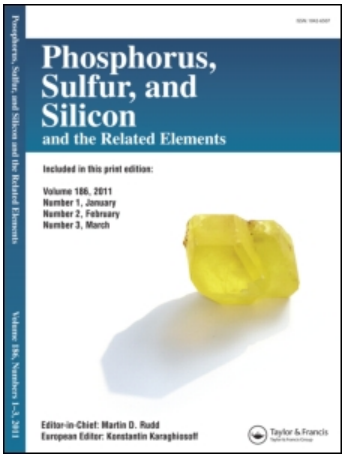

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Synthesis and Dynamic NMR Study of Atropisomerism in Stable 1,4-Diionic Phosphorus Compounds

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SYNTHESIS AND DYNAMIC NMR STUDY OF ATROPISOMERISM IN STABLE 1,4-DIIONIC PHOSPHORUS COMPOUNDS

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The addition of triphenylphosphine to acetylenic ketones in the presence of strong CH-acids, such as Meldrom's acid, N,N′*-dimethylbarbituric acid, dimedone, or indane-1,3-dione leads to 1,4-diionic organophosphorus compounds. Dynamic NMR study of these stable betaines show an unusually high sixfold energy barrier for rotation around the* sp^2-sp^3 *carbon-carbon single bond, which leads to an observable atropisomerism.*

Keywords: Acetylenic ketone; CH-acid; restricted rotation; stereochemistry; triphenylphosphine

INTRODUCTION

Organophosphorus compounds, that is, those bearing a carbon atom directly bound to a phosphorus atom, are synthetic targets of interest, not least because of their value for a variety of industrial, biological, and chemical synthetic uses.[1–3] As a result, a large number of methods have appeared describing novel syntheses of organophosphorus compounds. A number of reactions have been observed which involve 1,4-diionic phosphorus compounds as elusive transient species.[4–6] In all of the reactions in which this diionic system is postulated, the betaine cannot be isolated but appears to occur as an intermediate on the pathway to an observed product.

We have recently described[7–10] the synthesis of stable 1,4-diionic compounds from the reaction of triphenylphosphine and electron-deficient acetylenic esters in the presence of strong CH-acids. With

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the purpose of preparing betaines from electron-defficient acetylenic ketones, we performed the reaction of triphenylphosphine with ethynyl methyl or ethynyl phenyl ketone in the presence of strong CH-acids. Thus, reaction of the acetylenic ketone **1** with triphenylphosphine in presence of CH-acids, such as Meldrom's acid, *N*,*N*′-dimethylbarbituric acid, dimedone, or indane-1,3-dione, in dichloromethane as solvent, leads to betaines **3** in excellent yields (Scheme 1).

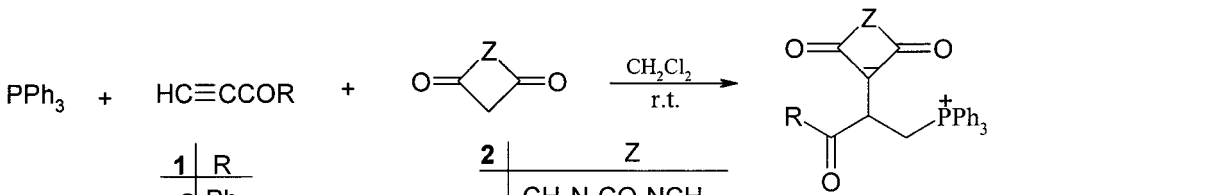
RESULTS AND DISCUSSION

This three component reaction produces the hitherto unknown phosphorus betaines **3a–h** in 76–95% yields. All the compounds are stable crystalline solids whose structures are fully supported by elemental analyses and IR, high-field ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and mass spectrometry.

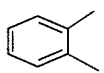
On the basis of the well established chemistry of phosphorus nucleophiles[2,3] it is reasonable to assume that betaine **3** results from initial addition of triphenylphosphine to the acetylenic ketone **1** and subsequent protonation of the reactive 1:1 adduct, followed by attack of the carbon atom of the anion of the CH-acid to the vinyltriphenylphosphonium cation **4** to generate ylide **5** which apparently isomerises, under the reaction conditions employed, to produce the 1,4-diionic compound **3** (Scheme 2).

