ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 7, pp. 1170–1176. © Pleiades Publishing, Ltd., 2007.
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Catalytic Hydrophosphorylation of Dialkyl 2-Allylmalonates

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Received April 5, 2007

Abstract—The reaction of dialkyl hydrogen phosphites and diphenylphosphine oxide with dialkyl 2-allylmalonates in the presence of $[Pd(Ph_3P)_4]$ is studied. The addition of the hydrophosphoryl compounds to the multiple bond is established to proceed by the Markovnikov rule. The reaction is accompanied by the side process of malonate dealkoxycarbonylation whose contribution to the main process depends on the nature of the reagents.

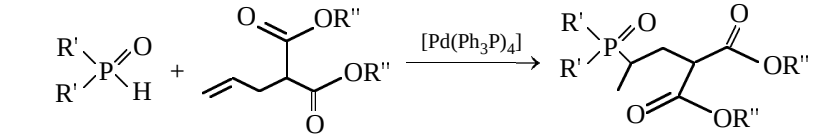
DOI: 10.1134/S1070363207070067

Catalytic hydrophosphorylation of unsaturated compounds with functional groups preliminary protected by easily removable protectors provides a perspective synthetic approach to functionally substituted phosphonates and phosphine oxides which present interest as compounds with potential biological activity or as precursors of such compounds.

Earlier [1] we reported the successful hydrophosphorylation of diethyl 2-allylmalonate with diethyl hydrogen phosphite in the presence of tetrakis(triphenylphosphine)palladium(0).

To study interrelation between the structure of unsaturated and hydrophosphoryl compounds and features of their reactions (first of all, reaction selectivity) and to synthesize new phosphonates and phosphine oxides interesting as starting materials for preparation of heterocyclic derivatives, we carried out catalytic hydrophosphorylation of dimethyl and dibutyl 2-allylmalonates with dialkyl hydrogen phosphites and diphenylphosphine oxide (Table 1) in the presence of 2 mol% of $[Pd(Ph_3P)_4]$ at 120°C for 20 h.

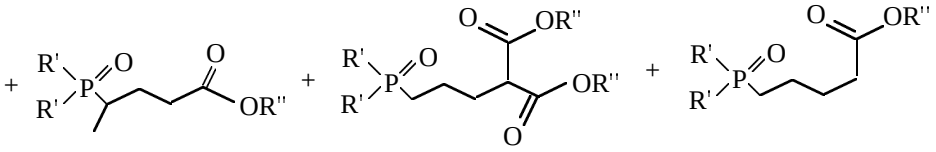
The process can be described by the following general scheme:



Ia, R' = MeO; **Ib**, R' = BuO; **Ic**, R' = Ph

IIa, R'' = Me; **IIb**, R'' = Bu

IIIa, R' = MeO, R'' = Me; **IIIb**, R' = BuO, R'' = Bu; **IIIc**, R' = Ph, R'' = Me; **IIId**, R' = Ph, R'' = Bu



IVa, R' = MeO, R'' = Me; **IVb**, R' = BuO, R'' = Bu; **IVc**, R' = Ph, R'' = Me; **IVd**, R' = Ph, R'' = Bu

Va, R' = MeO, R'' = Me; **Vb**, R' = BuO, R'' = Bu; **Vc**, R' = Ph, R'' = Me; **Vd**, R' = Ph, R'' = Bu

VIa, R' = MeO, R'' = Me; **VIb**, R' = BuO, R'' = Bu; **VIc**, R' = Ph, R'' = Me; **VId**, R' = Ph, R'' = Bu

The principal reaction products, dimethyl 2-[2-(dimethoxyphosphinoyl)propyl]malonate (**IIIa**) and dibutyl 2-[2-(dibutoxyphosphinoyl)propyl]malonate (**IIIb**), were isolated from the reaction mixtures as colorless viscous liquids by vacuum fractionation.

