0040-4020(94)00899-X

1-Alkoxycarbonylalkylidenetriphenylarsoranes: Preparation and Reactions

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Abstract: The higher homologues of the well-studied alkoxycarbonylmethylenetriphenylarsonium[1] ylide (3, R=H) can be easily obtained through the sequence: a), preparation of alkyl 2-trifloxyalkanoates (1); b), reaction between these trifloxyderivatives and triphenylphosphine to give 1-alkoxycarbonylalkyltriphenylarsonium triflates (2); and c), basic treatment of the triphenylarsonium triflates (2) with alumina-supported potassium fluoride to give 1-alkoxycarbonylalkyledenetriphenylarsonium ylides (3). These higher homologues of (3, R=H) react with aromatic aldehydes in good to excellent yields, and give rise to synthetically interesting "coupling" and cyclopropanation reactions.

Introduction

Preparation and reactions of arsonium salts and of their corresponding arsonium ylides (alkylidenearsoranes) have been much less intensively explored than those of phosphonium salts and phosphonium ylides (Wittig reagents) but according to general chemistry reasoning and to some experimental facts reported in the chemical literature[1, 2] it can be anticipated that, once prepared, arsonium ylides should be more reactive than the corresponding phosphonium ylides whilst the starting arsonium salts should be more difficult to prepare than the corresponding phosphonium salts; furthermore, use of the more reactive alkylarsines is unattractive because of their toxicity. Consequently, a search for a general quaternization procedure of *triphenylarsine* -a solid, rather unreactive, and easily available arsine- was justified and to take advantage of our experience in the phosphorous field[3,4,5], we directed our efforts to the preparation of 1-alkoxycarbonylalkyltriphenylarsonium salts.

Methoxycarbonylmethyltriphenylarsonium bromide is, up to now, the only known member of the above series. It is prepared by reaction of triphenylarsine with methyl bromoacetate[1,6,7] and easily converted into an arsorane that gives rise to interesting reactions (Wittig reactions with aldehydes *and* ketones; cyclopropanations; etc.)[1]. The scope of these reactions would be enlarged if the higher arsorane homologues were easily available but we have found that even the next member of the series, 1-alkoxycarbonylethyltriphenylphosphonium bromide, defeats a related preparation. In fact, ethyl 2-

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[1] In the present paper, alkoxy stands for either methoxy or ethoxy.

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bromopropanoate does not react with triphenylarsine under a variety of experimental conditions, including 20 h refluxing in toluene and 14 h refluxing in pyridine.

Preparation of 1-alkoxycarbonylalkyltriphenylarsonium triflates

According to related knowledge[8], alkyl 2-trifloxyalkanoates (trifluoromethanesulphonic acid esters of alkyl 2-hydroxyalkanoates, $F_3C-S(O_2)-O-CH(R)-COOR'$) (**1**) should be more reactive as arsine quaternizing agents than the usual 2-bromoderivatives and, *what is very important in the present context*, the leaving triflate should be much less nucleophilic than the bromide anion. Consequently, use of alkyl 2-trifloxyalkanoates, besides making quaternizations easier, would avoid the undesired secondary reaction depicted in Scheme 1, that is to be expected because in the phosphonium field[4] it takes place when the higher homologues of methyl bromoacetate are used as quaternizing agents and even when quaternization of polystyryldiphenylphosphine is intended with the proper methyl bromoacetate[3].
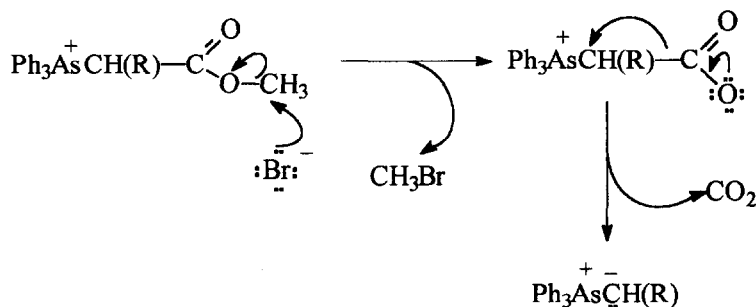
Scheme 1

We have found[5] that the needed reagents, alkyl 2-trifloxyalkanoates (**1**) can be easily prepared (yields around 80%) by reaction of alkyl 2-hydroxyalkanoates with triflic anhydride in the presence of anhydrous pyridine and using carbon tetrachloride as solvent. Many of the esters to be used as starting materials are commercially available substances and, in any case, other members of the series can be easily synthesized by such standard procedures as the sequence aldehyde, cyanohydrin, 2-hydroxyester (recently, an excellent method for the preparation of cyanohydrins has been reported[9]). In the present work, we have prepared two new members of the series: ethyl 2-trifloxybutanoate (**1**, R = R' = ethyl), starting from commercial ethyl 2-hydroxybutanoate, and methyl 2-trifloxytridecanoate (**1**, R = n-undecyl, R' = methyl), starting from methyl 2-hydroxytridercanoate prepared *via* cyanohydrin in a simpler procedure than the only one previously described[10]. Table 1.

