropenylbenzene	78	7.34 (d, 2, J = 9 Hz, arom), 7.20 (d, 2, J = 9 Hz, arom), 5.28 (s, 1, =CH), 5.02 (s, 1, =CH), 2.07 (s, 3, $-CH_3$)
16	*p*-methylphenyl	ethyl	B	Me_2SO	*p*-methylisopropenylbenzene	91	7.27 (d, 2, J = 8 Hz, arom), 7.01 (d, 2, J = 8 Hz, arom), 5.31 (s, 1, =CH), 5.01 (s, 1, =CH), 2.31 (s, 3, $-CH_3$), 2.14 (s, 3, $-CH_3$)
17	*p*-methoxyphenyl	methyl	B	benzene	*p*-methoxyisopropenylbenzene	83[a]	7.27 (d, 2, J = 9 Hz, arom), 6.71 (d, 2, J = 9 Hz, arom), 5.25 (s, 1, =CH), 4.92 (s, 1, =CH), 3.62 (s, 3, $-OCH_3$), 2.10 (s, 3, $-CH_3$)
18	*m*-methoxyphenyl	ethyl	A	Me_2SO	*m*-methoxyisopropenylbenzene	73	7.24–6.68 (m, 4, arom), 5.29 (s, 1, =CH), 5.03 (s, 1, =CH), 3.75 (s, 3, $-OCH_3$), 2.13 (s, 3, $-CH_3$)
19	*o*-methoxyphenyl	ethyl	B	Me_2SO	*o*-methoxyisopropenylbenzene	78	7.18–6.68 (m, 4, arom), 5.12 (s, 1, =CH), 5.04 (s, 1, =CH), 3.81 (s, 3, $-OCH_3$), 2.15 (s, 3, $-CH_3$)
20	*p*-(dimethylamino)phenyl	ethyl	C	Me_2SO	*p*-(dimethylamino)isopropenylbenzene	66	7.31 (d, 2, J = 8 Hz, arom), 6.61 (d, 2, J = 8 Hz, arom), 5.24 (s, 1, =CH), 4.89 (s, 1, =CH), 2.92 (s, 6, $-NCH_3$), 2.12 (s, 3, $-CH_3$)
21	*m*-(dimethylamino)phenyl	methyl	C	benzene	*m*-(dimethylamino)isopropenylbenzene	60[b]	7.27–6.56 (m, 4, arom), 5.33 (s, 1, =CH), 5.01 (s, 1, =CH), 2.84 (s, 6, $-NCH_3$), 2.12 (s, 3, $-CH_3$)
22	2-naphthyl	ethyl	A	Me_2SO	2-isopropenylnaphthalene	80[c]	7.82–7.34 (m, 7, arom), 5.47 (s, 1, =CH), 5.13 (s, 1, =CH), 2.22 (s, 3, $-CH_3$)
23	3-pyridyl	methyl	A	Me_2SO	3-isopropenylpyridine	60	8.56–7.13 (m, 4, arom), 5.38 (s, 1, =CH), 5.14 (s, 1, =CH), 2.20 (s, 3, $-CH_3$)
24	4-pyridyl	ethyl	A	Me_2SO		0[d]	
25	2-thienyl	ethyl	A	Me_2SO	2-isopropenylthiophene	71	7.19–6.87 (m, 3, arom), 5.36 (s, 1, =CH), 4.92 (s, 1, =CH), 2.15 (s, 3, $-CH_3$)
26	terephthalyl	dimethyl	B	Me_2SO	*p*-diisopropenylbenzene	50	7.40 (m, 4, arom), 5.37 (s, 2, =CH), 5.06 (s, 2, =CH), 2.05 (s, 6, $-CH_3$)
27	*trans*-cinnamyl	ethyl	A	Me_2SO	(*E*)-1-phenyl-3-methylbutadiene	52	6.03 (m, 5, arom), 5.68 (d, 1, J = 16 Hz, =CH–), 5.33 (d, 1, J = 16 Hz, =CH–), 4.19 (s, 1, =CH), 4.16 (s, 1, =CH), 1.60 (s, 3, $-CH_3$)

28	2-benzo[*b*]furyl	ethyl	B	Me_2SO	2-isopropenylbenzo[*b*]furan	28[e]	7.53-7.10 (m, 4, arom), 6.25 (s, 1, arom), 5.07 (s, 1, =CH), 4.90 (s, 1, =CH), 2.21 (s, 3, $-CH_3$)
29	phenylmethyl	neopentyl	B	Me_2SO	2-methyl-3-phenylpropene	71[f]	7.22 (m, 5, arom), 4.81 (s, 1, =CH), 4.75 (s, 1, =CH), 3.34 (s, 2, $-CH_2-$), 1.70 (s, 3, $-CH_3$)
30	cyclohexylmethyl	ethyl	B	THF	2-methyl-3-cyclohexylpropene	77	4.64 (m, 1, =CH), 4.57 (m, 1, =CH), 1.86 (d, 2, J = 7 Hz, $-CH_2-$), 1.76-0.75 (m, 7, $-CH_2-$), 1.64 (s, 3, $-CH_3$)
31	3-cyclohexenyl	methyl	B	benzene	4-isopropenylcyclohexene	55	5.57 (s, 2, =CH-), 4.59 (s, 2, $=CH_2$), 1.95 (m, 7, $-CH_2-$), 1.63 (s, 3, $-CH_3$)
32	*n*-(9-decenyl)	methyl	B	THF	2-methyl-1,12-dodecadiene	84	6.04-5.64 (m, 1, =CH-), 5.10-4.91 (m, 2, $=CH_2$), 4.68 (s, 2, $=CH_2$), 2.05 (t, 4, J = 7 Hz, $-CH_2-$), 1.74 (s, 3, $-CH_3$), 1.39 (m, 12, $-CH_2-$)
33	*n*-octyl	methyl	B	HMPA	2-methyl-1-decene	75	4.64 (s, 2, $=CH_2$), 2.00 (t, 2, J = 7 Hz, $-CH_2-$), 1.70 (s, 3, $-CH_3$), 1.32 (m, 12, $-CH_2-$), 0.88 (t, 3, J = 7 Hz, $-CH_3$)
34	4-ketocyclohexyl	methyl	B (5 equiv)	THF		78	4.65 (s, 2, $=CH_2$), 4.59 (s, 2, $=CH_2$), 2.45-1.75 (m, 9, $-CH_2-$), 1.68 (s, 3, $-CH_3$)
35	4-ketocyclohexyl trimethylenedithio acetal	methyl	B	THF		77	4.68 (s, 2, $=CH_2$), 2.88-2.62 (m, 4, $-SCH_2-$), 2.34 (m, 1, -CH), 2.08-1.53 (m, 10, $-CH_2-$), 1.68 (s, 3, $-CH_3$)
36	4-ketocyclohexyl ethylene acetal	methyl	B	THF		70	4.72 (s, 2, $=CH_2$), 3.91 (s, 4, $-OCH_2-$), 1.94-1.53 (m, 9, $-CH_2-$), 1.71 (s, 3, $-CH_3$)
37	4-(2′-tetrahydrofuranoxy)cyclohexyl	methyl	B	THF		55	5.29 (m, 1, $-OCH_2O-$), 4.67 (s, 2, $=CH_2$), 3.87 (m, 2, $-OCH_2-$), 3.51 (m, 1, -OCH-), 2.09-1.45 (m, 9, $-CH_2-$), 1.70 (s, 3, $-CH_3$)
38	4-ketocyclohexyl *p*-tosylhydrazone	methyl	B	THF		54	4.74 (s, 2, $=CH_2$), 2.34 (m, 4, $-CH_2-$), 2.18-1.43 (m, 5, $-CH_2$, -CH-), 1.72 (s, 3, $-CH_3$)
39	phenyl	2′-tetrahydro-furanyl[g]	B	Me_2SO	isopropenylbenzene	50	see entry 1
40	diphenylmethyl	methyl	B	benzene	2-methyl-3,3-diphenylpropene	51	7.23 (m, 10, arom), 5.04 (s, 1, -CH-), 4.70 (s, 1, =CH), 4.50 (s, 1, =CH), 1.90 (s, 3, $-CH_3$)

