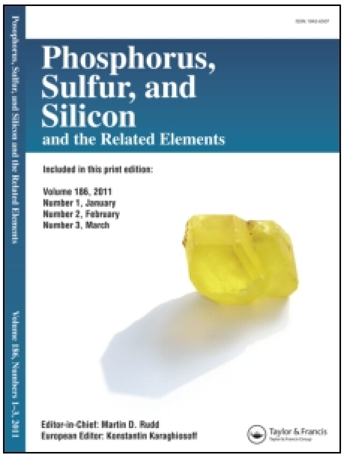

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CHEMISTRY OF PHOSPHORUS YLIDES 17. REACTIONS WITH PHOSPHACUMULENES X. THE BEHAVIOUR OF PHOSPHACUMULENES TOWARDS *o*-AND *p*-QUINONES. FACILE SYNTHESIS OF CYCLOBUTANEDIONE DERIVATIVES

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CHEMISTRY OF PHOSPHORUS YLIDES 17.[1] REACTIONS WITH PHOSPHACUMULENES X. THE BEHAVIOUR OF PHOSPHACUMULENES TOWARDS *o*- AND *p*-QUINONES. FACILE SYNTHESIS OF CYCLOBUTANEDIONE DERIVATIVES

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Dedicated to Professor H. J. Bestmann on the occasion of his 69th birthday

(Received October 17, 1994; in final form August 3, 1995)

The reactions of the active phosphacumulenes, (2-oxovinylidene)- (**7a**) and (2-thioxovinylidene)triphenylphosphorane (**7b**) with several *o*- (**8**, **12**, **14**, **16**) and *p*-quinones (**18**, **20**, **22**, **24**) have been studied. Phosphoranylidene-cyclobutanediones (**11a**, **13a**, **15a**, **17a**, **19a**, **21a**, **23a**, **25a**) and dithioxocyclobutylidenes (**11b**, **13b**, **15b**, **17b**, **19b**, **21b**, **23b**, **25b**) were obtained and identified on the basis of elemental analysis and spectroscopic studies.

Key words: Quinones, phosphacumulenes, cyclobutanediones, dithioxocyclobutylidenes.

INTRODUCTION

Bestmann[2] reported on the reactions of stabilized phosphonium ylides with *o*- and *p*-quinones. He found that alkoxycarbonylmethylenetriphenylphosphorane (**1**) do not undergo a double Wittig reaction with *o*-benzoquinone (**2**). Instead, monocarbonyl olefination takes place, followed by Michael addition of a second phosphorane molecule and elimination of triphenylphosphine, then alcohol to give the coumarin (**3**). In some cases cyclization occurs with the formation of the coumaran derivatives (**4**).[3,4] On the other hand, *p*-quinones (**5**) react with the stabilized phosphonium ylides (**1**) to give the corresponding complicated phosphonium ylide (**6**)[2] (Scheme I). The reaction of active phosphacumulenes (**7**) with aldehydes and ketones has been reported by Bestmann,[5] too. 1,3-cyclobutanediones have been isolated as reaction products.

The behaviour of active phosphacumulenes towards *o*- and *p*-quinones has not been investigated. Therefore, we have now studied the reaction of the active (2-oxovinylidene)-(**7a**) and (2-thioxovinylidene)triphenylphosphorane (**7b**) with tetrachloro-1,2-benzoquinone (**8**), acenaphthenequinone (**12**), 9,10-phenanthraquinone (**14**), 3,4-diphenylcyclo-butenedione (**16**), tetrachloro-1,4-benzoquinone (**18**), 2,5-diphenyl-*p*-benzoquinone (**20**), 9,10-anthraquinone (**22**) and 2,3-dimethyl-9,10-anthraquinone (**24**), and compared the reactivities of the active cumulative ylides (**7**) with those of known stabilized ylides (**1**) towards the above mentioned *o*- and *p*-quinones.