Table 1				
Preparation Yields and Spectral Data of Alkyl 2-Trifloxialkanoates (1)				
Compound 1 R R'	Yield (%)	IR (cm⁻¹)	¹H NMR (ppm)	¹³C NMR (ppm)
Et Et	84	2970, 2883, 1763, 1422, 1209, 1148, 1085, 1022, 967, 620	1.08 (3H, t), 1.33 (3H, t), 1.98 (2H, q), 4.27 (2H, q), 4.99 (1H, t)	13.92, 14.81, 31.74, 63.05, 84.12, 118.90, 167.74
C₁₁H₂₃ Me	61	2927, 2858, 1763, 1422, 1246, 1146, 951, 864, 614	0.87 (3H, t), 1.25 (16H, m), 1.96 (2H, m), 2.29 (2H, t), 3.83 (3H, s), 5.12 (1H, t)	14.52, 23.14, 24.87, 29.23, 29.80, 29.93, 30.04, 32.37, 53.57, 84.10, 118.91, 168.133

1-Alkoxycarbonylalkyltriphenylarsonium triflates {[RCH(COOR')AsPh₃]⁺ F₃C-SO₃⁻} (2) are prepared by quaternizing triphenylarsine with the corresponding alkyl 2-trifloxyalkanoate (1) (benzene, 50 °C, 48 h; yields from high to excellent) thus confirming the high reactivity of these alkylating reagents. The preparation of 1-methoxycarbonyldodecyltriphenylarsonium triflate (2, R = n-undecyl, R' = methyl) in more than 50% yield is worth pointing out. All the new arsonium triflates show satisfactory IR, and ¹H and ¹³C NMR spectra (Table 2).

Table 2				
Preparation Yields and Spectral Data of 1-Alkoxycarbonylalkyltriphenylarsonium Triflates (2)				
Compound 2 R R'	Yield (%)	IR (cm⁻¹)	¹H NMR (ppm)	¹³C NMR (ppm)
H Et	99	2983, 1716, 1439, 1254, 1154, 1030, 743, 635	3.61 (3H, s), 4.75 (3H, s), 7.70 (15H, m)	32.39, 54.13, 121.34, 131,41, 133.14 134.91, 166.43
Me Et	91	3062, 1742, 1441, 1268, 1225, 1154, 1084, 1032, 742, 639	1.01 (3H, t), 1.72 (3H, d), 4.03 (2H, q), 5.25 (1H, q), 7.65 (15H, m)	12.87, 13.44, 40.85, 63.13, 120.64, 130.85, 132.38, 132.94, 134.23, 167.71
Et Et	85	3064, 2941, 1740, 1441, 1264, 1225, 1154, 1030, 743, 637	1.04 (3H, t), 1.18 (3H, t), 2.08 (2H, m), 4.04 (2H, m), 5.02 (1H, t), 7.69 (15H, m)	13.33, 14.14, 22.76, 47.53, 63.60, 120.92, 131.52, 133.56, 134.98, 168.76
Pr Et	75	3064, 2970, 1733, 1441, 1262, 1225, 1154, 1032, 743, 637	0.96 (3H, t), 1.04 (3H, t), 1.60 (2H, m), 1.98 (2H, m), 4.05 (2H, m), 5.03 (1H, q), 7.74 (15H, m)	14.06, 14.12, 22.23, 30.87, 46.22, 63.69, 120.81, 131,57, 132.30, 133.53, 135.06, 168.70
Bu Et	74	3064, 2962, 1735, 1441, 1264, 1225, 1154, 1032, 743, 637	0.94 (3H, t), 1.12 (3H, t), 1.60 (4H, m), 2.00 (2H, m), 4.02 (2H, q), 5.03 (1H, t), 7.72 (15H, m)	13.73, 14.06, 22.21, 26.80, 30.95, 46.62, 63.80, 120.90, 131.45, 133.23, 135.02, 168.74
C₁₁H₂₃ Me	53	3064, 2927, 1733, 1441, 1262, 1225, 1154, 1032, 743, 639	0.83 (3H, t), 1.16 (16H, m), 1.60 (2H, m), 1.98 (2H, m), 3.54 (3H, s), 5.03 (1H, q), 7.69 (15H, m)	14.57, 23.11, 28.82, 28.96, 29.53, 29.75, 29.80, 29.97, 32.32, 46.49, 53.89, 120.80, 131.55, 133.49, 135.01, 169.46

One-pot As-Wittig reactions with aldehydes

1-Alkoxycarbonylalkylidenetriphenylarsoranes [RC(COOR')=AsPh₃] (3) belong to the stabilized arsonium ylide type and, in principle, they are isolable reagents; however, they are rather reactive towards humidity and air and one-pot As-Wittig reactions yield more satisfactory results than the two steps procedure.