The ^{31}P NMR spectra of these compounds contain signals characteristic of phosphonate phosphorus (Table 2). The ^{1}H NMR spectrum shows doubled doublet signal of the methyl group attached to the methine group at the phosphorus atom (0.96 ppm for

Table 1. Catalytic hydrophosphorylation of dialkyl 2-allylmalonates

Hydrophosphoryl compound	Unsaturated compound	Reaction products	Conversion, %	Reaction product ratio			
				III	**IV**	**V**	**VI**
Ia	**IIa**	**IIIa–VIa**	75.2	65.7	34.3	traces	0
Ib	**IIb**	**IIIb–VIb**		84.7	15.3	traces	0
Ic	**IIa**	**IIIc–VIc**	100	0	66.2	0	33.8
Ic	**IIb**	**IIId–VId**	60.4	0	100	0	traces

Table 2. Spectral characteristics of catalytic hydrophosphorylation products

Comp. no.	^{31}P NMR, δ, ppm	GC–MS data		
		retention time, min	quasimolecular ion $[M + H]^+$, *m/z*	mass spectrum, *m/z* (I_{rel})
IIIa	31.5	10.75	283	55.0 (12), 78.9 (15), 92.9 (9), 108.9 (45), 112.9 (16), 140.9 (26), 150.9 (100), 163.0 (22), 172.8 (25), 194.9 (28), 218.9 (28), 250.9 (9)
IVa	34.0	8.66	225	55.0 (36), 78.9 (42), 83.0 (49), 110.0 (94), 136.9 (87), 150.9 (100), 165.0 (23), 193.0 (22), 196.0 (16), 209.0 (3)
Va	33.5	11.74	283	55.0 (16), 78.9 (17), 94.0 (14), 108.9 (43), 124.0 (37), 151.0 (100), 163.0 (9), 191.0 (13), 219.0 (17), 251.1 (3)
IIIb	29.2	9.54	451	41.0 (14), 82.9 (58), 99.0 (9), 109.0 (7), 122.9 (28), 134.9 (14), 164.9 (21), 190.9 (46), 209.0 (22), 235.1 (100), 257.0 (24), 265.0 (29), 321.1 (6), 339.1 (8), 349.1 (14), 394.9 (12)
IVb	30.5	8.51	351	41.0 (21), 55.1 (14), 83.0 (69), 109.0 (7), 122.9 (16), 137.0 (21), 165.0 (100), 179.0 (7), 191.0 (5), 221.1 (14), 235.1 (25), 239.1 (11), 267.1 (7), 295.1 (23)
Vb		10.19 traces	451	41.0 (40), 56.1 (25), 73.0 (31), 83.0 (19), 99.0 (17), 109.0 (12), 123.0 (31), 137.1 (22), 153.0 (20), 165.0 (16), 191.0 (91), 207.0 (100), 235.1 (44), 265.0 (36), 281.0 (31), 321.3 (13), 340.7 (5), 377.3 (5), 395.2 (17)
IVc	35.2	14.31	317	46.9 (16), 51.0 (12), 77.0 (42), 83.0 (12), 125.0 (10), 153.0 (16), 183.0 (12), 201.0 (100), 202.0 (71), 229.0 (42), 288.1 (7), 315.1 (7)
VIc	29.3	15.43	317	51.0 (20), 77.0 (35), 107.0 (6), 137.0 (10), 152.0 (22), 153.0 (11), 183.0 (26), 201.0 (25), 277.0 (100), 278.1 (36)
IVd	33.4	15.26	359	55.0 (15), 76.9 (36), 82.9 (27), 124.9 (10), 153.0 (20), 182.9 (16), 200.9 (90), 201.9 (100), 218.9 (47), 228.9 (45), 257.0 (5), 277.0 (8), 285.0 (16), 301.0 (13), 330.0 (6), 357.1 (7)
VId	–	17.03 traces	359	–

IIIa and 0.83 ppm for **IIIb**), split due to spin–spin coupling with phosphorus (**IIIa**, $^3J_{HP}$ 7.5 Hz) and methine hydrogen (**IIIa**, $^3J_{HH}$ 7.5 Hz). These findings show that the addition of the phosphoryl group occurs by the internal rather than by the terminal carbon atom of the unsaturated fragment (as in the classical Pudovik reaction).