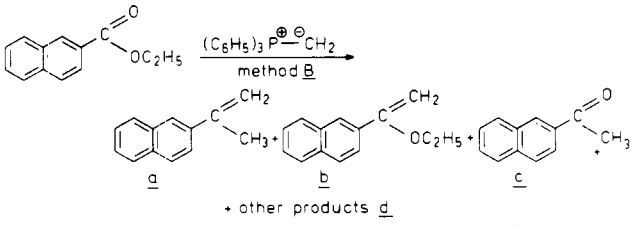
[a] And 3% α-methoxy-*p*-methoxystyrene. [b] The formed precipitate contained, apart from triphenylphosphine oxide, some *m*-(dimethylamino)benzoylmethylenetriphenylphosphorane. [c] And 8% 1-(2′-naphthyl)-1-ethoxyethene. [d] Only a 35% yield of 1-(4′-pyridyl)-1-ethoxyethene was obtained: NMR ($CDCl_3$) δ 8.45 (m, 2, arom), 7.41 (d, 2, J = 4 Hz, arom), 4.80 (d, 1, J = 3 Hz, =CH), 4.33 (d, 1, J = 3 Hz, =CH), 3.90 (q, 2, J = 7 Hz, $-OCH_2-$), 1.45 (t, 3, J = 7 Hz, $-CH_3$). [e] In addition a 42% yield of 1-(2′-benzofuryl)-1-ethoxyethene was obtained: NMR ($CDCl_3$) δ 7.53-7.10 (m, 4, arom), 6.88 (s, 1, arom), 5.00 (d, 1, J = 3 Hz, =CH), 4.30 (d, 1, J = 3 Hz, =CH), 3.80 (q, 2, J = 7 Hz, $-OCH_2-$), 1.30 (t, 3, J = 7 Hz, $-CH_3$). [f] In addition an 8% yield of benzyl methyl ketone was obtained: NMR ($CDCl_3$) δ 7.22 (m, 5, arom), 3.69 (s, 2, $-CH_2-$), 2.18 (s, 3, $-CH_3$). Heating of the isopropenyl compound formed gave isomerization to β,β-dimethylstyrene: NMR ($CDCl_3$) δ 7.22 (m, 5, arom), 6.27 (s, 1, =CH-), 1.94 (s, 3, $-CH_2$), 1.89 (s, 3, $-CH_2$). [g] Ester synthesized as described in the thesis of C. G. Kruse, Leiden, 1978.

Table II. Reaction of Aliphatic Diesters with Methylenetriphenylphosphorane



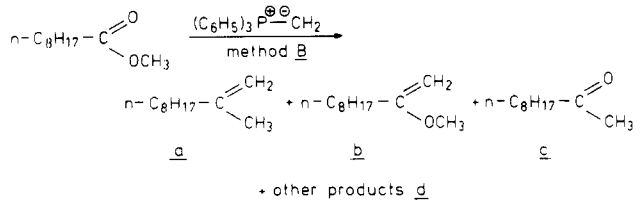
n	R_2	solvent	method	% yield	NMR δ ($CDCl_3$)
2	ethyl	THF	B	13	4.76 (s, 4, $=CH_2$), 2.40 (m, 4, $-CH_2-$), 1.80 (s, 6, $-CH_3$)
3	ethyl	benzene	B	15	4.70 (s, 4, $=CH_2$), 1.98 (t, 4, J = 7 Hz, $-CH_2-$), 1.69 (s, 6, $-CH_3$), 1.39 (t, 2, J = 7 Hz, $-CH_2-$)
4	ethyl	benzene	B	75	4.60, (s, 4, $=CH_2$), 2.00 (t, 4, J = 7 Hz, $-CH_2$), 1.64 (s, 6, $-CH_3$), 1.40 (m, 4, $-CH_2-$)
5	ethyl	THF	B	63	4.66 (s, 4, $=CH_2$), 2.00 (t, 4, J = 7 Hz, $-CH_2-$), 1.68 (s, 6, $-CH_3$), 1.36 (m, 6, $-CH_2-$)
10	methyl	benzene	B	81	4.60 (s, 4, $=CH_2$), 2.02 (t, 4, J = 7 Hz, $-CH_2-$), 1.64 (s, 6, $-CH_3$), 1.24 (m, 16, $-CH_2-$)

Table III. Reaction of Ethyl 2-Naphthoate with Methylenetriphenylphosphorane in Several Solvents



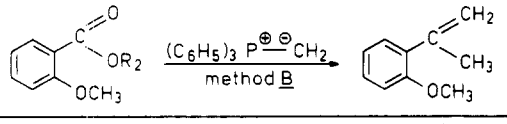
solvent	% yield	% product distribution a	b	c	d
benzene	93	63	21		16
THF	82	61	31	5	3
Me_2SO	88	89	11		
HMPA	91	59	41		

Table IV. Reaction of Methyl n-Nonanoate with Methylenetriphenylphosphorane in Several Solvents



solvent	% yield	% product distribution a	b	c	d
benzene	77	91	9		
THF	76	93	7		
Me_2SO	50	100			
HMPA	75	100			

Table V. Reaction of Various o-Methoxybenzoates with Methylenetriphenylphosphorane



R_2	% yield	reaction time, h[a]
methyl	64	1
ethyl	78	2
isopropyl	75	44
tert-butyl	0	44
neopentyl	85	20

[a] Reaction times are based on complete conversion of starting ester (analytical GC).

results obtained with 9-(ethoxycarbonyl)nonylidenetriphenylphosphorane. Best yields of the desired diethyl 10-substituted 9-nonadecene-1,19-dicarboxylate were obtained when the ylide was prepared in the presence of the ester. This was conveniently achieved by stirring the suspended phosphonium salt in dry HMPA of THF with 1 equiv of sodium hydride[21] and a trace of potassium hydride.[22] The choice of methyl esters is of particular importance here, because they react appreciably faster than the ethyl ester groups in ylide and reaction product. The formation of appreciable amounts of enol ether in the case of ethyl formate is not unexpected.[6]

Reaction of esters with the ylide from 5-(triphenylphosphonio)pentanoic acid (2 equiv of sodium hydride), a much used reagent in prostaglandin synthesis,[18] gives rise to the formation of 5-substituted 4-nonene-1,9-dicarboxylic acids, which can only be extracted from the reaction mixture with great difficulty. Reaction of the disodium dicarboxylates in situ with an excess of methyl iodide, however, provides the dimethyl esters in good yields. Best results were obtained in a solvent mixture of equal volumes of Me_2SO and THF.

Finally, Table XII shows the results obtained with 3-(2-methyl-1,3-dioxan-2-yl)propylidenetriphenylphosphorane. The ylide was prepared by both known methods.[19,20] Only moderate yields of 6-substituted 5-undecene-2,10-dione bis(ethylene acetals) were obtained, probably because of the presence of significant amounts of unprotected ketone in the starting phosphonium salts, even when these had been prepared with great care.

In summary, it can be said that in most cases, by the appropriate choice of reaction conditions, the reaction between esters and nonstabilized phosphoranes provides an excellent route for the direct conversion of these esters into branched olefins. Additional advantages of this method are that, contrary to e.g. a two-step conversion via Grignard addition and dehydration, acidic reaction conditions can be avoided and the double bond is formed specifically at the position of the ester carbonyl group.

Experimental Section

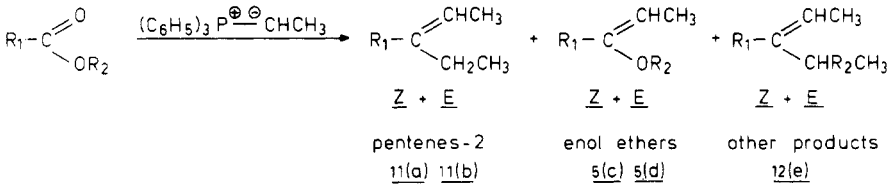
GC analyses were run on a Hewlett-Packard 402 gas chromatograph equipped with a flame ionization detector using a 2 m, 3% SE-30, Gaschrom Q 80–100 column. Preparative GC was carried out using a Varian 920 gas chromatograph equipped with

(20) J. A. Findlay, W. D. McKay, and W. S. Bowers, *J. Chem. Soc. C*, 2631 (1970).

(21) Sodium hydride was used as a 60% dispersion in oil and washed three times with dry n-pentane before use.

(22) Potassium hydride was used as a 24.4% dispersion in oil and was washed three times with dry n-pentane before use.