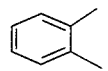
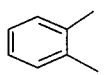
NMR spectroscopy was employed to distinguish structure **3** from the primary product, the ylide **5**. Thus, the ^{1}H NMR spectrum of each isolated product showed a methine and two diastereotopic methylene proton signals at about $\delta = 3.5$–5.5. Further evidence was obtained from the ^{13}C NMR spectra which displayed a CH_2—P doublet ($^{1}J_{CP} =$ 52–57 Hz) at about $\delta = 20$–23. Structure **3** was further confirmed by the ^{13}C NMR data for the CH-acid residue which exhibits local C_2 symmetry at ambient temperature. A cyclic six-membered ring structure for compound **3** is unlikely because it requires several chemical shift coincidences in the ^{1}H, and ^{13}C NMR spectra. If compound **3** had a cyclic structure, then we were to expect a doublet at about $\delta = 160$ for the *C*—O—P moiety in the ^{13}C NMR spectra. Moreover, the ^{31}P NMR spectra of compounds **3a–h** displayed signals at about $\delta = 23$–25 (downfield from 85% H_3PO_4). These shifts are similar to those observed for alkyltriphenylphosphonium iodide.[11,12] The ^{31}P chemical shift for a cyclic six-membered ring structure having a P—O bond is expected to be 80–90 ppm more shielded.[11–13,22]

Although the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra[12] of **3a–h**, it helps in assignment of the signals by

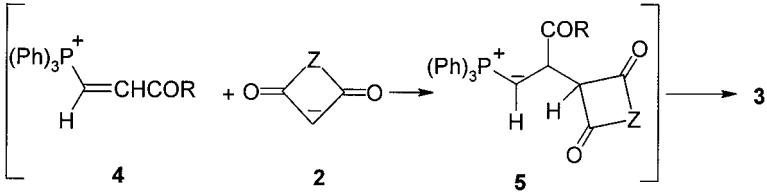


1	R
a	Ph
b	Me

2	Z
a	CH_3N-CO-NCH_3
b	O-$C(CH_3)_2$-O
c	CH_2-$C(CH_3)_2$-CH_2
d	

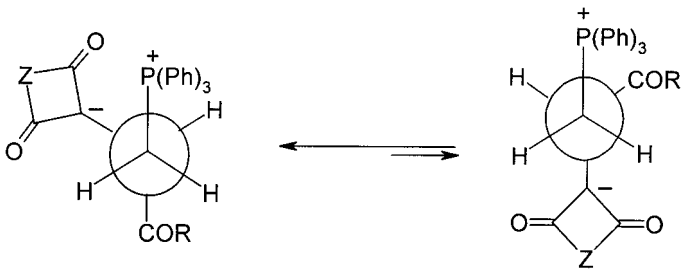
3	R	Z	%Yield
a	Ph	CH_3N-CO-NCH_3	93
b	Ph	O-$C(CH_3)_2$-O	86
c	Ph	CH_2-$C(CH_3)_2$-CH_2	83
d	Ph		76
e	Me	CH_3N-CO-NCH_3	95
f	Me	O-$C(CH_3)_2$-O	85
g	Me	CH_2-$C(CH_3)_2$-CH_2	83
h	Me		77

SCHEME 1



SCHEME 2 R = Me, Ph.

long-range coupling with ^{1}H and ^{13}C nuclei (see Experimental section). Of particular interest are the three-bond carbon-phosphorus coupling constants, $^{3}J_{CP}$, which provide information about the P—CH_2—C—C torsion. The $^{3}J_{CP}$ depends on conformation, as expected, *transoid* coupling being larger than *cisoid* ones. The Karplus relation can be derived from the data for organophosphorus compounds with tetra- and pentacoordinated phosphorus.[14] The observation of $^{3}J_{CP}$ of 9.7–13.7 Hz for the *C*=O group (see Experimental section), is in agreement with the *anti* arrangement of the P—CH_2—C—C(O) moiety (see Scheme 3). The $^{3}J_{CP}$ for the $C(CO)_2$ group is 1.2–4.8 Hz, which corresponds to a *gauch* arrangement.



SCHEME 3 R = Me, Ph.

The most noteworthy feature of the ^{1}H NMR spectrum of 2-(*N*,*N*′-dimethylbarbituric acid-5-yl-5-ylid)-1-phenyl-3-triphenylphosphoniopropanone (**3a**) in $CDCl_3$ at room temperature (25°C) is the *N*,*N*′-dimethyl barbituric acid residue which exhibits a slightly broad singlet (δ = 2.99 ppm) for the N—CH_3 groups. Near 50°C the broad line becomes sharper. Decreasing the temperature results in the splitting of the broad N—CH_3 resonance into a doublet with an intensity ratio of 1:1 (coalescence temperature, −18 ± 1°C). At −60°C, two fairly sharp singlets ($\Delta\nu$ = 135 Hz) are observed for the N—CH_3 groups.

