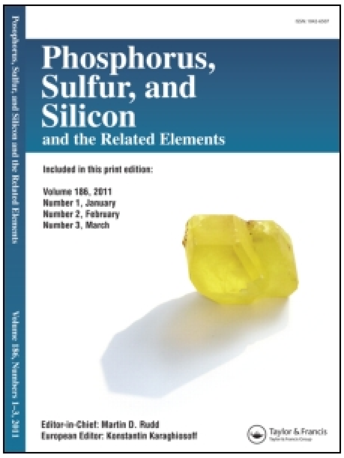

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CONVENIENT PREPARATION OF UNSYMMETRICALLY SUBSTITUTED BENZILS BY PERMANGANATE OXIDATION OF β-OXO PHOSPHORUS YLIDES

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CONVENIENT PREPARATION OF UNSYMMETRICALLY SUBSTITUTED BENZILS BY PERMANGANATE OXIDATION OF β-OXO PHOSPHORUS YLIDES

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Oxidative cleavage of a range of ylides **4** with R^1 and/or R^2 being aromatic groups, using $KMnO_4$ in a two-phase system, affords unsymmetrical benzils and 1-arylpropane-1,2-diones **5** in moderate to good yield, and the ylide formation and oxidation can be combined in a convenient one-pot method.

Key words: Phosphorus ylides, oxidation, 1,2-diketones, benzils, permanganate, oxoalkylidenetriphenylphosphoranes.

The formation and oxidative cleavage of β-oxoalkylidenetriphenylphosphoranes **4** provides convenient access to unsymmetrical 1,2-diketones **5**, allowing the overall coupling of an alkyl halide **1** with an acid chloride **3** to give the product in three steps. The oxidative cleavage of **4** to **5**[1] has been performed using a wide variety of reagents since it was first reported by Ramirez and coworkers using ozone in 1960.[2] Other oxidants used in early studies include peracetic acid,[3] benzoyl peroxide,[4] ethyl nitrite,[5] lead tetraacetate, iodobenzene diacetate and lead dioxide,[6] and sodium periodate.[7] More recently both triphenylphosphite ozonide[8] and *N*-sulfonyloxaziridines[9] have been reported to bring about the same transformation in excellent yield. There has been renewed interest in 1,2,3-tricarbonyl compounds since the discovery of this function in the immunosuppressant FK-506, and oxidative cleavage of α,α′-dioxo phosphorus ylides using singlet oxygen, ozone[10] and potassium peroxymonosulfate ("Oxone®")[11] has been used to gain access to α,β-dioxoesters and amides in this connection and also for synthesis of alkaloids[12] and bicyclomycin.[13] The corresponding reaction of ozone with sulfonium-,[14] pyridinium-,[15] and iodonium ylides[16] to produce 1,2,3-triones was also reported by Schank some years earlier.

In 1968 Zbiral and Rasberger[17] described the use of potassium permanganate in a two-phase system to oxidise six examples of ylides **4** with $R^1 = Pr^n$ and R^2 a variety of aliphatic groups. In this paper we report the successful extension of the $KMnO_4$ method to oxidative cleavage of a range of ylides **4** with R^1 and/or R^2 being aromatic groups which provides unsymmetrical benzils and 1-arylpropane-

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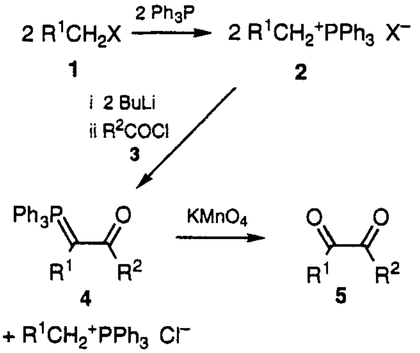

1,2-diones in good yield, and furthermore the combination of ylide formation and oxidation in a one-pot method.

The required ylides **4** were readily prepared in moderate to good yield by acylation of the appropriate ylides, generated from the phosphonium salts **2** and butyllithium, with acid chlorides **3** (0.5 equiv.).[18] Twelve examples with different aryl groups R^1 and R^2 were prepared for the first time and showed the expected spectroscopic and analytical properties.