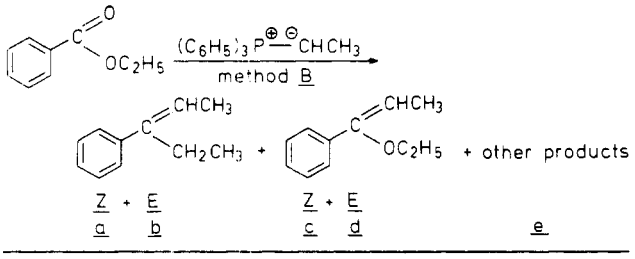
Table VI. Reaction of Esters with Ethylidenetriphenylphosphorane[a]



compd	R_1	R_2	method	% yield[b]	% product distribution: 2-pentenes total	2-pentenes Z(a)	2-pentenes E(b)	enol ethers Z(c) + E(d)	side products (e)
41	phenyl	methyl	A	58	99	77	22	1	
42	phenyl	ethyl	A	93	72	58	14	17	11
43	phenyl	isopropyl	A	83	86	69	17	6	8
44	*o*-methoxyphenyl	methyl	A	82	98	92	6	3	
45	*o*-methoxyphenyl	ethyl	A	90	89	84	5	6	5
46	*p*-methoxyphenyl	methyl	A	74	100	76	24		
47	*p*-methoxyphenyl	ethyl	A	92	88	69	19	10	2
48	*p*-bromophenyl	methyl	A	83	100	69	31		
49	*p*-bromophenyl	ethyl	A	83	63	42	21	27	10
50	3-pyridyl	methyl	A	72	92	62	30	4	
51	3-pyridyl	ethyl	A	78	69	49	20	21	10
52	4-pyridyl	methyl	A	81	97	64	33	3	
53	4-pyridyl	ethyl	A	78	67	45	22	26	7
54	*n*-nonyl	methyl	B	71	100				
55	*n*-9-decenyl	methyl	B	63	100				

[a] The NMR data are reported in Table XIII. [b] The total yield was obtained as the sum of the yields of the identified constituents.

Table VII. Reaction of Ethyl Benzoate with Ethylidenetriphenylphosphorane in Several Solvents



solvent	% yield[a]	% product distribution: a + b	a	b	c + d	e
benzene	96	83	71	12	17	
THF	77	73	57	16	20	7
Me_2SO	68	77	61	16	20	4
HMPA	89	29	23	6	65	5
tert-butyl alcohol	36[b]	100	57	43		

[a] The total yield was obtained as the sum of the yields of the identified constituents. [b] Also, 31% of *tert*-butyl benzoate was formed.

a thermal conductivity detector using a 6 m, 20% SE-30, Chromosorb W 60–80 column.

Proton magnetic resonance spectra were recorded on a Jeol-100 PFT spectrometer. Chemical shifts are reported in parts per million on the scale relative to tetramethylsilane as internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constants, and interpretation.

Mass spectral data were obtained with an AEI-MS 902 apparatus, ionization potential 70 eV. A "dry solvent" refers to solvents distilled from calcium hydride (DMF,[15] Me_2SO, HMPA), from lithium aluminum hydride (THF), or from potassium *tert*-butoxide (*tert*-butyl alcohol) or dried over sodium wire (benzene, diethyl ether, *n*-pentane).

The term "standard workup conditions" refers to the following product isolation procedure: pouring the reaction mixture onto a threefold quantity of an equal mixture of crushed ice and *n*-pentane, stirring overnight, filtration of the precipitate, separation of the *n*-pentane layer and extraction of the water/solvent layer twice with a 0.5-fold quantity of *n*-pentane, treatment of the combined *n*-pentane layers with anhydrous magnesium sulfate, filtration, solvent removal under reduced pressure and subjection of the resulting oil to short path distillation. The distillate was analyzed by NMR and analytical GC (product distribution). The reaction products were isolated by preparative GC and identified by analysis of their spectra, in particular NMR.

Method A. A dry, nitrogen-purged, 250-mL, three-neck, round-bottom flask, fitted with addition funnel, magnetic stirrer, and nitrogen system, was charged with 2.4 g of sodium hydride[21] and 35 mL of dry Me_2SO to prepare a dimethyl sulfoxide anion solution.[23] After stirring for 1 h at 70–80 °C the flask was cooled to room temperature and a solution of methyltriphenylphosphonium iodide (32.2 g, 0.08 mol) in 70 mL of dry Me_2SO was added over a 30-min period. Stirring was continued for 30 min. To this ylide solution the required ester (0.02 mol) was added in one portion at room temperature. Stirring was continued until no more starting ester was present (about 2 h as indicated by analytical GC). The reaction mixture was subjected to workup under standard conditions.

Method B.[10] To a dry, nitrogen-purged, 250-mL, round-bottom flask fitted with stopper and magnetic stirrer and charged with the required "salt-free" ylide[9] (0.04 mmol) in 100 mL of the indicated dry solvent, about 0.01 mol of the required ester was added in one portion at room temperature and the resulting mixture was stirred until all starting material had disappeared (about 2 h as indicated by analytical GC). The reaction mixture was subjected to workup under standard conditions.

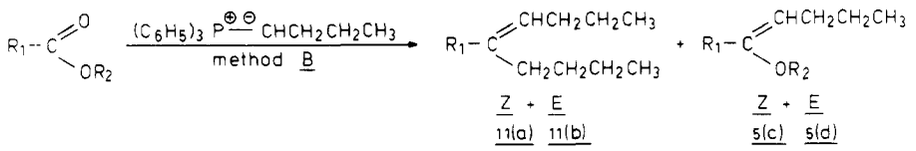
Method C.[10] Identical with method B, only the "salt-free" ylide solution[9] was heated to 50 °C, the required ester was added at this temperature, and stirring was continued at 50 °C until disappearance of the ester was indicated by GC.

9-(Ethoxycarbonyl)nonyltriphenylphosphonium Iodide. Ethyl 10-chlorodecanoate[24] was converted into ethyl 10-iododecanoate in 96% yield by refluxing with an equimolar quantity of sodium iodide in 2-butanone: bp 115–118 °C (0.02 mm). Refluxing the iodide with an equimolar quantity of triphenylphosphine in benzene for 24 h provided the title compound in 80% yield: mp 81–83 °C; NNR ($CDCl_3$) δ 7.78 (m, 15, arom), 4.08

(23) R Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(24) Generous gift from Naarden International N.V.

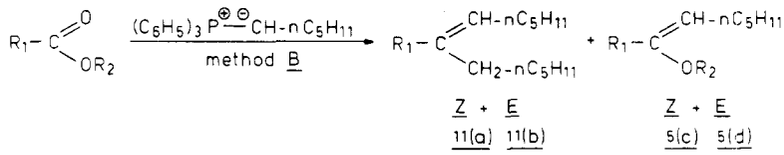
Table VIII.[a] Reaction of Esters with *n*-Butylidenetriphenylphosphorane



compd	R_1	R_2	solvent	% yield[b]	% product distribution			
					Z (a)	*E* (b)	*Z* (c)	*E* (d)
56	phenyl	methyl	Me_2SO	84	77	9	11	3
56	phenyl	methyl	benzene	53	20	5	56	19
57	H	ethyl	Me_2SO	47	80		7	13
57	H	ethyl	benzene	53	59		12	29
58	methyl	ethyl	Me_2SO	72	44	56		
59	*n*-octyl	methyl	Me_2SO	80	84		16	
59	n-octyl	methyl	Me_2SO[c]	71	100			

[a] The NMR data are reported in the Experimental Section. [b] The total yield was obtained as the sum of the yields of the identified constituents.

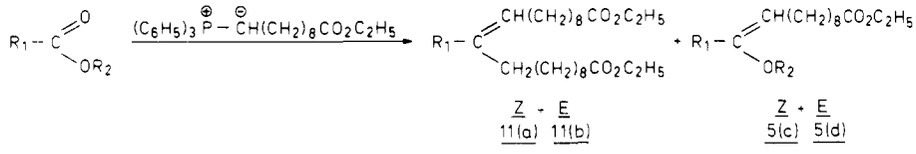
Table IX.[a] Reaction of Esters with *n*-Hexylidenetriphenylphosphorane



compd	R_1	R_2	method	% yield[b]	% product distribution			
					Z (a)	*E* (b)	*Z* (c)	*E* (d)
60	phenyl	methyl	A	81	95	5		
61	H	ethyl	B	83	84		7	9

[a] NMR data are reported in the Experimental Section. [b] The total yield was obtained as the sum of the yields of the identified constituents.

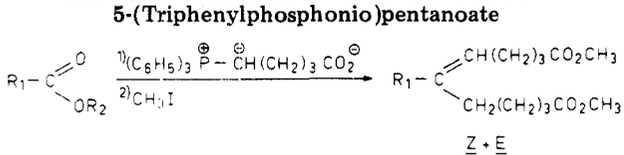
Table X.[a] Reaction of Esters with 9-(Ethoxycarbonyl)nonylidenetriphenylphosphorane



compd	R_1	R_2	solvent	% yield[b]	% product distribution			
					olefins		enol ethers	
					Z (a)	*E* (b)	*Z* (c)	*E* (d)
62	phenyl	methyl	THF	72	100	0		
62	phenyl	methyl	HMPA	50	90	10		
63	H	ethyl	THF	44	14		49	37
63	H	ethyl	HMPA	84	63		21	16

[a] The NMR data are reported in the Experimental Section. [b] The total yield was obtained as the sum of the yields of the identified constituents.