TABLE I Selected Proton Chemical Shifts (in ppm, Me_4Si) and Activation Parameters ($kJmol^{-1}$) for **3a–c** and **3g** in $CDCl_3$

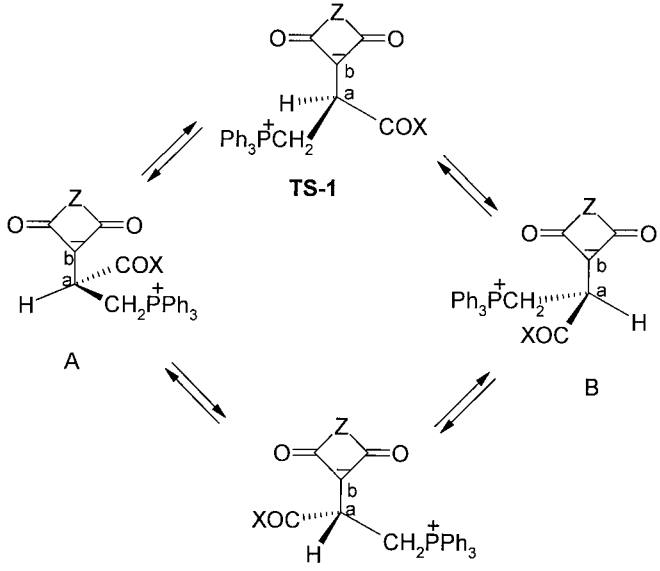
Compound	Temp (°C)	Resonance		$\Delta\nu$ (Hz)	k (s^{-1})	T_C (K)	$\Delta G^{\#}$
		NMe					
3a	25	2.99					
	−70	2.83	3.10	135	300	255	48.0 ± 2
		CMe_2					
3b	25	1.15					
	−70	0.87	1.29	210	466	258	49.6 ± 2
3c	25	0.61					
	−60	0.22	0.68	230	510	255	48.8 ± 2
3g	25	0.89					
	−60	0.82	0.73	46	102	246	50.3 ± 2

Although an extensive line–shape analysis in relation to the dynamic ^1H NMR effect observed for **3a** was not undertaken, the variable temperature spectra allowed to calculate the free energy barrier (if not the enthalpy and entropy of activation) for the dynamic NMR process in **3a**. From coalescence of the N-Me proton resonances and using the expression, $k = \pi\Delta\nu/\sqrt{2}$, we calculate that the first–order rate constant (k) for the dynamic NMR effect in **3a** is 300 s^{-1} at −18°C. Application of the absolute rate theory with a transmission coefficient of 1 gives a free–energy of activation ($\Delta G^{\#}$) of 48.0 ± 2 $kJmol^{-1}$, where all known sources of errors are estimated and included.[15] The experimental data available are not suitable for obtaining meaningful values of $\Delta H^{\#}$ and $\Delta S^{\#}$, even though the errors in $\Delta G^{\#}$ are not large.[16]

Similar dynamic ^1H NMR effects were observed for the CMe_2 proton resonances in **3b**, **3c**, and **3g**. The free-energy of activation obtained for these compounds are similar to that of **3a** (see Table I). The ^1H NMR spectrum of the indane-1,3-diione residue of compound **3d** at −60°C exhibits a complicated unsymmetrical pattern resulting from an ABCD spin system.

The barrier to rotation around the C_a—C_b bond in compounds **3a–h** is sixfold, as a result of the presence of the local C_2 axis in the plane of the ring (see Scheme 4). Sixfold barriers in general tend to be very low;[17] for example, that in nitromethane, which also has a local C_2 axis along the C—N bond of the nitro group, is about 25 $Jmol^{-1}$.[18] Methyl rotation in toluene is also nearly free the barrier being only 59 $Jmol^{-1}$.[19]

Since H is appreciably smaller than the COX and $CH_2P^+Ph_3$ groups (see Scheme 4), only conformers **A** and **B** need be considered, plus the lower of the two barriers between them, and the situation then formally resembles that in biphenyls with two maxima and two minima.



SCHEME 4 X = Me, Ph.