We have found very convenient the use as base of alumina supported potassium fluoride[11] for the *in situ* generation of arsonium ylides; in the presence of an aldehyde (up to now, only aromatic aldehydes have been studied) the expected Wittig reaction takes place affording in high yield *a single stereoisomer* of the

corresponding 2-alkyl-3-arylpropenoic ester (4) (Table 3). The spectral data, particularly the chemical shift of the C_3-hydrogen (always at δ 7.6-7.7) show that in all cases the (*E*)-stereoisomer is obtained.

Extensive informatizised search of the chemical literature[12] leads us to the conclusion that, even ignoring stereochemistry, the only propenoic esters (4) of Table 3 that have been satisfactorily described are those with Ar = phenyl and R = Me[5,13,14] or R = Et[13,14,15] or R = Pr[5,13] or R = Bu[5,15] and with Ar = 2-furyl and R = Me[14].

The easy preparation of methyl (*E*)-3-phenyl-2-undecylpropenoate in 80% yield should be emphasized because from this result it is fair to extrapolate that starting with the easily available 2-trifloxyalkanoates and triphenylarsine *propenoic esters with any 2-alkyl substituent* can be satisfactorily prepared. The procedure is far more simple and general that some others starting from sulfur derivatives[15], α-lithioalkylphosphonates[13] or α-halogenoderivatives and tributylstibine[14].

"Coupling" reaction

In view of the excellent yields obtained even in the reaction of aldehydes with the higher arsorane homologues, it was considered worthwhile to study their reaction with ketones (it has been reported that incontrast with the behaviour of the phosphorane derivative[16], alkoxycarbonylmethylidenetriphenylarsorane reacts with aliphatic ketones affording the corresponding unsaturated esters in acceptable yields[1]).

The one-pot Wittig reaction between cyclohexanone and 1-ethoxycarbonylethyltriphenylarsonium triflate (**2, R=Me**) was not very succesful: the highest yield in condensation product (ethyl 2-cyclohexylidenepropanoate, **5**) was about 15%. However, in the resulting reaction mixtures the presence of substancial amounts of diethyl (*Z*)-2,3-dimethylbutenedioate (**6**) was detected. A strong peak at δ 1.94, together with a "trace" peak at 2.07, in the ^{1}H NMR spectrum pointed to the *cis*-stereochemistry of the practically *single* isomer present in the mixture; this stereochemistry was confirmed by spontaneous conversion of the ester to the anhydride (IR carbonyl band at 1758 cm^{-1}) during its saponification.

   4   5   6
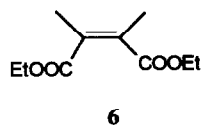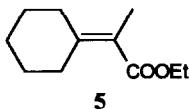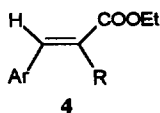
Confirming that the "coupled" product (**6**) is formed in the attack of the base (fluoride anion) on the arsonium salt (**2, R=Me**), we have found that treatment of this salt with alumina-supported potassium fluoride *in the absence* of any co-reagent affords diester (**6**) with a higher than 53% yield. Several assays (changes in reaction conditions; use of ultrasounds; previous conversion of the arsonium triflate into arsonium iodide) have been carried out to improve this yield but all of them have proved unsuccessful.

It is important to point out here that identical treatment of ethoxycarbonylmethyltriphenylarsonium triflate (**2, R=H**) afforded the corresponding Wittig reagent (**3, R=H**) and *no "coupling" reaction was observed*