To obtain further evidence for the structure of the reaction products and for a more detailed analysis of

side processes accompanying the catalytic hydrophosphorylation, we investigated the isolated individual compounds and reaction mixtures by means of gas chromatography–mass spectrometry (GC–MS). The mass spectra were obtained under chemical ionization (CI; reactant gas isobutane) and electron impact (EI) and are presented in Table 2. The EI mass spectra show no molecular ion peaks. The CI mass spectra contain strong quasimolecular ion peaks $[M + H]^+$.

The fragmentation patterns of the molecular ions of the phosphorylated carboxylic esters follow general regularities characteristic of esters [2, 3]. At the same time, the presence of the phosphoryl group endows the spectra with some specific features: formation of fragments via P–C bond cleavage followed by further fragmentation of the phosphorus-containing fragment.

The EI mass spectrum of compound **IIIa** characteristically shows $[M - CH_3O]^+$ ion peaks at *m/z* 251 (probably, the acyl-type ion $[(CH_3O)_2P(O)CH(CH_3)\cdot CH_2C(COOCH_3)C{\equiv}O]^+$), peaks of fragment ions formed by loss of the ester groups {$[M - CH(COOMe)_2]^+$, *m/z* 151} and the phosphoryl group {$[(CH_3O)_2P(O)]^+$, *m/z* 109}, and ions formed by further fragmentation of the latter ion {$[(CH_3O)POH]^+$, *m/z* 79}. Note that the formation of *m/z* 109 and 79 fragments is fairly characteristic of dimethoxyphosphinoyl compounds [4–7].

The reaction of dimethyl hydrogen phosphite with dimethyl 2-allylmalonate is less selective (Table 1) than the reaction of diethyl hydrogen phosphite with diethyl 2-allylmalonate [1]. Along with the principal reaction product **IIIa** (65.7% by ^{31}P NMR), a significant fraction (34.3%) of a compound which shows resonance in the region characteristic of phosphonates (δ_P 34.0 ppm) is formed. Its CI mass spectrum shows a quasimolecular ion $[M + H]^+$ peak at *m/z* 225.0, which allows this compound to be assigned structure **IVa** (dealkoxycarbonylation product). The EI mass spectrum contains fragment ions peaks at *m/z* 193 {$[M - CH_3O]^+$, 165 {$[M - COOMe]^+$}, 151 {$[M - CH_2COOMe]^+$}, and 137 {$[M - CH_2CH_2COOMe]^+$}. Such fragmentation patterns are fairly characteristic of dicarboxylic acids [2]. Furthermore, the EI mass spectrum contains peaks of phosphorus-containing fragments at *m/z* 110 $[(CH_3O)_2POH]^+$ and 79 $[CH_3OPOH]^+$, providing evidence for the presence of the dimethoxyphosphinoyl group in this compound.

At the same time, only trace amounts of the isomeric anti-Markovnikov adduct **Va** (δ_P 33.5 ppm) were detected. Compound **Va** was identified by the coincidence of its ^{31}P NMR and CI mass spectra with those of the compound prepared by addition of dimethyl hydrogen phosphite to dimethyl 2-allylmalonate under the conditions of radical initiation with benzoyl peroxide.

Dibutyl hydrogen phosphite reacts with dibutyl 2-allylmalonate with a higher selectivity (84.7%, Table 1), and dealkoxycarbonylation occurs to a minor extent.