CONCLUSION

The reaction of ethynyl methyl ketone or ethynyl phenyl ketone with triphenylphosphine in the presence of CH-acids, such as Meldrum's acid, *N*,*N*′-dimethylbarbituric acid, dimedone, or indane-1,3-diione provides a simple one-pot entry into the synthesis of stable crystalline 1,4-diionic organophosphorus compounds of potential interest. The present method carries the advantage that, not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modification. Dynamic NMR effects are observed in the ^{1}H NMR spectra of compounds **3a–c** and **3g** and are attributed to restricted rotation around the C—C single bond between the CH-acid residue and the rest of the molecule.

EXPERIMENTAL

Melting points were measured on an electrothermal 9100 apparatus. Elemental analyses for the C, H, and N were performed using a Heraeus

CHN-O-Rapid analyzer. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz respectively. ^{1}H, ^{13}C, and ^{31}P spectra were obtained on solutions in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard. Ethynyl phenyl ketone was prepared by addition of ethynylmagnesium bromide to benzaldehyde[20] and oxidation[21] of the obtained propargylic alcohol. Other chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and are used without further purification.

Preparation of 2-(*N,N′*-dimethylbarbituric acid-5yl-5-ylid)-1-phenyl-3-triphenylphosphoniopropanone 3a

General Procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and *N*,*N*′-dimethyl barbituric acid (0.14 g, 1 mmol) in dichloromethane (10 mL) was added dropwise a mixture of ethynyl phenyl ketone (0.13 g, 1 mmol) in dichloromethane (5 mL) at −5°C over 2 min. After 2 h the solvent was removed at reduced pressure. The solid residue was washed with diethyl ether (3 × 10 mL) and recrystallized from chloroform-ethyl acetate. Yellow crystals, m.p. 210–212°C (decomp.), 0.51g, yield 93%. Analysis: Calc. for $C_{33}H_{29}N_2O_4P$ (548.3): C, 72.28; H, 5.29; N, 5.11%; found: C, 72.1; H, 5.2; N, 5.0. IR (KBr) (ν_{max}, cm^{-1}): 1649 (C=O ketone), 1578 (2NC=O), 1422 (N_2C=O); δ_H($CDCl_3$): 3.00 (6H, s, 2 CH_3), 3.84 (1 H, ddd $^{2}J_{HH}$ 15.0 Hz, $^{3}J_{HH}$ 2.7 Hz, $^{2}J_{HP}$ 12.1 Hz, CH of PCH_2), 4.09 (1 H, ddd $^{2}J_{HH}$ 15.0 Hz, $^{3}J_{HH}$ 10.4 Hz, $^{2}J_{HP}$ 10.7 Hz, CH of PCH_2), 5.15 (1 H, ddd $^{3}J_{HH(anti)}$ 10.4 Hz, $^{3}J_{HH(gauche)}$ 2.7 HZ, $^{3}J_{HP}$ 9.9 Hz, CH), 7.2–8.0 (20 H, m, 4 C_6H_5). δ_c ($CDCl_3$): 22.5 (d, $^{1}J_{CP}$ 56.0 Hz, CH_2P), 27.1 (2 CH_3), 39.8 (CH), 85.7 [d $^{3}J_{CP}$ 2.3 Hz, $C(CO)_2$], 119.2 (d $^{1}J_{CP}$ 86.8 Hz, C_{ipso} of Ph_3P), 127.9 and 128.3 (CH of C_6H_5CO), 128.1 (d $^{3}J_{CP}$ 13.1 Hz, C_{meta} of Ph_3p), 131.2 (CH of C_6H_5CO), 133.7 (d $^{2}J_{CP}$ 9.9 Hz, C_{ortho} of Ph_3P), 134.4 (d $^{4}J_{CP}$ 2.8 Hz, C_{para} of Ph_3P), 135.9 (CH of C_6H_5CO), 153.0 (N—CO—N), 162.2 (2 C=O), 199.7 (d $^{3}J_{CP}$ 12.8 Hz, *C*OPh). δ_P ($CDCl_3$): 24.08 (Ph_3P^+-C); MS (*m/z*, %): 548 (M^+, 1), 286 (M^+ - PPh_3, 27), 262 (PPh_3, 100), 183 ($C_{12}H_8P$, 95), 77 (Ph, 93).