Table 3				
Preparation Yields and Spectral Data of Alkyl (E)-2-Alkyl-3-arylpropenoates (4)				
Compound 4		Yield (%)	IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
Ar	R				
2-furyl	Me	83	2980, 1705, 1635, 1390, 1368, 1210, 1180, 885, 740	1.35 (3H, t), 2.21 (3H, s), 4.25 (2H, q), 6.50 (1H, m), 6.61 (1H, d), 7.45 (1H, s), 7.54 (1H, d)	14.04, 14.30, 60.84, 112.01, 114.61, 125.05, 125.55, 143.89, 151.97, 168.53
C$_6$H$_5$	Me	79	2928, 1709, 1637, 1447, 1366, 1203, 1113, 766, 702	1.35 (3H, t), 2.12 (3H, s), 4.30 (2H, q), 7.42 (5H, s), 7.74 (1H, s)	14.56, 14.83, 61.37, 128.74, 128.85, 129.11, 130.13, 136.44, 139.15, 169.16
4-MeO-C$_6$H$_4$	Me	64	2960, 1700, 1630, 1510, 1365, 1305, 1178, 1120, 750	1.34 (3H, t), 2.12 (3H, s), 3.81 (3H, s), 4,27 (2H, q), 6.93 (2H, d), 7.39 (2H, d), 7.65 (1H, s)	14.58, 14.86, 55.76, 61.25, 114.31, 128.98, 131.91, 138.84, 139.15, 160.11, 169.15
4-Cl-C$_6$H$_4$	Me	80	2980, 1710, 1635, 1490, 1365, 1200, 1115, 840, 750	1.34 (3H, t), 2.12 (3H, s), 4.25 (2H,q), 7.35 (4H,m), 7.64 (1H,s)	13.99, 14.26, 60.93, 128.54, 129.15, 130.83, 134.30, 137.22, 168.90
2-furyl	Et	92	2975, 1706, 1634, 1368, 1287, 1239, 1208, 1179, 1125, 1020, 745	1.13(3H,t),1.33(3H,t),2.73(2H,q) 4.25(2H,q),6.50(1H,m),6.60 (1H,d) 7.38 (1H, s), 7.52 (1H, d)	13.92, 14.81, 21.74, 61.-20, 112.45, 115.10, 125.37, 131.91, 144.51, 152.11, 168.74
C$_6$H$_5$	Et	93	2979, 1710, 1632, 1447, 1368, 1289, 1237, 1202, 1127, 1047, 700	1.18 (3H, t), 1.35 (3H, t),, 2.55 (2H, q), 4.28 (2H, q), 7.37 (5H, m), 7.65 (1H, s)	14.39, 14.822, 21.30, 61.22, 128.74, 128.93, 129.67, 135.53, 136.34, 138.78, 168.83
4-MeO-C$_6$H$_4$	Et	95	2977, 1706, 1607, 1513, 1302, 1237, 1202, 1177, 1126, 1048, 834	1.19(3H,t),1.35(3H,t),2.56(2H,q) 3.83 (3H,s), 4.27 (2H,q), 6.92 (2H,d), 7.36 (2H,d), 7.60 (1H,s)	14.24, 14.84, 21.25, 55.77, 61.10, 114.41, 128.80, 131.47, 133.37, 138.46, 160.17, 169.07
4-Cl-C$_6$H$_4$	Et	90	2979, 1710, 1636, 1491, 1368, 1235, 1128, 1092, 762	1.16 (3H, t), 1.35 (3H, t), 2.52 (2H, q), 4.28 (2H, q), 7.33 (4H, m), 7.58 (1H, s)	14.56, 14.83, 61.37, 128.744, 128.85, 129.11, 130.13, 136.44, 139.15, 169.16
2-furyl	Pr	84	2963, 1706, 1634, 1372, 1223, 1207, 1128, 1021, 743	0.99 (3H, t), 1.33 (3H, t), 1.55 (2H, m), 2.69 (2H, t), 4.25 (2H, q), 6.49 (1H m), 6.58 (1H, d), 7.40 (1H, s), 7.52 (1H, d)	14.16, 14.27, 22.22, 29.75, 60.68, 111.91, 114.60, 125.28, 130.02, 143.93, 151.70, 168.42
C$_6$H$_5$	Pr	89	2960, 1709, 1623, 1453, 1369, 1225, 1128, 1056, 699	0.96 (3H, t), 1.35 (3H, t), 1.60 (2H, m), 2.48 (2H, m), 4.27 (2H, q), 7.36 (5H, s), 7.66 (1H, s)	14.70, 14.81, 23.13, 30.03, 61.22, 128.70, 128.92, 129,69, 134.33, 136.42, 139.07, 169.03
4-MeO-C$_6$H$_4$	Pr	78	2962, 1706, 1607, 1512, 1256, 1223, 1177, 1128, 754	0.99(3H,t),1.34(3H,t),1.61 (2H,m),2.48(2H,m),3.83(3H,s), 4.26(2H,q),6.92(2H,d),7.35(2H, d),7.61(1H,s)	14.75, 14.84, 23.00, 30.03, 55.77, 61.10, 114.41, 128.87, 131.50, 132.19, 138.74, 161.15, 169.16
4-Cl-C$_6$H$_4$	Pr	82	2964, 1711, 1632, 1492, 11273, 1225, 1131, 10944, 756	0.95 (3H, t), 1.35 (3H, t), 1.58 (2H, m), 2.42 (2H, m), 4.27 (2H, q), 7.34 (4H, m), 7.59 (1H, s)	14.67, 14.79, 23.04, 29.99, 61.35, 128.73, 129.18, 129.89, 130.95, 131.27, 134.95, 169.03
2-furyl	Bu	81	2960, 1706, 1632, 1465, 1372, 1262, 1208, 1129, 745	0.95 (3H, t), 1.33 (3H, t), 1.44 (4H, m), 2.70 (2H, t), 4.25 (2H, q), 6.50 (1H, m), 6.58 (1H, d), 7.39 (1H, s), 7.52 (1H, d)	14.46,, 14.81, 23.36, 28.13, 31.65, 61.21, 112.43, 115.06, 125.60, 130.77, 144.43, 152.23, 168.94
C$_6$H$_5$	Bu	82	2977, 1710, 1631, 1449, 1370, 1237, 1202, 1127, 698	0.92 (3H, t), 1.35 (3H, t), 1.51 (4H, m), 2.53 (2H, t), 4.27 (2H, q), 7.37 (5H, s), 7.65 (1H, s)	13.87, 14.32, 22.84, 27.26, 31.46, 60.74, 128.20, 128.42, 129.20, 133.97, 135.93, 138.42, 168.55
4-MeO-C$_6$H$_4$	Bu	85	2960, 1706, 1607, 1513, 1254, 1202, 1177, 1131, 830	0.94 (3H, t), 1.34 (3H, t), 1.60 (4H, m), 2.50 (2H, m), 3.83 (3H, s), 4.26 (2H, q), 6.92 (2H, d), 7.35 (2H, d), 7.59 (1H, s)	13.97, 14.35, 22.98, 27.29, 31.33, 56.28, 60.62, 113.84, 128.38, 131.66, 131.83, 138.09, 159.65, 168.03
4-Cl-C$_6$H$_4$	Bu	74	2960, 1711, 1632, 1491, 1248, 1200, 1131, 1094, 818	0.91 (3H, t), 1.35 (3H, t), 1.52 (4H, m), 2.45 (2H, m), 4.27 (2H, q), 7.32 (4H, m), 7.58 (1H, s)	14.84, 14..29, 22.81, 27.23, 31.34, 60.85, 128.67, 128.92, 130.46, 134.59, 137.04, 168.27
C$_6$H$_5$ (methyl instead of ethyl ester)	C$_{11}$H$_{23}$	80	2927, 2856, 1715, 1630, 1438, 1243, 1202, 1131, 768, 698	0.88 (3H, t), 1.26 (16H, m), 1.50 (2H, m), 2.49 (2H, m), 3.81 (3H, s), 7.36 (5H, m), 7.65 (1H, s)	14.63, 23.20, 28.04, 29.75, 29.84, 30.09, 30.15, 32.42, 52.44, 128.76, 128.93, 129.70, 134.19, 136.34, 139.20, 169.50