The ylides were subjected to oxidation, using the conditions described by Zbiral and Rasberger,[17] by stirring with excess $KMnO_4$ in a two phase system of toluene and water in the presence of magnesium sulfate. Even at 50–60°C the reactions were slow requiring from 20–120 h for maximum conversion. After the appropriate time, separation of the organic phase, evaporation and removal of the triphenylphosphine oxide by chromatography afforded the desired 1,2-diketones **5** in moderate to good yield (Table I).

Although the procedure was generally satisfactory, some limitations were discovered. Thus ylide **4e** with the strongly electron withdrawing dinitrophenyl group failed to give any of the diketone, presumably due to the low electron density at the ylide carbon atom. A range of examples **4** with $R^1 = CO_2Me$ were also examined but these were recovered unchanged even after prolonged reaction times, again due to excessive delocalisation of the electron density by the second carbonyl group. This observation, which rules out the use of this method to obtain α,β-dioxoesters, contrasts with the use of singlet oxygen, oxone® or ozone which are successful for these cases.[11,12]

The cinnamoyl ylide **4o** also gave no useful products with only benzaldehyde being identified, clearly resulting from oxidative cleavage of the C=C double bond. The compound **4** (R^1 = Ph, R^2 = CH=CHPh) gave a similar result and this is consistent with the previous observation[17] that the method was unsuccessful for a crotonyl ylide. For these cases it is again preferable to use singlet oxygen or oxone® which are compatible with the presence of an alkene double bond.[11]

The function of the magnesium sulfate described in the literature procedure[17] is not clear but it is obviously beneficial since attempts to either omit it or replace it by a classical phase transfer catalyst, benzyltriethylammonium chloride, resulted in a substantial reduction in yield in the oxidation of **4a**. It most likely acts as a buffer to prevent the aqueous layer becoming too strongly basic during the course of the reaction.

TABLE I

Oxidation of ylides **4** to give α-diketones **5**

	R^1	R^2	Reaction time, h	Yield of **5** %	m.p. °C	lit. m.p. °C
a	Ph	Ph	20	96	95–96	94–95^{19}
a'	Ph	Ph	45	70‡	"	"
b	Ph	$\text{4-NO}_2\text{C}_6\text{H}_4$	30	65	140–141	141–142^{20}
c	Ph	$\text{2-NO}_2\text{C}_6\text{H}_4$	72	58	98–99	102^{21}
d	Ph	$\text{3-NO}_2\text{C}_6\text{H}_4$	120	30	115–117	120^{21}
e	Ph	$\text{2,4-(NO}_2)_2\text{C}_6\text{H}_3$	150	~0		
f	Ph	$\text{4-MeC}_6\text{H}_4$	70	63	26–28	31^{22}
g	Ph	$\text{2,4,6-(Me)}_3\text{C}_6\text{H}_2$	70	17	135–137	137^{22}
h	Ph	$\text{4-ClC}_6\text{H}_4$	72	52	71–73	73^{22}
i	Ph	$\text{4-BrC}_6\text{H}_4$	40	42	81–83	86.5^{22}
j	Ph	Me	40	43	b.p.$_{16}$ 118–120	b.p.$_{20}$ 126–128^{23}
k	Me	Ph	40	42	"	"
l	Me	$\text{4-MeC}_6\text{H}_4$	24	43	b.p.$_{17}$ 115–118	b.p.$_5$ 117–120^{24}
m	Me	$\text{4-ClC}_6\text{H}_4$	40	39	36–38	35–36^{25}
n	Me	$\text{4-BrC}_6\text{H}_4$	24	20	44–47	46^{26}
o	Me	PhCH=CH	70	0		
p	$\text{4-ClC}_6\text{H}_4$	Ph	40	74	71–73	73^{22}
q	$\text{4-ClC}_6\text{H}_4$	$\text{4-MeC}_6\text{H}_4$	50	62	122–124	116–117^{27}
r	$\text{4-BrC}_6\text{H}_4$	Ph	50	50	83–84	86.5^{22}
s	$\text{4-BrC}_6\text{H}_4$	$\text{4-MeC}_6\text{H}_4$	50	53	129–131	136–137^{28}
t	$\text{4-BrC}_6\text{H}_4$	$\text{4-ClC}_6\text{H}_4$	60	74‡	197–199	203–204^{29}

‡ Overall yield from **2** and **3** using one-pot method.