Table XI.[a] Reaction of Esters with Sodium 5-(Triphenylphosphonio)pentanoate



compd	R_1	R_2	% yield	% product distribution	
				Z (a)	*E* (b)
64	phenyl	methyl	83	36	64
65	H	ethyl	21	100	
66	9-decenyl	methyl	74	100	

[a] The NMR-data are reported in the experimental section.

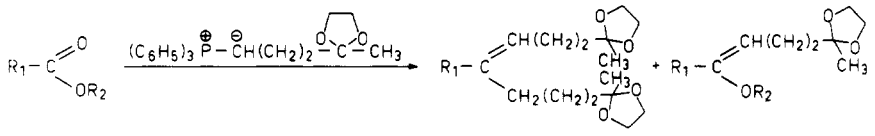
(q, 2, J = 7 Hz, $-CH_2O-$), 3.60 (m, 2, $-CH_2P-$), 2.26 (t, 2, J = 7 Hz, $-CH_2-$), 1.64 (m, 4, $-CH_2-$), 1.24 (m, 13, $-CH_2-$, $-CH_3$).

Reaction of Esters with 9-(Ethoxycarbonyl)-nonylidenetriphenylphosphorane (see Table X). To a dry, nitrogen-purged, 250-mL, round-bottom flask, equipped with a magnetic stirrer and a nitrogen filled balloon at the top, was added 1.60 g (0.04 mol) of sodium hydride[21] and a trace of potassium hydride,[22] 100 mL of the desired dry solvent, and 23.5 g (0.04 mol) of 9-(ethoxycarbonyl)nonyltriphenylphosphonium iodide. This suspension was stirred at room temperature for 48 h. The reaction mixture was worked up by standard procedures.

Diethyl (*Z*)-10-phenyl-9-nonadecene-1,19-dicarboxylate (62a): NMR ($CDCl_3$) δ 7.22 (m, 5, arom), 5.40 (t, 1, J = 7 Hz, $=CH-$), 4.08 (q, 4, J = 7 Hz, $-OCH_2-$), 2.24 (t, 4, J = 7 Hz, $-CH_2-$), 1.90 (m, 4, $-CH_2-$), 1.59 (m, 4, $-CH_2-$), 1.24 (m, 28, $-CH_2-$, $-CH_3$); ^{13}C NMR ($CDCl_3$) arom δ 141.1 (C_1), 127.9 (C_2), 128.4 (C_3), 127.2 (C_4), olefin δ 141.7–126.2, carbonyl δ 173.5, $-OC-$ δ 60.0, $-CH_3$ δ 14.3, side chains δ 34.4 (C_1), 25.1 (C_2), 28.8, 29.2, 29.4 ($-CH_2-$), allyl $-CH_2-$ δ 30.1, 39.4; M_w = 486.3685; $C_{31}H_{50}O_4$ = 486.3709.

Diethyl (*E*)-10-phenyl-9-nonadecene-1,19-dicarboxylate (62b): NMR ($CDCl_3$) δ 7.22 (m, 5, arom), 5.62 (t, 1, J = 7 Hz, $=CH-$), 4.08 (q, 4, J = 7 Hz, $-OCH_2-$), 2.24 (t, 4, J = 7 Hz, $-CH_2-$),

Table XII.[a] Reaction of Esters with 3-(2-Methyl-1,3-dioxalan-2-yl)propylidenetriphenylphosphorane



Z + E 11(a) 11(b) Z + E 5(c) 5(d)

compd	R_1	R_2	method	solvent	% yield[b]	product distribution in %: olefins Z (a)	olefins E (d)	enol ethers Z (c)	enol ethers Z (d)
67	phenyl	methyl	B	Me_2SO	48	51	33	16	
68	*p*-methylphenyl	methyl	A	Me_2SO/THF (1/1)	66	86	14		
69	H	ethyl	B	Me_2SO	30	60		20	20
69	H	ethyl	B	benzene	53	42		33	25
70	*n*-9-decenyl	methyl	B	Me_2SO/THF (1/1)	44	99		1	

[a] The NMR data are reported in the Experimental Section. [b] The total yield was obtained as the sum of the yields of the identified constituents.

1.90 (m, 4, $-CH_2-$), 1.59 (m, 4, $-CH_2-$), 1.24 (m, 28, $-CH_2-$, $-CH_3$).

Diethyl 9-nonadecene-1,19-dicarboxylate (63a, 63b): NMR ($CDCl_3$) δ 5.35 (t, 2, J = 7 Hz, =CH–), 4.13 (q, 4, J = 7 Hz, $-CH_2O-$), 2.31 (t, 4, J = 7 Hz, $-CH_2-$), 2.05 (m, 4, $-CH_2-$), 1.64 (m, 4, $-CH_2-$), 1.26 (m, 28, $-CH_2-$, $-CH_3$); M_w = 410.3398; $C_{25}H_{46}O_4$ = 410.3395.

Ethyl (*Z*)-10-ethoxy-9-decene-1-carboxylate (63c): NMR ($CDCl_3$) δ 5.88 (d, 1, J = 7 Hz, =CH–), 4.30 (d of t, 1, J = 7, 7 Hz, =CH–), 4.10 (q, 2, J = 7 Hz, $-CH_2O-$), 3.74 (q, 2, J = 7 Hz, $-OCH_2-$), 2.27 (t, 2, J = 7 Hz, $-CH_2-$), 2.02 (m, 2, $-CH_2-$), 1.61 (m, 2, $-CH_2-$), 1.26 (m, 16, $-CH_2-$, $-CH_3$).

Ethyl (*E*)-10-ethoxy-9-decene-1-carboxylate (63d): NMR ($CDCl_3$) δ 6.18 (d, 1, J = 12 Hz, =CH–), 4.72 (d of t, 1, J = 7, 12 Hz, =CH–), 4.10 (q, 2, J = 7 Hz, $-CH_2O-$), 3.67 (q, 2, J = 7 Hz, $-OCH_2-$), 2.27 (t, 2, J = 7 Hz, $-CH_2-$), 2.02 (m, 2, $-CH_2-$), 1.61 (m, 2, $-CH_2-$), 1.26 (m, 16, $-CH_2-$, $-CH_3$).

5-(Triphenylphosphonio)pentanoic Acid Iodide. 5-Bromopentanoic acid was refluxed with an equimolar quantity of sodium iodide in 2-butanone. Filtration of the precipitated sodium bromide and evaporation of the solvent provided a brown solid. This solid was dissolved in benzene and the rest of the sodium bromide was filtered off. The benzene solution was dried ($MgSO_4$) and filtered and an equimolar quantity of triphenylphosphine was added. The resulting solution was refluxed for 48 h. The precipitate was filtered off. A 90% yield of the title compound was obtained: white crystals; mp 167–170 °C; NMR ($CDCl_3$) δ 10.47 (s, 1, –OH), 7.72 (m, 15, arom), 3.62 (m, 2, $-CH_2P-$), 2.48 (t, 2, J = 7 Hz, $-CH_2-$), 1.90 (m, 4, $-CH_2-$).

Reaction of Esters with Sodium 5-(Triphenylphosphonio)pentanoate (see Table XI). To a dry, nitrogen-purged, 250-mL, three-neck, round-bottom flask, equipped with a nitrogen system and a magnetic stirrer, 2.80 g (0.07 mol) of sodium hydride[21] and 50 mL of dry Me_2SO were added. The solution was stirred for 2 h at 60–70 °C to obtain a dimethyl sulfoxide anion solution.[23] The solution was cooled to room temperature and 50 mL of dry THF was added. In one portion 19.6 g (0.04 mol) of (triphenylphosphonio)pentanoic acid iodide was added. Stirring was continued for 1 h. To this solution 0.01 mol of the desired ester was added in one portion. Stirring was continued for 47 h. Neutralization of this solution with dilute acid and workup according to the standard procedure yielded the dicarboxylic acid in low yields. Addition of an excess of methyl iodide (14.2 g; 0.10 mol) instead of neutralization and additional stirring for 20 h yielded, after the standard workup procedure, the corresponding dimethyl dicarboxylates.