Selected data for 2-(isopropylidenemalonate-5-yl-5-ylid)-1-phenyl-3-triphenylphosphoniopropanone ***3b***. White crystals, m.p. 190–193°C (decomp.), 0.46 g, yield 86%. Analysis: Calc. for $C_{33}H_{29}O_5P$ (536.3): C, 73.88; H, 5.41% found: C, 73.7; H, 5.3. IR (KBr) (ν_{max}, cm^{-1}): 1677 (C=O ketone), 1587 (C=O ester); δ_H ($CDCl_3$): 1.15 (6 H, s, 2 CH_3), 3.98–4.02 (2 H, m, CH_2P), 4.91–4.96 (1 H, m, CH), 7.28–7.85 (20 H, m, 4 C_6H_5).

δ_C ($CDCl_3$): 22.2 (d $^1J_{CP}$ 53 Hz), 25.8 (2 CH_3), 39.9 (CH), 73.9 [d $^3J_{CP}$ 4 Hz, *C*$(CO)_2$], 101.0 (*C*Me_2), 119.4 (d $^1J_{CP}$ 86.6 Hz, C_{ipso} of Ph_3P), 127.9 and 128.2 (CH of C_6H_5CO), 129.9 (d $^3J_{CP}$ 12.6 Hz, C_{meta} of Ph_3P), 131.9 (CH of C_6H_5CO), 133.7 (d $^2J_{CP}$ 9.8 Hz, C_{ortho} of Ph_3P), 134.4 (d $^4J_{CP}$ 2.8 Hz, C_{para} of Ph_3P), 136.4 (CH of C_6H_5CO), 165.5 (2 C=O), 199.5 (d $^3J_{CP}$ 10.7 Hz, COPh). δ_p ($CDCl_3$): 24.33 (Ph_3P^+-C); MS. (*m/z*, %): 262 (PPh_3, 51), 274 (M^+ -PPh_3, 5), 183 ($C_{12}H_8P$, 15), 105 (PhCO, 100).

Selected data for2-(5,5-dimethycyclohexane-1,3-dione-2yl-2-ylid)-1-phenyl-3-triphenylphosphoniopropanone ***3c***. White crystals, m.p. 110°C (decomp.), 0.44 g, yield 83%. Analysis: Calc. for $C_{35}H_{33}O_3P$ (532.3): C, 78.95; H, 6.20% found: C, 78.6; H, 6.3. IR (KBr) (ν_{max}, cm^{-1}): 1660 (C=O of PhCO), 1477 (C=O); δ_H ($CDCl_3$): 0.61 (6 H, s, 2 CH_3), 1.68 (2 H, d $^2J_{HH}$ 16 Hz, 2CH), 1.89 (2 H, d $^2J_{HH}$ 16 Hz, 2CH, 3.65 (1 H, ddd $^2J_{HH}$ 15.4 Hz, $^3J_{HH}$ 8.2 Hz, $^2J_{PH}$ 10.3 Hz, CH of CH_2P), 4.07 (1 H, ddd $^2J_{HH}$ 15.4 Hz, $^3J_{HH}$ 4.5 Hz, $^2J_{PH}$ 12.2 Hz, CH of CH_2P), 5.09 (1H, ddd $^3J_{HH(gauche)}$ 4.5 Hz, $^3J_{HH(anti)}$ 8.2 Hz, $^3J_{PH}$ 10.6 Hz, CH), 7.22–7.83 (20 H, m, 4 C_6H_5). δ_C ($CDCl_3$): 22.1 (d, $^1J_{CP}$ 52 Hz, CH_2P), 28.9 (C*M*e$_2$), 31.3 (CMe_2), 39.1 (CH), 49.3 (CH_2), 109.0 [d $^3J_{CP}$ 4.8 Hz, *C*(CO_2)], 120.2 (d $^1J_{CP}$ 86.6 Hz, C_{ipso} of Ph_3P), 127.6 and 128.4 (CH of C_6H_5CO), 129.8 (d $^3J_{CP}$ 13 Hz, C_{meta} of Ph_3P), 131.6 (CH of C_6H_5CO), 133.7 (d $^2J_{CP}$ 9.9 Hz, C_{ortho} of Ph_3P), 134.2 (d $^4J_{CP}$ 2.8 Hz, C_{para} of Ph_3P), 136.7 (CH of C_6H_5CO), 189.3 (2 C=O), 201.7 (d $^3J_{CP}$ 9.7 Hz, *C*OPh), δ_p ($CDCl_3$): 24.19 (Ph_3P^+-C); MS (*m/z*, %): 270 (M^+ - PPh_3, 17), 262 (PPh_3, 95), 183 ($C_{12}H_8P$, 100), 105 (PhCO, 95).