A general problem encountered in the preparation of stabilised ylides such as **4** is that they are often reluctant to crystallise in pure form from the oil obtained on evaporation of the reaction solution. Since they are hydrolysed on attempted chromatography and decompose on attempted sublimation, the only available option is trituration which can result in poor yields of pure product from what is inherently a high yielding reaction. Since the solvent used for preparation and oxidation of **4** was the same we decided to investigate direct oxidation of the crude ylide solution without isolation. Thus the toluene solution from reaction of **2** with **3** was filtered to remove the unwanted quaternary phosphonium salt, $KMnO_4$, $MgSO_4$ and water were added and the oxidation was performed as usual. In the case of **4a** this gave benzil in a yield equivalent to that obtained by isolating the ylide and then oxidising it separately. This one-pot method was then applied to a case **4t** in which the ylide could not readily be obtained in pure form, and gave excellent results with the diketone **5t** obtained in 74% overall yield from **2** and **3**.

In summary we have demonstrated that the use of $KMnO_4$ in a two phase system gives good results for the oxidation of a variety of ylides **4** containing aromatic groups, R^1 and/or R^2, to provide convenient access to unsymmetrically substituted benzils and 1-arylpropane-1,2-diones in reasonable overall yield from alkyl halides **1** and acid chlorides **3**. The efficiency of the sequence can be further enhanced by combining the ylide preparation and oxidation in a one-pot procedure. The method is not, however, suitable for the more highly stabilised ylides with strongly electron withdrawing groups R^1 or for examples containing an alkene double bond.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were obtained on Nujol mulls. NMR spectra were recorded at 100 MHz for ^1H and at 32 MHz for ^{31}P, both on solutions in $CDCl_3$. Coupling constants are in Hz. Mass spectra were obtained using electron impact at 70 eV. Dry toluene was freshly distilled from sodium.

Preparation of β-Oxoalkylidenetriphenylphosphoranes **4**. A solution of the appropriate quaternary phosphonium chloride **2** (25 mmol) in dry toluene (100 ml) was stirred under N_2 while *n*-butyllithium in hexane (25.5 mmol) was added. After 15 min a solution of the appropriate acid chloride **3** (12.5 mmol) in dry toluene (10 ml) was added dropwise and the resulting mixture stirred for 3 h. It was then filtered and the filtrate evaporated to give a solid which was recrystallised from ether/hexane to give the product. If evaporation gave an oil, crystallisation was induced by trituration with ether. Using this procedure the following ylides **4** were prepared:

(α-Benzoyl-α-phenylmethylene)triphenylphosphorane **4a** as colourless crystals (72%), m.p. 188–190°C (lit.,[18] 192–194°C); δ_P +15.7.

(α-4-Nitrobenzoyl-α-phenylmethylene)triphenylphosphorane **4b** as orange crystals (61%), m.p. 231–233°C (Found: C, 76.4; H, 5.0; N, 2.5. $C_{32}H_{24}NO_3P$ requires C, 76.6; H, 4.8; N, 2.8%); ν_{max}/cm^{-1} 1596, 1542, 1510, 1438, 1347, 1252, 1109, 967, 867, 762, 727, 711 and 698; δ_H 7.94 (2 H, half of AB pattern, *J* 8), 7.65–7.35 (17 H, m) and 6.95–6.8 (5 H, m); δ_P +17.0; m/z 501 (M^+, 100%), 454 (2), 379 (20), 351 (5), 349 (4), 337 (5), 303 (5), 277 (25), 262 (33), 223 (33), 201 (23), 183 (35) and 77 (76). Preparation of this compound has been described briefly but it was not characterised.[30]