at all. Neither was it observed in the alumina-supported potassium fluoride treatment of methyl- and phenyl-carbonylmethyltriphenylarsonium chlorides.
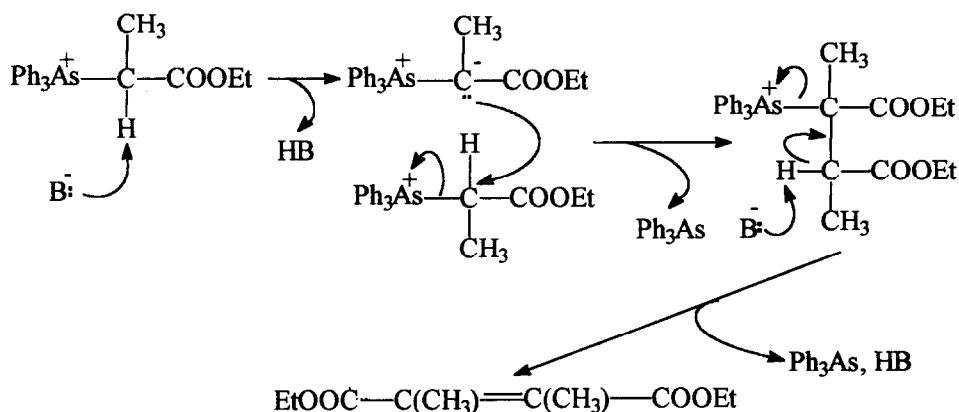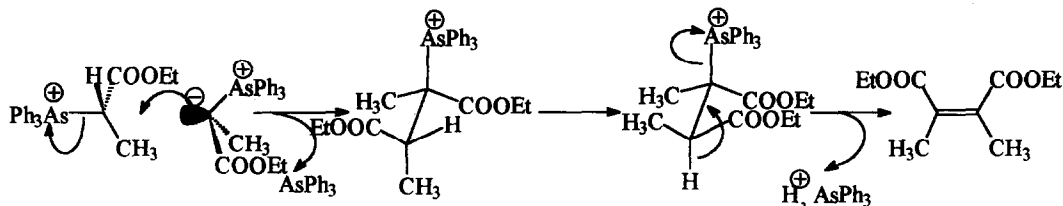