The fragmentation of the molecular ion of the main reaction product **IIIb** characteristically involves consecutive loss of butene molecules from the phosphoryl group. The EI mass spectrum contains $[M - COOBu]^+$ (*m/z* 349), $[M - CH(COOBu)_2]^+$ (*m/z* 235), $[(C_4H_9O)P(O)(OH)CHCH_3]^+$ (*m/z* 165), and $[(HO)_2\cdot P(O)CHCH_3]^+$ (*m/z* 109) ion peaks. The EI mass spectrum of dealkoxycarbonylation product **IVb** contains $[M - CH_2COOBu]^+$ (*m/z* 235) and $[(C_4H_9O)P(O)\cdot (OH)CHCH_3]^+$ (*m/z* 165) ion peaks. The result of the reactions of diphenylphosphine oxide with dimethyl and dibutyl 2-allylmalonates was rather unexpected: The dealkoxycarbonylation process here prevailed. The main reaction products were alkyl 4-(diphenyl0 phosphinoyl)- and 5-(diphenylphosphinoyl)hexanoates **IVc**, **IVd** and **VIc**. The mass spectrum of product **IVc** contains a quasimolecular ion peak at *m/z* 317. Fragment ion peaks are observed at *m/z* 229 {$[M - CH_2COOMe]^+$}, 201 {$[Ph_2PO]^+$}, 153 {$[PhP(O)\cdot CH_2CH_3]^+$}, and 77 (Ph^+). Furthermore, the chromatogram of the reaction mixture contains a peak related to the isomeric compound (*m/z* 317, retention time 15.43 min). The regioselectivity of the addition of phosphine oxide to the multiple bond under the applied experimental conditions is much lower than with dialkyl hydrogen phosphites (Table 2).

The reaction of dipenylphosphine oxide with dibutyl 2-allylmalonate proceeds similarly. The main reaction pathway involves formation of compound **IVd** (quasimolecular ion at *m/z* 359). The EI mass spectrum contains peaks at *m/z* 301 {$[Ph_2P(O)CH\cdot (CH_3)CH_2CH_2COO]$}, 285 {$[Ph_2P(O)CH(CH_3)CH_2\cdot CH_2C{-}O]^+$}, 229 {$[Ph_2P(O)CHCH_3]^+$}, 201 {$[Ph_2PO]^+$}, 202 {$Ph_2P(O)H^+$}, 153 {$[PhP(O)CH_2\cdot CH_3]^+$}, and 77 ($Ph^+$).

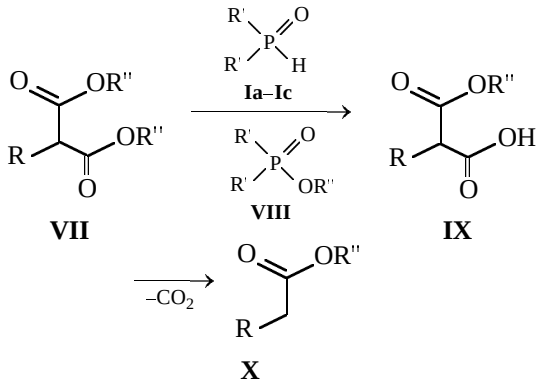
The reaction of diphenylphosphine oxide with dibutyl 2-allylmalonate is characterized by a much higher regioselectivity of the addition of the phosphoryl fragment to the double bond. Product **VId** was detected in trace amounts.

The fact that in some cases the reaction of hydrophosphoryl compounds with 2-allylmalonates proceeds unselectively prompted us to a more detailed study of side processes. There are many reported examples of dealkoxycarbonylation of 2-substituted methyl and ethyl malonates in the presence of nucleo-

philic reagents (potassium fluoride, sodium cyanide, and even such a weak nucleophile as the chloride anion in NaCl) [8–11]. The mechanism of dealkoxycarbonylation proposed in [9] includes nucleophilic attack of the anion on the carbonyl group followed by elimination. However, some weak acids, such as boric [12] and stearic [13], were also successfully applied as dealkoxycarbonylation catalysts. In all the described examples, one of the alkoxycarbonyl groups was eliminated to form the corresponding monocarboxylic acid ester.