(α-2-Nitrobenzoyl-α-phenylmethylene)triphenylphosphorane **4c** as orange crystals (50%), m.p. 191–193°C (Found: C, 76.8; H, 5.0; N, 2.8. $C_{32}H_{24}NO_3P$ requires C, 76.6; H, 4.8; N, 2.8%); ν_{max}/cm^{-1} 1612, 1577, 1520, 1350, 1242, 1140, 1108, 1005, 963, 846, 760, 745, 723, 701 and 694; δ_H 7.8–7.4 (15 H, m), 7.4–7.15 (4 H, m) and 6.95–6.8 (5 H, m); δ_P +16.6; m/z 501 (M^+, 1.2%), 453 (0.4), 396 (1), 379 (1), 367 (26); 277 (11), 262 (100), 183 (21), 108 (14), 105 (54) and 77 (15).

(α-3-Nitrobenzoyl-α-phenylmethylene)triphenylphosphorane **4d** as orange crystals (50%), m.p. 235–237°C (Found: C, 76.8; H, 4.7; N, 2.7. $C_{32}H_{24}NO_3P$ requires C, 76.6; H, 4.8; N, 2.8%); ν_{max}/cm^{-1} 1595, 1575, 1500, 1351, 1310, 1254, 1145, 1105, 1002, 970, 913, 898, 833, 825, 725 and 695; δ_H 8.31 (1 H, m), 7.99 (1 H, m), 7.8–7.35 (15 H, m), 7.3–7.2 (2 H, m) and 6.96–6.85 (5 H, m); δ_P +17.1; m/z 501 (M^+, 18%), 379 (4), 277 (8), 262 (6), 223 (6), 201 (4), 183 (10), 165 (4), 150 (2) and 78 (100).

(α-2,4-Dinitrobenzoyl-α-phenylmethylene)triphenylphosphorane **4e** as orange crystals (33%), m.p. 229–230°C (Found: C, 70.4; H, 4.2; N, 5.4. $C_{32}H_{23}N_2O_5P$ requires C, 70.3; H, 4.2; N, 5.1%); ν_{max}/cm^{-1} 1597, 1548, 1522, 1350, 1155, 1108, 1030, 967, 902, 749, 725, 715, 705 and 693; δ_H 8.59 (1 H, d, *J* 2), 8.09 (1 H, dd, *J* 8, 2), 7.7–7.4 (16 H, m) and 6.95–6.8 (5 H, m); δ_P +17.2; m/z 546 (M^+, 0.7%), 379 (1), 367 (21), 277 (19), 262 (100), 201 (7), 183 (23), 105 (45) and 77 (18).

(α-4-Methylbenzoyl-α-phenylmethylene)triphenylphosphorane **4f** as colourless crystals (77%), m.p. 239–240°C (Found: C, 84.3; H, 5.7. $C_{33}H_{27}OP$ requires C, 84.2; H, 5.8%): ν_{max}/cm^{-1} 1596, 1575, 1496, 1262, 1182, 1133, 1108, 974, 833, 750 and 699; δ_H 7.65–7.55 (6 H, m), 7.45–7.3 (11 H, m), 6.91 (1 H, s), 6.88 (6 H, m) and 2.21 (3 H, s); δ_P +15.4; m/z 470 (M^+, 100%), 379 (6), 277 (8), 262 (28), 201 (7), 192 (48), 183 (23), 165 (11), 119 (16), 108 (10), 91 (10) and 78 (18).

(α-Phenyl-α-2,4,6-trimethylbenzoylmethylene)triphenylphosphorane **4g** as pale brown crystals (50%), m.p. 138–140°C (Found: C, 84.15; H, 6.1. $C_{35}H_{31}OP$ requires C, 84.3; H, 6.3%); ν_{max}/cm^{-1} 1590,

1440, 1262, 1194, 1178, 1113, 1030, 1000, 972, 858, 799, 753, 725 and 697; δ_H 7.75–7.6 (6 H, m), 7.5–7.3 (9 H, m), 6.77 (5 H, s), 6.58 (2 H, s), 2.31 (6 H, s) and 2.11 (3 H, s); δ_P +15.1; m/z 498 (M^+, 0.01%,), 497 (0.03), 478 (0.02), 278 (94), 277 (100), 201 (36), 199 (22), 185 (17), 183 (24), 152 (13) and 77 (62).