(*Z*)-5-Phenyl-4-nonene-1,9-dicarboxylic acid: NMR ($CDCl_3$) δ 10.92 (s, 2, –OH), 7.24 (m, 5, arom), 5.41 (t, 1, J = 7 Hz, =CH–), 2.32 (m, 8, $-CH_2-$), 1.76 (m, 6, $-CH_2-$); ^{13}C NMR ($CDCl_3$) arom δ 140.7 (C_1), 128.0 (C_2), 128.1 (C_3), 127.8 (C_4), olefin δ 142.7–126.2, C=O δ 179.1, $-CH_2-$, C_3 piece δ 33.9 (C_1), 24.8 (C_2), C_4 piece δ 33.5 (C_1), 24.5 (C_2), 27.8 (C_3), allyl $-CH_2-$ δ 28.0–38.8.

(*E*)-5-Phenyl-4-nonene-1,9-dicarboxylic acid: NMR ($CDCl_3$) δ 10.92 (s, 2, –OH), 7.24 (m, 5, arom), 5.61 (t, 1, J = 7 Hz, =CH–), 2.32 (m, 8, $-CH_2-$), 1.76 (m, 6, $-CH_2-$); ^{13}C NMR ($CDCl_3$) identical to *Z* isomer, except allyl $-CH_2-$ δ 28.0 and 29.2.

4-Nonene-1,9-dicarboxylic acid: NMR ($CDCl_3$) δ 9.64 (s, 2, –OH), 5.37 (t, 2, J = 7 Hz, =CH–), 2.29 (t, 4, J = 7 Hz, $-CH_2-$), 2.02 (m, 4, $-CH_2-$), 1.65 (m, 6, $-CH_2-$).

Dimethyl (*Z*)-5-phenyl-4-nonene-1,9-dicarboxylate (64a): NMR ($CDCl_3$) δ 7.25 (m, 5, arom), 5.38 (t, 1, J = 7 Hz, =CH–), δ 3.62 (s, 3, $-OCH_3$), 3.56 (s, 3, $-OCH_3$), 2.26 (m, 8, $-CH_2-$), 1.68 (m, 6, $-CH_2-$); ^{13}C NMR ($CDCl_3$) arom δ 140.8 (C_1), 128.1 (C_2), 128.3 (C_3), 129.7 (C_4), olefin δ 141.7 and 126.3, C=O δ 173.5, $-OCH_3$ δ 51.1, $-CH_2-$, C_3 piece δ 33.8 (C_1), 27.5 (C_2), C_4 piece δ 33.4 (C_1), 25.2 (C_2), 28.3 (C_3), allyl $-CH_2-$ δ 29.8 and 39.0; M_w = 318.1825; $C_{19}H_{26}O_4$ = 318.1831.

Dimethyl (*E*)-5-phenyl-4-nonene-1,9-dicarboxylate (64b): NMR ($CDCl_3$) δ 7.25 (m, 5, arom), 5.60 (t, 1, J = 7 Hz, =CH–), 3.62 (s, 3, $-OCH_3$), 3.56 (s, 3, $-OCH_3$), 2.26 (m, 8, $-CH_2-$), 1.68 (m, 6, $-CH_2-$); ^{13}C NMR ($CDCl_3$) identical to *Z* isomer, except allyl $-CH_2-$ δ 29.8, 29.4.

Dimethyl 4-nonene-1,9-dicarboxylate (65): NMR ($CDCl_3$) δ 5.37 (t, 2, J = 7 Hz, =CH–), 3.60 (s, 3, $-OCH_3$), 2.31 (t, 4, J = 7 Hz, $-CH_2-$), 2.02 (m, 4, $-CH_2-$), 1.65 (m, 6, $-CH_2-$).

Dimethyl 5-(9′-decenyl)-4-nonene-1,9-dicarboxylate (66): NMR ($CDCl_3$) δ 5.82 (m, 1, =CH–), 5.09–4.87 (m, 3, $=CH_2$, =CH–), 3.58 (s, 6, $-OCH_3$), 2.29 (t, 4, J = 7 Hz, $-CH_2-$), 1.98 (m, 8, $-CH_2-$), 1.64–1.24 (m, 18, $-CH_2-$); M_w = 380.2921; $C_{23}H_{40}O_4$ = 380.2927.

3-(2-Methyl-1,3-dioxolan-2-yl)propyltriphenylphosphonium Iodide. α-Acetyl-γ-butyrolactone was converted into 5-chloro-2-pentanone according to a known procedure[25] in 61% yield. The chloride was converted in 80% yield into 5-iodo-2-pentanone (potassium iodide in 2-butanone).[19,20] This ketone was converted into its ethylene acetal in 76% yield according to literature procedures.[19,20] The use of a water separator was found to improve the yield of acetal considerably. The phosphonium salt was obtained according to a literature procedure in 94% yield.[19,20] Despite the use of dry reagents, this salt was found to contain varying amounts of the phosphonium salt of the unprotected ketone:[26] mp 167–170 °C; NMR ($CDCl_3$) δ 7.80 (m, 15, arom), 3.86 (s, 4, $-OCH_2-$), 3.72 (m, 2, $-CH_2P-$), 2.02 (m, 2, $-CH_2-$), 1.76 (m, 2, $-CH_2-$), 1.21 (s, 3, $-CH_3$).

Reaction of Esters with 3-(2-methyl-1,3-dioxolan-2-yl)-propylidenetriphenylphosphorane (see Table XII). The ylide was prepared salt free according to a literature procedure (sodium amide in liquid ammonia).[19,20]

(*Z*)-6-Phenyl-5-undecene-2,10-dione bis(ethylene acetal) (67a): NMR ($CDCl_3$) δ 7.25 (m, 5, arom), 5.45 (t, 1, J = 7 Hz, =CH–), 3.75 (s, 8, $-OCH_3$), 2.29 (m, 4, $-CH_2-$), 1.63 (m, 6, $-CH_2-$), 1.19 (s, 6, $-CH_3$).

(25) G. W. Cannon, R. C. Ellis, and J. R. Leal, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 597.

(26) Detectable in the NMR spectrum by the methyl ketone signal at δ 2.19.

Table XIII. ^{1}H NMR Data of Branched Olefins 11 and Enol Ethers 6, Obtained by Reaction of Esters with Alkylidenetriphenylphosphoranes