Scheme 2

Ignoring, for the moment, stereochemical questions, a plausible mechanism for the reaction that leads to diethyl 2,3-dimethylbutenedioate (**6**) is that given in Scheme 2. According to this mechanism, the *simultaneous* presence of arsonium cation and arsonium ylide is necessary for the coupling reaction to take place; in other words, the arsonium cation deprotonation rate cannot be very much faster than the global "coupling" reaction rate. The different behaviour of arsonium triflates (**2**, R=H) and (**2**, R=Me) can be explained on these grounds.

In the final step of Scheme 2, the proper arsonium ylide could act as base, feeding back arsonium cation; that means that, starting from arsonium ylide, a catalytic amount of arsonium cation would be sufficient for the whole "coupling" process to take place. This is precisely the justification given to explain the *thermal decomposition* (heating in benzene-ether solution) of benzylidenetriphenylarsorane into triphenylarsine and a mixture of stilbene isomers (70-80% yield)[17].

The *cis*-configuration of the resulting diethyl 2,3-dimethylbutenedioate can be rationalized (Scheme 3) by accepting that in the S_N2 step the biggest and positive substituent group of the ylide (Ph_3As^+) takes a position in between the smallest group (H) and the electronegative group (COOEt) of the onium cation at the same time that the two COOEt groups remain as far as possible one from the other; an that a *trans*-stereochemistry holds in a concerted (E_2) elimination step.
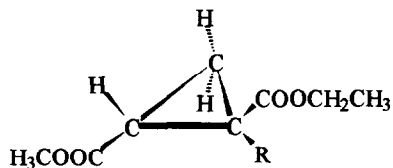
The "coupling" reaction offers interesting synthetic possibilities and it is the authors feeling that by controlling the initial arsonium salt/base ratio and the temperature; or by using mixtures of arsonium salt and arsorane; or by appealing to some other experimental trick, a useful "coupling" reaction could be performed in many cases.

Scheme 3

Cyclopropanation reactions

The stabilised methoxycarbonylmethylenetriphenylphosphorane *does not* react with α,β-unsaturated esters but methoxycarbonylmethylenetriphenylarsorane *does* affording sterically defined cyclopropane derivatives in moderate to excellent yields[1]. Here we report that *one-pot* reactions between methyl acrylate and higher homologues of ethoxycarbonylmethylenetriphenylarsorane (generated by basic treatment with alumina-supported potassium fluoride of the corresponding triphenylarsonium triflate) afforded *trans*-cyclopropane-1,2-dicarboxylic esters in very good yield (Table 4); for instance, preparation of ethyl *trans*-1-butyl-2-methoxycarbonylcyclopropanecarboxylate (7, R = Bu) in 76% is remarkable. The ^{1}H NMR spectra of the resulting cyclopropane-1,2-dicarboxylic diesters establishes their *trans* configuration.

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Table 4				
Preparation Yields and Spectral Data of *trans*-Cyclopropane-1,2-dicarboxylic Esters (7)				
Compound 7 R	Yield (%)	IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
Me	61	2985, 1729, 1443, 1389, 1283, 1162, 1073, 1028, 868, 770	1.25 (3H, t), 1.31 (1H, q), 1.39 (3H, s), 1.56 (1H, q), 2.32 (1H, q), 3.70 (3H, s), 4.13 (2H, q)	13.54, 14.60, 21.57, 27.53, 28.07, 52.46, 61.74, 171.45, 173.89
Bu	76	2960, 2869, 1729, 1445, 1393, 1320, 1273, 1206, 1160, 1098, 1034, 870	0.88 (3H, t), 1.26 (3H, t), 1.31 (4H, m), 1.34 (1H, q), 1.53 (1H, q), 1.77 (2H, m), 2.34 (1H, q), 3.71 8(3H, s), 4.15 (2H, q)	14.40, 14.57, 20.85, 23.20, 27.45, 30.45, 32.83, 52.46, 61.57, 171.70, 173,28

For R equal to an alkyl of *any* length, the present cyclopropanation procedure appears far more simple and general than others based in the use of diazoderivatives and transition metal promoters or catalysts[18, 19] or in the use of 2-chloroesters under phase transfer conditions[20].

At this point, it is worth pointing out that, if the presence of some residual benzoylmethyl triphenylarsonium salt is accepted, the excellent yield in *trans*-1,2,3-tribenzoylcyclopropane obtained in the

"coupling" reaction followed by a cyclopropanation reaction. The presence of some arsonium salt justifies the formation of 1,2-dibenzoylethene through a "coupling" reaction (see above) that would be "captured" immediately by another arsorane molecule in a cyclopropanation reaction. Incidentally, we have not detected the presence of triethyl 1,2,3-trimethylcyclopropane-1,2,3-tricarboxylate in the "coupling" reaction reported above.