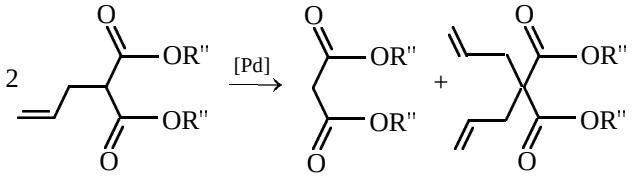
The most interesting case of decarboxylation of malonates (and related compounds) in the presence of transition metal compounds is the formation of palladium π-allyl complexes in the reactions of 2-propylenemalonic acids, their acid amides, 2-propylenecyanoacetic acids, and 2-propyleneacylacetic acids with palladium chloride at room temperature [14]. The reactions involved cleavage of the carboxyl group with simultaneous coordination of the compound (as a π-allyl ligand) to the metal atom.

The reaction mixtures after completion of the catalytic hydrophosphorylation reaction contained products of hydrogen substitution in the hydrophosphoryl group by alkoxy and even alkyl groups of the starting ester. For example, the reaction of dimethyl hydrogen phosphite with dimethyl 2-allylmalonate involved, as a side process, formation of trimethyl phosphate which was identified by the coincidence of its mass spectrum with the spectrum from the NIST Chemistry WebBOOK database [7]. In the reactions of diphenylphosphine oxide with dimethyl and dibutyl 2-allylmalonates, the contents of methyl diphenylphosphinate and butyl diphenylphosphinate were comparable with the content of the main (target) compound. In this connection we consider the most probable the following dealkoxycarbonylation scheme. In the first step, hydrophosphoryl compound **I** (a weak acid) reacts with ester **VII** to form incomplete malonic ester **IX**. Further thermal decarboxylation of compound **IX** proceeds.



After completion of hydrophosphorylation of dimethyl 2-allylmalonate, the chromatogram of the reaction mixture showed three peaks with RT 6.45, 6.84, and 7.41 min. The CI mass spectra contained quasimolecular $[M + H]^+$ ion peaks at *m/z* 213. Along with this base peak, the CI mass spectrum of the first compound contained weak peaks at *m/z* 181 $\{[M - CH_3O]^+\}$ and 153 $\{[M - C_3H_5 \cdot H_2O]^+\}$, and the CI mass spectra of the second and third compounds, peaks at *m/z* 171 $\{[M - C_3H_5]^+\}$ and 153 $\{[M - C_3H_5 \cdot H_2O]^+\}$. In the EI mass spectrum, molecular ions peaks were not observed, and the maximum *m/z* value corresponds to the fragment ion $[M - C_3H_5]^+$ considered above. Among light fragment ions peaks in the EI mass spectra of these compounds, we can mention a strong peak at *m/z* 59, which we assign to the $^+COOCH_3$ ion. These fragments are typical of esters, and a similar peak was registered, e.g., in the mass spectrum of dimethyl malonate. The molecular weights obtained from the CI mass spectra, and the presence of fragment ions formed by loss of the allyl and methoxycarbonyl groups allowed us to identify these products as dimethyl 2,2-diallylmalonate (**XIIa**) and compounds **XIIIa** and **XIVa** formed by isomerization (most probably, carbocyclization) under the action of the palladium complex.

These compounds are most probably formed by "disproportionation" of the parent 2-allylmalonates in the Pd-catalyzed allylic substitution with allyl "transfer" from one 2-allylmalonate molecule to the other.

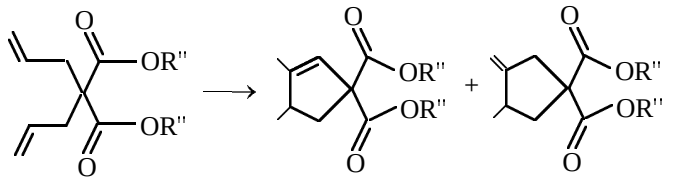


Ia, Ib **XIa, XIb** **XIIa, XIIb**

Evidence for this assumption comes from published data on Pd(0)-catalyzed allylation of malonates, with allyl compounds as a source of the allyl group (allyl acetate, allyl aryl ethers, etc.) [15, 16]. The latter form with the parent Pd(0) complex oxidative addition products (π-allyl complexes) that further react with malonates to afford 2-allylmalonic esters.