no.	compd	chemical shifts δ (ppm) and coupling constants J (Hz)
		Branched Olefins
41a	(*Z*)-3-phenyl-2-pentene	7.39–7.02 (m, 5, arom), 5.49 (q, 1, J = 7, =CH-), 2.35 (q, 2, J = 7, -CH_2-), 1.55 (d, 3, J = 7, -CH_3), 0.94 (t, 3, J = 7, -CH_3)
41b	*E* isomer	7.32–7.12, 5.69, 2.52, 1.88, 0.98
44a	(*Z*)-3-(*o*-methoxyphenyl)-2-pentene[a]	7.33–6.84 (m, 4, arom), 5.59 (q, 1, J = 7, =CH-), 3.76 (s, 3, -OCH_3), 2.32 (q, 2, J = 7, -CH_2-), 1.45 (d, 3, J = 7, -CH_3), 0.94 (t, 3, J = 7, -CH_3)
44b	*E* isomer[b]	7.31–6.86, 5.45, 3.80, 2.50, 1.78, 0.87
46a	(*Z*)-3-(*p*-methoxyphenyl)-2-pentene	7.03 (d, 2, J = 8, arom), 6.48 (d, 2, J = 8, arom), 5.84 (q, 1, J = 7, =CH-), 3.76 (s, 3, -OCH_3), 2.33 (q, 2, J = 7, -CH_2-), 1.56 (d, 3, J = 7, -CH_3), 0.93 (t, 3, J = 7, -CH_3)
46b	*E* isomer	7.23, 6.79, 5.63, 3.77, 2.48, 1.76, 0.98
48a	(*Z*)-3-(*p*-bromophenyl)-2-pentene	7.42 (d, 2, J = 8, arom), 6.96 (d, 2, J = 8, arom), 5.52 (q, 1, J = 7, =CH-), 2.35 (q, 2, J = 7, -CH_2-), 1.53 (d, 3, J = 7, -CH_3), 0.95 (t, 3, J = 7, -CH_3)
48b	*E* isomer	7.39, 7.17, 5.70, 2.51, 1.80, 0.99
50a	(*Z*)-3-(3′-pyridyl)-2-pentene	8.38 (m, 2, arom), 7.45–7.13 (m, 2, arom), 5.57 (q, 1, J = 7, =CH-), 2.36 (q, 2, J = 7, -CH_2-), 1.52 (d, 3, J = 7, -CH_3), 0.93 (t, 3, J = 7, -CH_3)
50b	*E* isomer	8.55–7.09, (m, 4, arom), 5.70, 2.50, 1.80, 0.96
52a	(*Z*)-3-(4′-pyridyl)-2-pentene	8.51 (d, 2, J = 6, arom), 7.03 (d, 2, J = 6, arom), 5.57 (q, 1, J = 7, =CH-), 2.33 (q, 2, J = 7, -CH_2-), 1.53 (d, 3, J = 7, -CH_3), 0.92 (t, 3, J = 7, -CH_3)
52b	*E* isomer	8.46, 7.20, 5.92, 2.49, 1.79, 0.97
54a,b	(*Z*)- and (*E*)-3-ethyl-2-dodecene	5.14 (q, 1, J = 7, =CH-), 1.96 (m, 4, -CH_2-), 1.55 (d, 3, J = 7, -CH_3), 1.27 (m, 18, -CH_2), 0.94 (t, 3, J = 7, -CH_3), 0.88 (t, 3, J = 7, -CH_3)
55a,b	(*Z*)- and (*E*)-3-ethyl-2,12-tridecadiene	5.75 (m, 1, =CH-), 5.17–4.86 (m, 3, =CH_2, =CH-), 2.01 (m, 6, -CH_2), 1.55 (d, 3, J = 7, -CH_3), 1.29 (m, 12, -CH_2-), 0.95 (t, 3, J = 7, -CH_3)
56a	(*Z*)-5-phenyl-4-nonene	7.31–7.06 (m, 5, arom), 5.43 (t, 1, J = 7, =CH-), 2.36 (t, 2, J = 7, -CH_2-), 1.93 (d of t, 2, J = 7, -CH_2-), 1.31 (m, 6, -CH_2-), 0.83 (m, 6, -CH_3)
56b	*E* isomer	7.27, 5.62, 2.48, 2.18, 1.32, 0.99
57a	(*Z*)- and *E*-4-nonene	5.33 (t, 2, J = 4, =CH-), 2.13 (m, 4, -CH_2-), 1.36 (m, 6, -CH_2), 0.90 (t, 6, J = 7, -CH_3)
58a	(*Z*)-5-methyl-4-nonene	5.10 (t, 1, J = 7, =CH-), 1.93 (m, 4, -CH_2-), 1.58 (s, 3, -CH_3), 1.34 (m, 6, -CH_2-), 0.90 (t, 6, J = 7, -CH_3)
58b	*E* isomer	5.10, 1.93, 1.68, 1.34, 0.90
59a,b	(*Z*)- and (*E*)-5-*n*-butyl-4-tridecene	5.19 (t, 1, J = 7, =CH-), 1.99 (m, 6, -CH_2-), 1.31 (m, 18, -CH_2-), 0.93 (t, 9, J = 7, -CH_3)
60a	(*Z*)-7-phenyl-6-tridecene	7.16 (m, 5, arom), 5.43 (t, 1, J = 7, =CH-), 2.35 (m, 2, -CH_2-), 1.92 (d of t, J = 7, -CH_2-), 1.25 (m, 14, -CH_2-), 0.84 (t, 6, J = 7, -CH_3)
60b	*E* isomer	7.16, 5.64, 2.47, 2.18, 1.25, 0.84
61a,b	(*Z*)- and (*E*)-6-tridecene	5.36 (t, 2, J = 4, =CH-), 2.04 (m, 4, -CH_2-), 1.31 (m, 14, -CH_2-), 0.88 (t, 6, J = 7, -CH_3)
		Enol Ethers
42c	(*Z*)-1-phenyl-1-ethoxypropene	7.18–7.05 (m, 5, arom), 5.31 (q, 1, J = 7, =CH-), 3.67 (q, 2, J = 7, -OCH_2-), 1.79 (d, 3, J = 7, -CH_3), 1.26 (t, 3, J = 7, -CH_3)
43c	(*Z*)-1-phenyl-1-isopropoxypropene	7.47–7.21 (m, 5, arom), 5.31 (q, 1, J = 7, =CH-), 3.94 (sept, 1, J = 7, -CH), 1.78 (d, 3, J = 7, -CH_3), 1.19 (d, 6, J = 7, -CH_3)
44c	(*Z*)-1-(*o*-methoxyphenyl)-1-methoxypropene	7.31–6.81 (m, 4, arom), 5.05 (q, 1, J = 7, =CH-), 3.85 (s, 3, -OCH_3), 3.42 (s, 3, -OCH_3), 1.80 (d, 3, J = 7, -CH_3)
45c	(*Z*)-1-(*o*-methoxyphenyl)-1-ethoxypropene[c]	7.46–6.80 (m, 4, arom), 5.10 (q, 1, J = 7, =CH-), 3.78 (s, 3, -OCH_3), 3.78 (q, 2, J = 7, -OCH_2-), 1.79 (d, 3, J = 7, -CH_3), 1.28 (t, 3, J = 7, -CH_3)
45d	*E* isomer[d]	7.46–6.82, 4.87, 3.81, 3.97, 1.44, 1.20
47c	(*Z*)-1-(*p*-methoxyphenyl)-1-ethoxypropene	7.38 (d, 2, J = 8, arom), 6.81 (d, 2, J = 8, arom), 5.25 (q, 1, J = 7, =CH-), 3.85 (s, 3, -OCH_3), 3.70 (q, 2, J = 7, -OCH_2-), 1.79 (d, 3, J = 7, -CH_3), 1.28 (t, 3, J = 7, -CH_3)
49c	(*Z*)-1-(*p*-bromophenyl)-1-ethoxypropene	7.41 (d, 2, J = 8, arom), 7.23 (d, 2, J = 8, arom), 5.35 (q, 1, J = 7, =CH-), 3.65 (q, 2, J = 7, -OCH_2), 1.77 (d, 3, J = 7, -CH_3), 1.27 (t, 3, J = 7, -CH_3)
49d	*E* isomer	7.41, 6.89, 4.79, 3.74, 1.66, 1.31
50c	(*Z*)-1-(3′-pyridyl)-1-methoxypropene	8.64–7.09 (m, 4, arom), 5.42 (q, 1, J = 7, =CH-), 3.51 (s, 3, -OCH_3), 1.80 (d, 3, J = 7, -CH_3)

51c	(*Z*)-1-(3′-pyridyl)-1-ethoxypropene	3.72 (s, 1, arom), 8.50 (d, 1, *J* = 4, arom), 7.47 (d, 1, *J* = 8, arom), 7.27 (m, 1, arom), 5.47 (q, 1, *J* = 7, =CH–), 3.73 (q, 2, *J* = 7, $-OCH_2-$), 1.83 (d, 3, *J* = 7, $-CH_3$), 1.31 (t, 3, *J* = 7, $-CH_3$)
52c	(*Z*)-1-(4′-pyridyl)-1-methoxypropene	8.53 (m, 2, arom), 7.28 (m, 2, arom), 5.71 (q, 1, *J* = 7, =CH–), 3.57 (s, 3, $-OCH_3$), 1.85 (d, 3, *J* = 7, $-CH_3$)
53c	(*Z*)-1-(4′-pyridyl)-1-ethoxypropene	8.47 (d, 2, *J* = 6, arom), 7.26 (d, 2, *J* = 6, arom), 5.65 (q, 1, *J* = 7, =CH–), 3.68 (q, 2, *J* = 7, $-OCH_2-$) 1.81 (d, 3, *J* = 7, $-CH_3$), 1.29 (t, 3, *J* = 7, $-CH_3$)
56c	(*Z*)-1-phenyl-1-methoxy-1-pentene	7.48–7.22 (m, 5, arom), 5.32 (t, 1, *J* = 7, =CH–), 3.54 (s, 3, $-OCH_3$), 2.28 (d of t, 2, *J* = 7, $-CH_2-$), 1.46 (t of t, *J* = 7, and 7, $-CH_2-$), 1.00 (t, 3, *J* = 7, $-CH_3$)
56d	*E* isomer	7.48–7.22, 4.74, 3.60, 2.05, 1.46, 0.91
57c	(*Z*)-1-ethoxy-1-pentene	5.89 (d, 1, *J* = 7, =CH–), 4.34 (d of t, *J* = 7 and 7, =CH–), 3.76 (q, 2, *J* = 7, $-OCH_2-$), 1.91 (d of t, *J* = 7 and 7, $-CH_2-$), 1.34 (m, 2, $-CH_2-$), 0.91 (t, 3, *J* = 7, $-CH_3$)
57d	*E* isomer	6.17 (d, 1, *J* = 13, =CH–), 4.76 (d of t, *J* = 13 and 7, =CH–), 3.69, 1.91, 1.34, 0.91
59c,d	(*Z*)- and (*E*)-5-methoxy-4-tridecene	4.48 (t, 1, *J* = 7, =CH–), 3.49 (s, 3, $-OCH_3$), 2.39 (t, 2, *J* = 7, $-CH_2-$), 1.99 (m, 2, $-CH_2-$), 1.31 (m, 14, $-CH_2-$), 0.93 (t, 3, *J* = 7, $-CH_3$)
61c	(*Z*)-1-ethoxy-1-heptene	5.90 (d, 1, *J* = 7, =CH–), 4.33 (d of t, 1, *J* = 7 and 7, =CH–), 3.75 (q, 2, *J* = 7, $-OCH_2-$), 1.96 (m, 2, $-CH_2-$), 1.30 (m, 6, $-CH_2-$), 0.89 (t, 3, *J* = 7, $-CH_3$)
61d	*E* isomer	6.42 (d, 1, *J* = 13, =CH–), 4.73 (d of t, 1, *J* = 13 and 7, =CH–), 3.68, 1.96, 1.30, 0.89

[a] MS: M_w 176.1198, calcd for $C_{12}H_{16}O$ 176.1201. [b] MS: M_w 176.1196. [c] MS: M_w 192.1157, calcd for $C_{12}H_{16}O_2$ 192.1150. [d] MS: M_w 192.1158.