EXPERIMENTAL

All the starting materials, with the exception of methyl 2-hydroxytridecanoate, were commercially available and were purchased either from Aldrich Chemical Co. or from Fluka Chemie A.G. NMR spectra were recorded on a Varian Gemini 200 spectrometer and IR spectra on a Nicolet FT-IR 510 instrument. Nitrogen or argon atmospheres and carefully redistilled and conveniently dried solvents were used throughout. With the exception of the preparation of methyl 2-hydroxytridecanoate, general procedures are here described; specific data are given in Tables 1, 2, 3 and 4.

Preparation of methyl 2-hydroxytridecanoate.- A saturated solution of sodium bisulfite (20 mL) was added to a well stirred mixture of sodium cyanide (470 mg, 10 mmol) and dodecanal (920 mg, 5 mmol); ice (20 g) was added to the reaction mixture during the slow addition of the first half of the bisulfite solution. After 8 h at r. t., the resulting crude cyanohydrine (1 g) was collected, washed with water and directly mixed with methanol (30 mL) and conc. sulfuric acid (15 mL). The reaction mixture was refluxed overnight, cooled and poured over water (100 mL). The resulting mixture was extracted with ether, the ethereal layer dried over anh. sodium sulfate, the solvent removed *in vacuo*, and the crude methyl 2-hydroxytridecanoate was distilled under reduced pressure. Yield: 320 mg (30%). IR (cm^{-1}): 3453 (O-H), 1740 (C=O). ^{1}H NMR (ppm): 0.88 (3H, t), 1.18 (20H, m), 1.65 (2H, m), 3.79 (3H, s), 4.20 (1H, dd). ^{13}C NMR (ppm): 14.59 (CH$_3$), 23.18 (CH$_2$), 25.22 (CH$_2$), 30.04 (six overlapping CH$_2$), 32.40 (CH$_2$), 34.86 (CH$_2$), 52.98 (OCH$_3$), 70.98 (CH), 176.25 (C=O).

Preparation of alkyl 2-trifloxyalkanoates (1).[5]- Alkyl 2-hydroxyalkanoate (6.0 mmol) was mixed with anhydrous pyridine (6.0 mmol) in anhydrous carbon tetrachloride (20 mL). The resulting solution was cooled to -24°C and then trifluoromethanesulphonic anhydride (6.0 mmol) was added and a white suspension was formed. After 1 h, the suspension was warmed to room temperature and filtered by passing through a small silica-gel column. Removal of solvents afforded the corresponding ethyl 2-trifloxyalkanoates (1) in about 80 % yields and pure enough (spectral analysis) to be used without further purification. Preparation yields and spectral data of the previously undescribed alkyl 2-trifloxyalkanoates are collected in Table 1.

Preparation of 1-alkoxycarbonylalkyltriphenylarsonium triflates (2).- A solution of alkyl 2-trifloxyalkanoate **(1)** (5 mmol) and triphenylarsine (6 mmol) in toluene (25 mL) was heated to 75-85°C and kept for 48 h. The resulting arsonium triflates were then insolubilized by adding anhydrous ether and filtered off. This procedure did not work in the case of 1-methoxycarbonyldodecyltriphenylarsonium triflate because of the solubility of this salt in ether; in this case, the salt was purified by removing solvents *in vacuo* and filtering the residue through a silica-gel column , using as eluent a 3:2:2 (v/v/v) mixture of acetonitrile: chloroform: hexane. Preparation yields and spectral data of salts **(2)** are collected in Table 2.

"One-pot" As-Wittig reactions: prepartion of alkyl (E)-2-alkyl-3-arylpropenoates (4).- A suspension formed with the arsonium triflate (0.2 mmol), aryl aldehyde (1 mmol), and potassium fluoride on aluminum oxide as base (1 mmol) in acetonitrile (5 mL) was stirred for 48 h at r.t. After that, the solvent was removed and the residue was filtered through a silica-gel column using as eluent a 9:1 (v/v) mixture of hexane: methylene chloride. Eluate evaporation afforded the corresponding ester **(4)**. Preparation yields and spectral data of esters **(4)** are collected in Table 3

"Coupling" reaction: preparation of diethyl (Z)-2,3-dimethylbutenedioate (6).- Potassium fluoride on aluminium oxide (0.8 mmol) and 1-ethoxycarbonylethyltriphenylarsonium triflate (0.2 mmol) were added to acetonitrile (3 mL) and the resulting suspension was stirred for 48 h at r. t. After that, solvent was removed and the residue was filtered through a silica-gel column using as eluent a 9:1 (v/v) mixture of hexane: chloroform; diester **(6)** was isolated by evaporation of the eluate. Yield: 53%. IR: strongest peak at 1720 cm^{-1}. ^{1}H NMR (ppm): 1.29 (6H, t), 1.94 (6H, s), 4.19 (4H, q). ^{13}C NMR (ppm): 14.48 (CH$_3$), 14.65 (CH$_3$), 61.54 (CH$_2$), 133.77 (C=), 169.41 (C=O).