Selected data for 2-(indane-1,3-dione-2yl-2-ylid)-1-phenyl-3-triphenylphosphoniopropanone ***3d***. Yellow crystals, m.p. 137–138°C (decomp.), 0.41 g, yield 76%. Analysis: Calc. for $C_{36}H_{27}O_3P$ (538.3); C, 80.30; H, 5.02%; found: C, 80.2; H, 5.1. IR (KBr) (ν_{max}, cm^{-1}): 1671 (CO of PhCO), 1533 (C=O); δ_H ($CDCl_3$): 3.78 (1 H, ddd $^3J_{HH}$ 3.3 Hz, $^2J_{HH}$ 15.1 Hz, $^3J_{HP}$ 11.6 Hz, CH of CH_2P), 4.19 (1 H, ddd $^2J_{HH}$ 15.1 Hz, $^3J_{HH}$ 10.4 Hz, $^2J_{HP}$ 10.8 Hz, CH of CH_2P), 4.88 (1 H, ddd $^3J_{HH(gauche)}$ 3.3 Hz, $^3J_{HH(anti)}$ 10.4 Hz, $^3J_{PH}$ 9.9 Hz, CH), 7.0–8.0 (24 H, m, 4 C_6H_5 and C_6H_4), δ_c ($CDCl_3$): 22.7 (d, $^1J_{CP}$ 55.2 Hz, CH_2P), 37.1 (CH), 100.4 [d $^3J_{CP}$ 1.2 Hz, *C*$(CO)_2$], 117.5(CH of C_6H_5CO), 118.8 (d $^1J_{CP}$ 86.6 Hz, C_{ipso} of Ph_3P), 128.0 (CH of C_6H_4), 128.8 and 129.2 (CH of C_6H_5CO), 129.8 (d $^3J_{CP}$ 13 Hz, C_{meta} of Ph_3P), 132.4 (CH of C_6H_5CO), 133.6 (d $^2J_{CP}$ 9.9 Hz, C_{ortho} of Ph_3P), 134.2 (d $^4J_{CP}$ 2.8 Hz, C_{para} of Ph_3P), 135.3 (CH of C_6H_4), 139.7 (CH of C_6H_4), 189.6 (2 C=O), 197.1 (d $^3J_{CP}$ 12.3 Hz, *C*OPh). δ_p ($CDCl_3$): 24.11 (Ph_3P^+-C); MS (*m/z*, %): 538 (M^+, 1), 262 (PPh_3, 95), 183 ($C_{12}H_8P$, 100), 105 (PhCO, 55), 108 (PhP, 60).

Selected data for 2-(N,N′-dimethylbarbituric acid-5yl-5-ylid)-1-methyl-3-triphenylphosphoniopropanone ***3e***. Yellow crystals, m.p. 150–151°C (decomp.), 0.92 g, yield 95%. Analysis: Calc. for $C_{28}H_{27}N_2O_4P$ (486.3); C, 69.13; H, 5.59; N, 5.75%; found: C, 69.1.; H, 5.6; N, 5.7 IR (KBr) (ν_{max}, cm^{-1}): 1704 (C=O ketone), 1653 (2 NC=O), 1565 (N_2C=O), 1428 (P–Ph), 1103 (P–Ph), 998 (P–Ph).δ_H ($CDCl_3$): 1.97 (3 H, s, CH_3), 3.00 (6H, s, 2 CH_3), 3.72 (1H, ddd $^2J_{HH}$ 15.4 Hz, $^3J_{HH(anti)}$ 9.5 Hz, $^2J_{HP}$ 11.9 Hz, CH of PCH_2), 3.76 (1H, ddd $^3J_{HP}$ 11.3 Hz, $^3J_{HP(gauche)}$ 3.84 Hz, $^2J_{HP}$ 11.9 Hz, CH of PCH_2), 4.2 (1H, ddd, $^3J_{HP}$ 11.3 Hz, $^3J_{HH(anti)}$ 9.0 Hz, $^3J_{HH(gauche)}$ 3.77 Hz, CH), 7.45–7.7 (15 H, m, 3 C_6H_5). δ_c ($CDCl_3$): 21.26 (d, $^1J_{CP}$ 56.7 Hz, CH_2P), 25.95 (d, $^4J_{CP}$ 11.8 Hz, CH_3), 26.66 (N-CH_3), 43.00 (d, $^2J_{CP}$ 6.7 Hz, CH), 84.35 [d, $^3J_{CP}$ 2.6 Hz, $C(CO)_2$], 118.56 (d, $^1J_{CP}$ 86.8 Hz, C_{ipso} of Ph_3P), 129.14 (d, $^3J_{CP}$ 12.4 Hz, C_{meta} of Ph_3P), 133.1 (d, $^2J_{CP}$ 9.8 Hz C_{ortho} of Ph_3P), 133.89 (d, $^4J_{CP}$ 2.8 Hz, C_{para} of Ph_3P), 152.56 (N–CO–N), 162.2 (2 C=O), 208.59 (d $^4J_{CP}$ 13.2 Hz, $COCH_3$). δ_P ($CDCl_3$): 23.7 (Ph_3P^+-C). MS (*m/z*, %): 486 (M^+, 1), 262 (PPh_3, 65), 224 (M–CH_3CO, 15), 183 ($C_{12}H_8P$, 100), 108 (PPh, 95), 43 (CH_3CO, 22).