(*E*)-6-Phenyl-5-undecene-2,10-dione bis(ethylene acetal) (67b): NMR ($CDCl_3$) δ 7.25 (m, 5, arom), 5.45 (t, 1, *J* = 7 Hz, =CH–), 3.75 (s, 8, $-OCH_2-$), 3.71 (s, 4, $-OCH_2-$), 2.29 (m, 2, $-CH_2-$), 1.63 (m, 4, $-CH_2-$), 1.15 (s, 3, $-CH_3$).

(*Z*)-6-(*p*-Methylphenyl)-5-undecene-2,10-dione bis(ethylene acetal) (68a): NMR ($CDCl_3$) δ 7.02 (m, 4, arom), 5.38 (t, 1, *J* = 7 Hz, =CH–), 3.58 (s, 8, $-OCH_2-$), 2.30 (s, 3, (s, 3, $-CH_3$), 2.04 (m, 4, $-CH_2-$), 1.63 (m, 6, $-CH_2-$), 1.22 (s, 6, $-CH_3$); M_w = 360.2314; $C_{22}H_{32}O_4$ = 360.2301.

(*E*)-6-(*p*-Methylphenyl)-5-undecene-2,10-dione bis(ethylene acetal) (68b): NMR ($CDCl_3$) δ 7.02 (m, 4, $-CH_2-$), 1.62 (m, 6, $-CH_2-$), 1.22 (s, 6, $-CH_3$).

5-Undecene-2,10-dione bis(ethylene acetal) (69a, 69b): NMR ($CDCl_3$) δ 5.37 (t, 2, *J* = 7 Hz, =CH–), 3.87 (s, 8, $-OCH_2-$), 2.09 (m, 4, $-CH_2-$), 1.63 (m, 6, $-CH_2-$), 1.31 (s, 6, $-CH_3$).

(*Z*)-1-Ethoxy-1-hexen-5-one ethylene acetal (69c): NMR ($CDCl_3$) δ 5.87 (d, 1, *J* = 7 Hz, =CH–), 4.30 (d of t, 1, *J* = 7, 7 Hz, =CH–), 3.82 (s, 4, $-OCH_2-$), 3.68 (q, 2, *J* = 7 Hz, $-OCH_2-$), 2.02 (m, 2, $-CH_2-$), 1.62 (m, 2, $-CH_2-$), 1.14 (s, 3, $-CH_3$), 1.18 (t, 3, *J* = 7 Hz, $-CH_3$).

(*E*)-1-Ethoxy-1-hexen-5-one ethylene acetal (69d): NMR ($CDCl_3$) δ 6.21 (d, 1, *J* = 12 Hz, =CH–), 4.52 (d of t, 1, *J* = 12, 7 Hz, =CH–), 3.82 (s, 4, $-OCH_2-$), 3.62 (q, 2, *J* = 7 Hz, $-OCH_2$), 2.02 (m, 2, $-CH_2-$), 1.62 (m, 2, $-CH_2-$), 1.14 (s, 3, $-CH_3$), 1.18 (t, 3, *J* = 7 Hz, $-CH_3$).

(*Z*)- + (*E*)-6-(9-Decenyl)-5-undecene-2,10-dione bis(ethylene acetal) (70a, 70b): NMR ($CDCl_3$) δ 5.96–5.56 (m, 1, =CH–), 5.38 (t, 1, *J* = 7 Hz, =CH–), 5.08–4.88 (m, 2, =CH–), 3.84 (s, 8, $-OCH_2-$), 2.04 (m, 8, $-CH_2-$), 1.66 (m, 4, $-CH_2-$), 1.28 (m, 18, $-CH_2-$, $-CH_3$).

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Registry No. **13**, 93-89-0; **14**, 7335-27-5; **15**, 5798-75-4; **16**, 94-08-6; **17**, 94-30-4; **18**, 10259-22-0; **19**, 7335-26-4; **20**, 10287-53-3; **21**, 16518-65-3; **22**, 3007-91-8; **23**, 93-60-7; **24**, 2459-09-8; **25**, 2810-04-0; **26**, 120-61-6; **27**, 1205-84-1; **28**, 3199-61-9; **29**, 70812-80-5; **30**, 5452-75-5; **31**, 6493-77-2; **32**, 111-81-9; **33**, 1731-84-6; **34**, 6297-22-9; **35**, 70850-30-5; **36**, 26845-47-6; **37**, 70812-81-6; **38**, 70812-82-7; **39**, 3333-44-6; **40**, 3469-00-9; **41a**, 4165-78-0; **41b**, 4701-36-4; **41c**, 4518-65-4; **41d**, 4541-69-9; **42c**, 70812-83-8; **42d**, 70812-84-9; (*Z*)-**42e**, 70812-85-0; (*E*)-**42e**, 70812-86-1; **43c**, 70812-87-2; **43d**, 70812-88-3; (*Z*)-**43e**, 70812-89-4; (*E*)-**43e**, 70812-90-7; **44a**, 66702-38-3; **44b**, 66702-37-2; **44c**, 58889-99-9; **44d**, 58889-98-8; **45c**, 66702-40-7; **45d**, 66702-39-4; (*Z*)-**45e**, 70812-91-8; (*E*)-**45e**, 70812-92-9; **46a**, 18322-83-3; **46b**, 18421-23-3; **46c**, 58889-89-7; **46d**, 58889-88-6; **47c**, 70812-93-0; **47d**, 70812-94-1; (*Z*)-**47e**, 70812-95-2; (*E*)-**47e**, 70812-96-3; **48a**, 70812-97-4; **48b**, 70812-98-5; **49c**, 70812-99-6; **49d**, 70813-00-2; (*Z*)-**49e**, 70813-01-3; (*E*)-**49e**, 70813-02-4; **50a**, 70813-03-5; **50b**, 70813-04-6; **50c**, 70813-05-7; **50d**, 70813-06-8; **51c**, 70813-07-9; **51d**, 70813-08-0; (*Z*)-**51e**, 70813-09-1; (*E*)-**51e**, 70813-10-4; **52a**, 70813-11-5; **52b**, 70813-12-6; **52c**, 70813-13-7; **52d**, 70813-14-8; **53c**, 70813-15-9; **53d**, 70813-16-0; (*Z*)-**53e**, 70813-17-1; (*E*)-**53e**, 70850-24-7; **54a**, 70813-18-2; **54b**, 70813-19-3; **55a**, 70813-20-6; **55b**, 70813-21-7; **56a**, 70813-22-8; **56b**, 70813-23-9; **56c**, 70813-24-0; **56d**, 70813-25-1; **57a**, 10405-84-2; **57b**, 10405-85-3; **57c**, 16627-08-0; **57d**, 16627-09-1; **58a**, 2807-33-2; **58b**, 2807-34-3; **59a**, 70813-26-2; **59b**, 70813-27-3; **59c**, 70850-35-0; **59d**, 70864-66-3; **60a**, 70813-28-4; **60b**, 70813-29-5; **61a**, 6508-77-6; **61b**, 6434-76-0; **61c**, 16627-10-4; **61d**, 16627-11-5; **62a**, 70813-30-8; **62b**, 70813-31-9; **63a**, 70813-32-0; **63b**, 70850-36-1; **63c**, 70813-33-1; **63d**, 70813-34-2; **64a**, 70813-35-3; **64b**, 70850-37-2; **65a**, 70813-36-4; **65b**, 70813-37-5; **66a**, 70813-38-6; **66b**, 70813-39-7; **67a**, 70813-40-0; **67b**, 70813-41-1; **67c**, 70813-42-2; **67d**, 70813-43-3; **68a**, 70813-44-4; **68b**, 70813-45-5; **69a**, 70813-46-6; **69b**, 70813-47-7; **69c**, 70813-48-8; **69d**, 70813-49-9; **70a**, 70813-50-2; **70b**, 70813-51-3; **70c**, 70813-52-4; **70d**, 70813-53-5; isopropenylbenzene, 98-83-9; *p*-chloroisopropenylbenzene, 1712-70-5; *p*-bromoisopropenylbenzene, 6888-79-5; *p*-methylisopropenylbenzene, 1195-32-0; *p*-methoxyisopropenylbenzene, 1712-69-2; *m*-methoxyisopropenylbenzene, 25108-57-0; *o*-methoxyisopropenylbenzene, 10278-02-1; *p*-(dimethylamino)isopropenylbenzene, 25108-56-9; *m*-(dimethylamino)isopropenylbenzene, 35843-88-0; 2-isopropenylnaphthalene, 3710-23-4; 3-isopropenylpyridine, 15825-89-5; 2-isopropenylthiophene, 30616-73-0; *p*-diisopropenylbenzene, 1605-18-1; (*E*)-1-phenyl-3-methylbutadiene, 49623-06-5; 2-isopropenylbenzo[*b*]furan, 56426-65-4; 2-methyl-3-phenylpropene, 3290-53-7; 2-methyl-3-cyclohexylpropene,