Cyclopropanation reactions: preparation of ethyl trans-*1-alkyl-2-methoxycarbonylcyclopropanecarboxylates (7).-* Arsonium triflate (0.5 mmol), methyl acrylate (1.0 mmol) and potassium fluoride on aluminium oxide (1 mmol) were added to acetonitrile (3 mL). The resulting suspension was stirred for 48 h at r. t. , the solvent was removed and the residue was passed through a silica-gel column using as eluent a 9:1 (v/v) mixture of hexane: methylene chloride. Eluate evaporation afforded the desired compound **(7)**. Preparation yields and spectral data of diesters **(7)** are collected in Table 4

ACKNOWLEDGEMENTS

REFERENCES AND NOTES

01. Huang, Yaozeng; Sheng, Yanchang *Adv. Organometallic Chem.* **1982**, *20*, 113-157.

02. Lloyd, D.; Gosney, I.; Ormiston, R. A. *Chem. Soc. Rev.* **1987**, *16*, 45-74.

03. Castells, J.; Font, J.; Virgili, A. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1-6.

04. Pórtulas, J.; Sánchez-Ferrando, F.; Sánchez-Pardo, J. *Tetrahedron Lett.* **1976**, 3617-3618

05. Castells, J.; López-Calahorra, F.; Yu, Zhanru *Chinese J. Reac. Polymers* **1993**, *2*, 156-163.

06. Hendrickson, J. B.; Spenger, R. E.; Sims, J. J. *Tetrahedron* **1963**, *19*, 707-713.

07. Dale, A. J.; Froyen, P. *Acta Chem. Scand.* **1971**, *25*, 1452-1456.

08. Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1981**, *103*, 1283-1285.

09. Ohno, H.; Mori, A.; Inoue, S. *Chemistry Lett.* **1993**, 375-378.

10. Orito, K.; Seki, Y.; Suginome, H.; Iwadare, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2013-2017.

11. Mélot, J.-M.; Texier-Boullet, F.; Foucaud, A. *Synthesis* **1987**, 364-366.

12. Search of general structure ArCH=CRCOOEt, with Ar = 2-furyl or phenyl or 4-methoxyphenyl or 4-chlorophenyl and R = methyl or ethyl or n-propyl or n-butyl, afforded the following CAS RN: 1734-78-07, 4071-41-4, 7042-34-4, 7042-33-3, 13329-06-7, 52750-05-7, 53618-36-3, 53618-42-1, 54110-97-3, 60754-34-9, 60754-33-8, 81787-40-8, 81787-39-5, 82826-13-9, 92576-43-7, 115754-00-2, 119346-66-6, 119870-81-4, 123827-87-2, 123827-88-3. Perusal of chemical references related to those RN led to the given conclusion.

13. Tay, M. K.; About-Jaudet, E.; Collignon, N.; Teulade, M. P.; Savignac, Ph. *Synthetic Comm.* **1988**, *18*, 1349-1362.

14. Huang, Yao-Zeng; Chen, Chen; Shen, Yanchang *J. Organometallic Chem.* **1989**, *366*, 87-93.

15. Tanikaga, R.; Miyashita, K.; Ono, N.; Kaji, A. *Synthesis* **1982**, 131-132.

16. Maercker, A. The Wittig reaction. In *Organic reactions, Vol. 14*; Adams, R. Ed.; John Wiley and Sons, Inc. York, 1965; pp 270-490.

17. Nesmeyanov, N. A.; Pravdina, V. V.; Reutov, O. A. *J. Org. Chem. U.S.S.R.* (Engl. trans.) **1967**, *3*, 574.

18. Doyle, M. P.; Dorow, R. L.; Tamblyn, W. H. *J. Org. Chem.* **1982**, *47*, 4059-4068.

19. Majchrzak, M. W.; Kotelko, A.; Lambert, J. B. *Synthesis* **1983**, 469-470.

20. Yan, Chaoguo; Kong, Qiangzhi; Lu, Wenxing; Wu, Jitao *Synthetic Commun.* **1992**, *22*, 1651-1653.

21. Johnson, A. W.; Schubert, H. *J. Org. Chem.* **1970**, *35*, 2678-2680.