Further evidence in favor of allyl migration in 2-allylmalonic esters is provided by the reported isomerization of dimethyl 2-methyl-2-(3-methyl-1-vinylbut-2-enyl)malonate into dimethyl 2-methyl-2-[(2*E*)-5-methylhexa-2,4-dienyl)]malonate on heating with $[Pd(Ph_3P)_4]$ [15]. This reaction can only proceed via C–C bond cleavage. This fact provides convincing evidence for mobility of groups with an allylic double

bond in substituted malonic esters. The 2,2-diallylmalonic ester formed in this reaction undergo further Pd(0)-catalyzed transformations forming cyclic derivatives. Such cyclizations of esters of 2,2-diallyl- [17, 18], 2-allyl-2-(2-bromoallyl)malonic acids [19–21], and related compounds with allyl substituents [22] occur in the presence of transition metal salts and complexes, such as $(CH_3COO)_2Pd$ [17], $[RhCl(Ph_3P)_3]$ [17, 18], $[Pd(Ph_3P)_4]$ [19], catalytic Pd complexes prepared in situ [20–21], and, in some cases, ever without catalyst [22]. Depending on the reaction conditions and catalyst, these reactions afford various isomeric cyclic compounds. A possible route of their formation is follows:



XIIa, XIIb **XIIIa, XIIIb** **XIVa, XIVb**

To confirm our assumptions, we studied transformations of an unsaturated compound, dimethyl 2-allylmalonate, in the presence of a hydrophosphorylation catalyst, but in the absence of a hydrophosphoryl compound, under conditions modeling conditions of such reactions. We found that heating of dimethyl 2-allylmalonate (**Ia**) in the presence of tetrakis(triphenylphosphine)palladium(0) at 120°C for 20 h results in partial transformation of compound **Ia** into dimethyl malonate (**XIa**) and dimethyl 2,2-diallylmalonate (**XIIa**), as follows from the appearance in the ^1H NMR spectrum of additional signals due to the methylene group of dimethyl malonate (singlet at 3.36 ppm) and the allyl group in dimethyl 2,2-diallylmalonate [δ_H, ppm: 5.03 m (CH_2=) and 5.59 m (=CH)], shifted slightly upfield compared to the signals of the related groups in the parent unsaturated compound **Ia** [δ_H, ppm: 5.05 m (CH_2=) and 5.73 m (=CH)]. The conversion of dimethyl 2-allylmalonate was 22%. It is important to note that we observed in this experiment no isomerization of the unsaturated compound with migration of the allylic double bond. Analysis of the reaction mixtures after completion of the hydrophosphorylation reaction also revealed no isomerization of the parent dimethyl 2-allylmalonate. Heating of dimethyl hydrogen phosphite with dimethyl 2-allylmalonate under analogous conditions but without catalyst induced no reactions. Hence, the observed regioselectivity of the hydrophosphorylation reaction is not a result of preliminary isomerization of 2-allylmalonate into 2-propenylmalonate under the action of either the metal complex catalyst or hydrophosphoryl compound, but results from intracoordination transformations in metal complex intermediates.

Thus, the dealkoxycarbonylation reactions observed in all cases, while to quite different extents, most probably directly involve the hydrophosphoryl compound and is primarily controlled by its nature. Cyclization processes contribute little into the overall reaction, but they present interest in terms of further research into the synthesis of cyclic phosphorylated derivatives on the basis of 2,2-diallylmalonic esters.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were registered on a Brucker AC 200 at 200.13 (^1H) and 80.01 (^{31}P) MHz, solvent $CDCl_3$. The chemical shifts were measured in ppm relative to TMS (^1H) and 85% H_3PO_4 (^{31}P). The measurements were performed without additional reference compounds, and the signals frequencies were related to residual proton signals of the deuterated solvent.