Selected data for 2-(isopropylidenemalonate-5-yl-ylid)-1-methyl-3-triphenylphosphoniopropanone ***3f***. White crystals, m.p. 160°C (decomp.) 0.8 g, yield 85%. Analysis: Calc. for $C_{28}H_{27}O_5P$ (474.3): C, 70.87; H, 5.73%; found: C, 70.6; H, 5.7. IR (KBr) (ν_{max}, cm^{-1}): 1699 (C=O ketone), 1653, (C=O ester), 1579 (Ph), 1430 (P–Ph), 1203 (C–O ester), 1105 (P–Ph), 990 (P–Ph). δ_H ($CDCl_3$): 1.45 (6H, s, 2 CH_3), 2.1 (3 H, s, CH_3) 3.69 (1H, ddd $^2J_{HH}$ 15.6 Hz, $^2J_{HP}$ 11.2 Hz, $^3J_{HH(anti)}$ *8.9 Hz*, CH of CH_2P), 3.93 (1H, ddd, $^2J_{HH}$ 15.6 Hz, $^2J_{HP}$ 12.6 Hz, $^3J_{HH(gauche)}$ 3.67 Hz, CH_2P), 4.00 (1H, ddd, $^3J_{HP}$ 12.7 Hz, $^3J_{HH(anti)}$ 8.8 Hz, $^3J_{HH(gauche)}$ 3.67 Hz, CH), 7.5–7.8 (15H, m, 3 C_6H_5). δ_C ($CDCl_3$): 21.24 (d, $^1J_{CP}$ 53.8 Hz, CH of CH_2P), 25.64 ($2CH_3$), 26.31 (CH_3), 43.44 (d, $^2J_{CP}$ 2.9 Hz, CH), 72.23 [d, $^3J_{CP}$ 3.8 Hz, $C(CO)_2$], 100.7 (CMe_2), 119.0 (d, $^1J_{CP}$ 9.8 Hz, C_{ipso} of Ph_3P), 129.48 (d, $^3J_{CP}$ 12.5 Hz, C_{meta} of Ph_3P), 133.10 (d, $^2J_{CP}$ 9.8 Hz, C_{ortho} of Ph_3P), 133.98 (d, $^4J_{CP}$ 2.8 Hz, C_{para} of Ph_3P), 165.66 (2 C=O), 208.61 (d, $^4J_{CP}$ 11.2 Hz, C=O). δ_P ($CDCl_3$): 24.33 (Ph_3P^+-C). MS (*m/z*, %): 262 (PPh_3, 95), 183 ($C_{12}H_8P$, 100), 108 (PPh, 80), 43 (CH_3CO, 93).

Selected data for 2-(5,5-dimethylcyclohexane-1,3-dione-2-yl-2-ylid)-1-methyl-3-triphenylphosphoniopropanone ***3g***. White crystals, m.p. 117–119°C (decomp.), 0.81 g, yield 85%. Analysis: Calc. for $C_{30}H_{31}O_3P$ (470.3); C, 76.57; H, 6.64%; found: C, 76.3; H, 6.6. IR (KBr) (ν_{max}, cm^{-1}): 1690 (C=O, H_3C–C=O), 1652, 1564 (2 C=O), 1475 (Ph), 1423 (P–Ph), 1105 (P–Ph), 990 (P–Ph). δ_H ($CDCl_3$): 0.84 (6H, s, $2CH_3$), 1.69 (2H, d, $^2J_{HH}$ 15.7 Hz, CH_2), 1.87 (2H, d, $^2J_{HH}$ 15.9 Hz, CH_2), 1.88 (3H, s, CH_3), 3.5 (1H, ddd, $^2J_{HH}$ 15.6 Hz, $^2J_{HP}$ 11.1 Hz, $^3J_{HH(anti)}$ 9.0 Hz, CH of