(α-4-Chlorobenzoyl-α-phenylmethylene)triphenylphosphorane **4h** as colourless crystals (20%), m.p. 241–242°C (Found: C, 78.5; H, 5.0. $C_{32}H_{24}ClOP$ requires C, 78.3; H, 4.9%); ν_{max}/cm^{-1} 1590, 1572, 1502, 1255, 1173, 1131, 1110, 1018, 972, 860, 838, 752, 727 and 697; δ_H 7.65–7.3 (17 H, m), 7.1–7.0 (2 H, m) and 6.92–6.8 (5 H, m); δ_P +16.1; m/z 492 (^{37}Cl-M^+, 39%), 490 (^{35}Cl-M^+, 100), (15), 351 (5), 337 (4), 303 (4), 277 (13), 262 (28), 214 (25), 212 (75), 201 (18), 183 (28) and 139 (8).

(α-4-Bromobenzoyl-α-phenylmethylene)triphenylphosphorane **4i** as pale yellow crystals (32%), m.p. 248–249°C (Found: C, 71.7; H, 4.5. $C_{32}H_{24}BrOP$ requires C, 71.8; H, 4.5%); ν_{max}/cm^{-1} 1588, 1570, 1500, 1443, 1437, 1260, 1174, 1130, 1107, 1070, 1014, 972, 858, 834, 750, 718 and 696; δ_H 7.65–7.2 (19 H, m) and 6.93–6.8 (5 H, m); δ_P + 16.2; m/z 536, 534 (M^+, 40, 40%), 379 (8), 277 (27), 262 (48), 258 (29), 256 (29), 201 (23), 183 (46), 165 (23), 108 (17) and 77 (100).

(α-Acetyl-α-phenylmethylene)triphenylphosphorane **4j** as colourless crystals (75%), m.p. 162–166°C (lit.,[18] 166–168°C); δ_P +15.6.

(α-Benzoylethylidene)triphenylphosphorane **4k** as colourless crystals (80%), m.p. 162–164°C (lit.,[18] 170–172°C); δ_P +17.8.

(α-4-Methylbenzoylethylidene)triphenylphosphorane **4l** as colourless crystals (81%), m.p. 175–177°C (lit.,[31] 176–177°C); δ_P +17.6.

(α-4-Chlorobenzoylethylidene)triphenylphosphorane **4m** as yellow crystals (25%), m.p. 172–173°C (lit.,[31] 175–176°C); δ_P +18.3.

(α-4-Bromobenzoylethylidene)triphenylphosphorane **4n** as pale brown crystals (37%), m.p. 187–190°C (lit.,[31] 193–194°C); δ_P +18.2.

(α-Cinnamoylethylidene)triphenylphosphorane **4o** as yellow crystals (60%), m.p. 205–207°C; (lit.,[18] 205–208°C); δ_P +18.7.

(α-Benzoyl-α-4-chlorophenylmethylene)triphenylphosphorane **4p** as yellow crystals (10%), m.p. 248–249°C (Found: C, 78.5; H, 5.2. $C_{32}H_{24}ClOP$ requires C, 78.3; H, 4.9%); ν_{max}/cm^{-1} 1587, 1504, 1370, 1268, 1253, 1132, 1112, 1105, 1093, 1032, 974, 869, 796, 763, 730, 724 and 695; δ_H 7.56–7.21 (17 H, m), 7.17–7.05 (3 H, m) and 6.82 and 6.72 (4 H, AB pattern, *J* 8); δ_P + 15.7; m/z 492 (^{37}Cl-M^+, 15%), 490 (^{35}Cl-M^+, 40), 415 (2), 413 (6), 277 (66), 262 (100), 212 (41), 201 (30), 183 (76), 108 (32), 105 (38), 78 (57) and 77 (55).