The GC–MS analysis of the reaction mixtures and isolated individual compounds was carried out on a Finnigan Trace DCQ instrument with a BPX-5 30 × 0.32 capillary column (SGE). Injector temperature 280°C, transfer line temperature 300°C, temperature program: from 80°C (1 min) to 320°C (5 min) at a rate of 15°C/min.

Conditions of EI ionization: 70 eV, ion source temperature 200°C. Conditions of chemical ionization: 120 eV, ion source temperature 200°C, reactant gas isobutane (flow rate 0.4 ml/min). Conditions of direct inlet analysis: DEP probe (fast evaporation from a platinum wire), heating rate 200°C/s, chemical ionization with isobutane.

Dimethyl 2-allylmalonate and dibutyl 2-allylmalonate were synthesized according to [23], dimethyl hydrogen phosphate, according to [24], diphenylphos-

phine oxide, according to [25], and tetrakis(triphenylphosphine)palladium(0), according to [26].

Hydrophosphorylation of unsaturated compounds was carried out by heating in the presence of 2 mol% of $[Pd(Ph_3P)_4]$ in a dry ampule purged with argon for 20 h at 120°C. Analysis of the reaction mixtures was performed using ^{31}P NMR spectroscopy and GC–MS. Compounds **IIIa** and **IIIb** were isolated by vacuum fractionation.

Dimethyl 2-[2-(dimethoxyphosphinoyl)propyl]malonate (IIIa) was prepared from 1.05 g dimethyl hydrogen phosphite and 1.03 g of dimethyl 2-allylmalonate in the presence of 219 mg of $[Pd(Ph_3P)_4]$, yield 451 mg (26.7%), bp 131°C (3 mm Hg). ^1H NMR spectrum, δ, ppm: 0.98 d.d (CH_3CH, 3H, J_{HH} 7.5, J_{HP} 7.5 Hz), 1.59–1.75 m [$CH_2CH\cdot(COOMe)_2$, 2H], 2.59 m (CH, 1H), 3.66?3.70 m [CH_3O, 12H, $CH(COOMe)_2$, 1H].

Dibutyl 2-[2-(dibutoxyphosphinoyl)propyl]malonate (IIIb) was prepared from 2.30 g of dibutyl hydrogen phosphite and 3.04 g of dibutyl 2-allylmalonate in the presence of 274 mg of $[Pd(Ph_3P)_4]$, yield 1.09 g (20.4%), bp 175°C (3 mm Hg). ^1H NMR spectrum, δ, ppm: 0.83 t (CH_3, 12H, J_{HH} 7.1 Hz), 0.96 d.d (CH_3CH, 3H, J_{HH} 7.5, J_{HP} 7.5 Hz), 1.27 m (CH_2, 8H, J_{HH} 7.0 Hz), 1.53 m (CH_2, 8H, J_{HH} 7.0 Hz), 1.66 m [$CH_2CH(COOBu)_2$, 2H], 2.51 m (CH, 1H), 3.67 m [$CH(COOBu)_2$, 1H], 3.91 m (CH_2O, 4H), 4.03 m (CH_2O, 4H).

Radical reaction of hydrophosphoryl compounds with dimethyl 2-allylmalonate *(general procedure).* A mixture of hydrophosphoryl compound, 15.3 mmol, and 15.3 mmol of dialkyl 2-allylmalonate was heated under argon in the presence of 3.10 mmol of a radical initiator (benzoyl peroxide or AIBN) at 100°C for 10 h or illuminated with unfiltered light of a DT-220 high-pressure mercury lamp for 20 h. According to ^{31}P NMR data, the conversion in the reaction of dimethyl hydrogen phosphite with dimethyl 2-allylmalonate was 60.4% and in the reaction of diphenylphosphine oxide with dimethyl 2-allylmalonate 79.5% (UV initiation) or 100% (AIBN initiation).

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 04-03-32 632a) and Administration of St. Petersburg (project no. PD06-1.3-61).

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