3990-93-0; 4-isopropenylcyclohexene, 26325-89-3; 2-methyl-1,12-dodecadiene, 34386-65-7; 2-methyl-1-decene, 13151-27-4; 1-isopropenyl-4-methylenecyclohexane, 499-97-8; 1-isopropenyl-4-ketocyclohexyltrimethylene dithioacetal, 70813-54-6; 1-isopropenyl-4-ketocyclohexyl ethylene acetal, 70850-38-3; 1-isopropenyl-4-(2'-tetrahydrofuranoxy)cyclohexane, 70813-55-7; 1-isopropenyl-4-ketocyclohexane, 22460-53-3; 2-methyl-3,3-diphenylpropene, 70813-56-8; $EtO_2C(CH_2)_2CO_2Et$, 123-25-1; $EtO_2C(CH_2)_3CO_2Et$, 818-38-2; $EtO_2C(CH_2)_4CO_2Et$, 141-28-6; $EtO_2C(CH_2)_5CO_2Et$, 2050-20-6; $MeO_2C(CH_2)_{10}CO_2Me$, 1731-79-9; $CH_3C(=CH_2)(CH_2)_2C(=CH_2)CH_3$, 627-58-7; $CH_3C(=CH_2)(CH_2)_3C(=CH_2)$, 51708-83-9; $CH_3C(=CH_2)(CH_2)_4C(=CH_2)CH_3$, 59840-10-7; $CH_3C(=CH_2)(CH_2)_5C(=CH_2)CH_3$, 20054-25-5; $CH_3C(=CH_2)(CH_2)_{10}C(=CH_2)CH_3$, 22080-36-0; 1-ethoxy-1-(2-naphthyl)ethene, 70813-57-9; 1-(2-naphthyl)ethanone, 93-08-3; $CH_3(CH_2)_7C(=CH_2)OCH_3$, 54123-72-7; 1-methylethyl *o*-methoxybenzoate, 944-95-6; 1,1-dimethylethyl *o*-methoxybenzoate, 16537-20-5; 2,2-dimethylpropyl *o*-methoxybenzoate, 66702-44-1; methyl benzoate, 93-58-3; 1-methylethyl benzoate, 939-48-0; ethyl *p*-methoxybenzoate, 94-30-4; methyl *p*-bromobenzoate, 619-42-1; ethyl 3-pyridylcarboxylate, 614-18-6; methyl 4-pyridylcarboxylate, 2459-09-8; methyl *n*-nonylcarboxylate, 110-42-9; ethyl benzoate, 93-89-0; ethyl acetate, 141-78-6; methyl *p*-methylbenzoate, 99-75-2; (*Z*)-5-phenyl-4-nonene-1,9-dicarboxylic acid, 70813-58-0; (*E*)-5-phenyl-4-nonene-1,9-dicarboxylic acid, 70813-59-1; 4-nonene-1,9-dicarboxylic acid, 70813-60-4; 9-(ethoxycarbonyl)nonyltriphenylphosphonium iodide, 70813-61-5; 9-(ethoxycarbonyl)nonyltriphenylphosphorane, 70813-62-6; 5-(triphenylphosphonio)pentanoic acid iodide, 70813-63-7; sodium 5-(triphenylphosphonio)pentanoate, 41723-91-5; 3-(2-methyl-1,3-dioxolan-2-yl)propyltriphenylphosphonium iodide, 70813-64-8; 3-(2-methyl-1,3-dioxolan-2-yl)propylidenetriphenylphosphorane, 3054-93-1; ethyl 10-chlorodecanoate, 70813-65-9; triphenylphosphine, 603-35-0.

Synthesis and Stereochemistry of Ethyl (*E*)-3-Methyl-3-phenylglycidate and (*E*)- and (*Z*)-1,3-Diphenyl-2-buten-1-one Oxide

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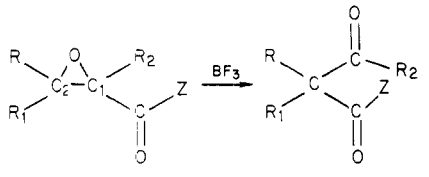
The absolute configurations of (+)-(2*S*,3*R*)-Ethyl (*E*)-3-methyl-3-phenylglycidate (1) and (+)-(2*S*,3*R*)-(*E*)- and (−)-(2*S*,3*S*)-(*Z*)-1,3-diphenyl-2-buten-1-one oxide (dypnone oxide) have been assigned. The resolution of sodium (*E*)-3-methyl-3-phenylglycidate (4) and an asymmetric epoxidation of 1,3-diphenyl-2-buten-1-one are described.

When 1,2-epoxycarbonyl compounds are treated with Lewis acids, 1,3-dicarbonyl products may be formed from the 1,2 migration of the carbonyl group (eq 1).[2,3] Carbonyl

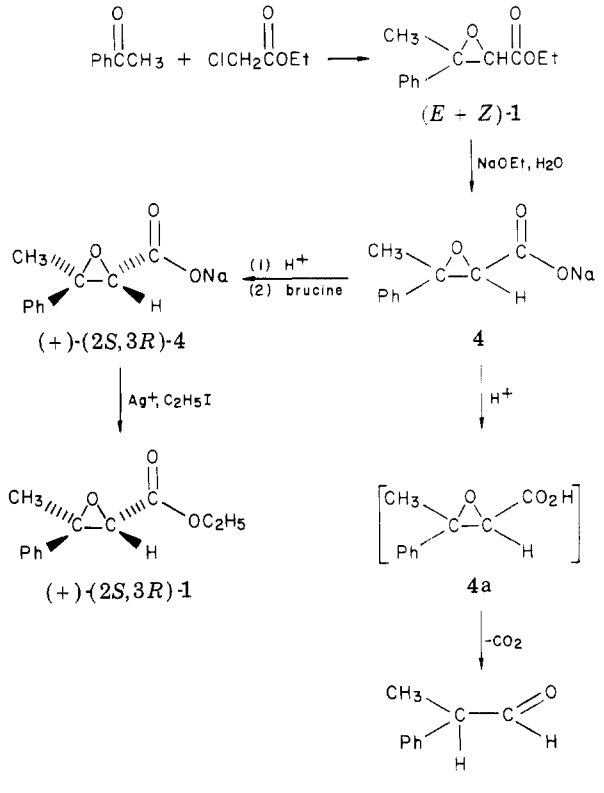


(1)

migrations have been observed with epoxy ketones,[4] esters,[5] and thiol esters.[6] These intramolecular[7] rearrangements have been established to be concerted processes that proceed with complete inversion of configuration at the migration terminus.[8] We have been able to ascertain the overall stereochemistry of these transformations by employing model substrates in optically active form and establishing the absolute configuration and optical purity of both starting material and rearrangement products (eq 1).

An examination of the literature revealed that very few derivatives of glycidic acids have been prepared in optically active form.[9] Fortunately, the optically active glycidic ester 1 had been reported and its absolute configuration assigned.[10] We chose (+)-sodium 2-methyl-2-phenylglycidate as the pivotal intermediate in our mechanistic scheme since it is the precursor to 1 and we felt that we could devise a method to stereospecifically convert it to

Scheme I



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