CH_2P), 3.9 (1H, ddd, $^3J_{HH}$ 15.5 Hz, $^2J_{HP}$ 14.5 Hz, $^3J_{HH(gauche)}$ 3.83 Hz, CH of CH_2P), 4.23 (1H, ddd, $^3J_{HP}$ 11.8 Hz, $^3J_{HH(anti)}$ 8.7 Hz, $^3J_{HH(gauche)}$ 3.8 Hz, CH), 7.5–7.7 (15H, m, 3 C_6H_5). δ_C ($CDCl_3$): 20.74 (d, $^1J_{CP}$ 53.7 Hz, CH_2P), 26.04 (d, $^4J_{CP}$ 5.2 Hz, H_3C—C=O), 28.45 [$C(CH_3)_2$], 30.87 (2Me), 41.85 (CH), 49.31 ($2CH_2$), 107.05 [d, $^3J_{CP}$ 3.9 Hz, $C(CO)_2$], 119.63 (d, $^1J_{CP}$ 86.9 Hz C_{ipso} of Ph_3P), 129.24 (d, $^3J_{CP}$ 121.5 Hz, C_{meta} of Ph_3P), 133.13 (d, $^2J_{CP}$ 9.9 Hz, C_{ortho} of Ph_3P), 133.65 (d, $^4J_{CP}$ 2.6 Hz, C_{para} of Ph_3P), 189.96 (2 C=O), 209.44 (d, $^4J_{CP}$ 11.06 Hz, C=O). δ_p ($CDCl_3$): 24.51 (Ph_3P^+-C). MS (*m/z*, %): 470 (M^+, 1), 262 (PPh_3, 100), 183 ($C_{12}H_8P$, 55), 108 (PPh, 15), 43 (CH_3CO, 18).

Selected data for 2-(indane-1,3-dione-2-yl-2-yild)-1-methyl-3-triphenylphosphoniopropanone ***3h***. Yellow crystals, m.p. 120–121°C (decomp.), 0.72 g, yield 75%. Analysis: Calc. for $C_{31}H_{28}O_3P$ (476.3): C, 77.64; H, 5.88%; found: C, 77.7; H, 5.8. IR (KBr) (ν_{max}, cm^{-1}): 1693 (H_3C—C=O), 1636, 1602 (2C=O), 1528 (Ph), 1423 (P—Ph), 1104 (P—Ph), 991 (P—Ph). δ_H ($CDCl_3$): 2.0 (3H, s, CH_3), 3.7 (1H, m, CH of CH_2P), 3.8–4.1 (2H, m, CH, CH_2P), 7.0–7.7 (19H, m, 3 C_6H_5, C_6H_4). δ_c ($CDCl_3$): 20.6 (d, $^1J_{CP}$ 56.4 Hz, CH of CH_2P), 26.55 (H_3C—C=O), 40.67 (d, $^2J_{CP}$ 2.0 Hz, CH), 99.87 [d, $^3J_{CP}$ 2.4 Hz, $C(CO)_2$], 116.89 (CH of C_6H_4), 118.07 (d, $^1J_{CP}$ 86.65 Hz, C_{ipso} of Ph_3P), 128.80 (CH of C_6H_4), 129.34 (d, $^3J_{CP}$ 12.6 Hz, C_{meta} of Ph_3P), 133.00 (d, $^2J_{CP}$ 10.2 Hz, C_{ortho} of Ph_3P), 133.78 (d, $^4J_{CP}$ 2.8 Hz, C_{para} of Ph_3P), 139.24 (C_{ipso} of C_6H_4), 189.76 (2 C=O), 207.6 (d, $^4J_{CP}$ 13.3 Hz, C=O) δ_p ($CDCl_3$): 24.18 (Ph3P+-C). MS (*m/z*, %): 476 (M^+, 1), 262 (PPh_3, 82), 183 ($C_{12}H_8P$, 100), 108 (PhP, 65), 43 (CH_3CO, 71).

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