(α-4-Chlorophenyl-α-4-methylbenzoylmethylene)triphenylphosphorane **4q** as pale yellow crystals (51%), m.p. 240–241°C (Found: C, 78.7; H, 5.4. $C_{33}H_{26}ClOP$ requires C, 78.5; H, 5.2%); ν_{max}/cm^{-1} 1614, 1578, 1370, 1310, 1258, 1182, 1132, 110, 1090, 972, 872, 837, 823, 765, 750, 727, 722, and 695; δ_H 7.65–7.3 (17 H, m), 6.95–6.7 (6 H, m) and 2.27 (3 H, s); δ_P +15.5; m/z 506 (^{37}Cl-M^+, 32%), 504 (^{35}Cl-M^+, 76), 415 (3), 413 (11), 277 (51), 262 (74), 228 (34), 226 (100), 201 (4), 183 (87), 91 (34), 78 (77) and 77 (47).

(α-Benzoyl-α-4-bromophenylmethylene)triphenylphosphorane **4r** as pale yellow crystals (64%), m.p. 245–246°C (Found: C, 71.95; H, 4.6. $C_{32}H_{24}BrOP$ requires C, 71.8; H, 4.5%); ν_{max}/cm^{-1} 1580, 1260, 1250, 1125, 1108, 1101, 1070, 1028, 1007, 968, 790, 758, 725, 712, 705 and 689; δ_H 7.65–7.3 (17 H, m), 7.15–7.10 (3 H, m) and 6.98 and 6.68 (4 H, AB pattern, *J* 8); δ_P +15.7; m/z 536 and 534 (^{81}Br- and ^{79}Br-M^+, 54%), 459 (7), 457 (10), 303 (6), 277 (26), 262 (45), 258 (45), 256 (45), 183 (55), 165 (25), 105 (36) and 78 (100).

(α-4-Bromophenyl-α-4-methylbenzoylmethylene)triphenylphosphorane **4s** as pale yellow crystals (71%), m.p. 234–236°C (Found: C, 72.4; H, 4.9. $C_{33}H_{26}BrOP$ requires C, 72.3; H, 4.8%); ν_{max}/cm^{-1} 1607, 1572, 1435, 1365, 1260, 1179, 1120, 1100, 1072, 1008, 968, 835, 817, 752, 740, 715 and 693; δ_H 7.67–7.3 (17 H, m), 6.99 and 6.92 (4 H, AB pattern, *J* 8), 6.68 (2 H, m) and 2.27 (3 H, s); δ_P + 15.4; m/z 550 and 548 (^{81}Br- and ^{79}Br-M^+, 32%), 469 (3), 459 (4), 457 (4), 272 (32), 270 (35), 262 (38), 183 (46), 119 (34), 108 (18), 91 (26) and 78 (100).

Oxidation of Ylides **4** *to give α-Diketones* **5**. A mixture of the ylide **4** (0.5 mmol), potassium permanganate (0.15 g, 0.95 mmol), anhydrous magnesium sulfate (0.5 g), toluene (20 ml) and water (20 ml) was stirred vigorously at 50–60°C until TLC showed disappearance of the starting ylide. The organic layer was then separated, washed with water, dried over $MgSO_4$ and evaporated. The residue was purified by rapid column chromatography on silica using Et_2O to remove most of the Ph_3PO, followed by extraction with hexane which left any remaining phosphine oxide and unreacted ylide undissolved. Individual reaction times, yields and m.p. or b.p. of the products **5** are given in Table I.

One-Pot Procedure for Preparation and Oxidation of Ylides **4**. The standard procedure for formation of **4** was followed as above up to the stage of filtering the reaction mixture. The filtrate was then directly stirred with magnesium sulfate (12.0 g), potassium permanganate (3.6 g, 23 mmol) and water (40 ml) until reaction was complete as judged by TLC. Work up as above gave the products **5**. Individual reaction times, yields and m.p. or b.p. of the products are given in Table I.

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