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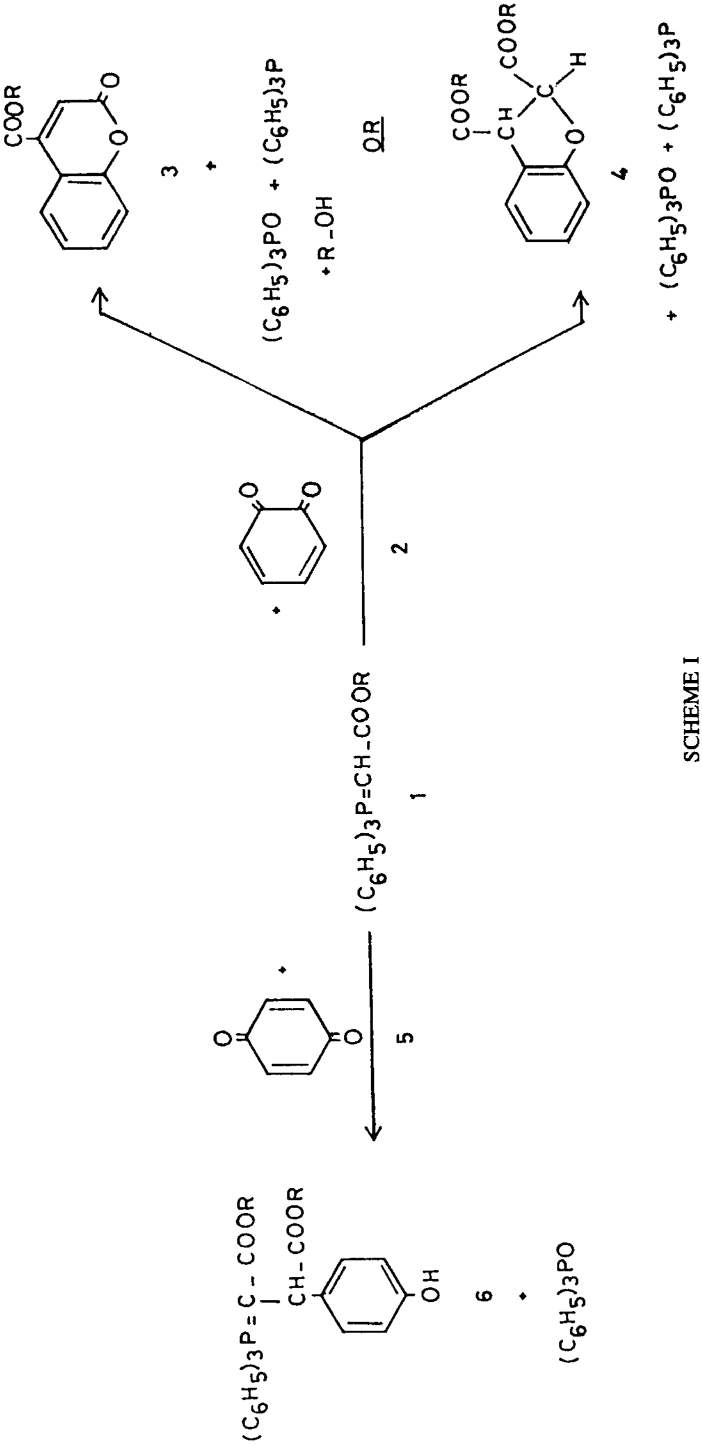
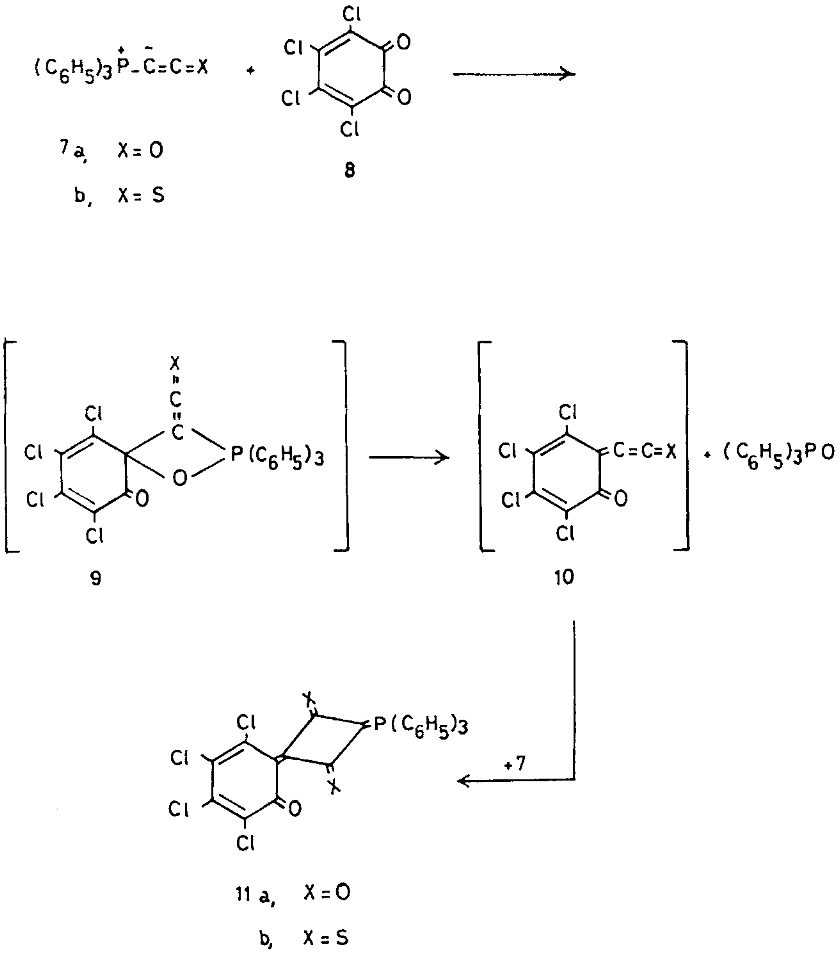
† Author to whom correspondence should be addressed.


(C6H5)3P=CH-COOR
1
2
5
COOR
3
+ (C6H5)3PO + (C6H5)3P
+ R-OH
OR
COOR
CH
COOR
C
H
O
4
+ (C6H5)3PO + (C6H5)3P
(C6H5)3P = C - COOR
CH-COOR
OH
6
+ (C6H5)3PO

SCHEME I



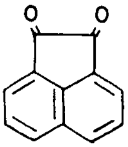
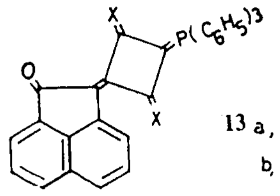
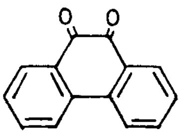
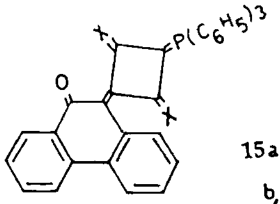
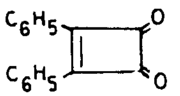
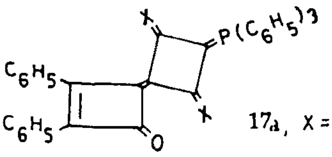
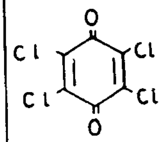
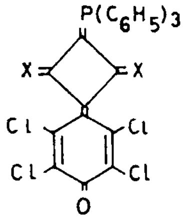
SCHEME II

RESULTS AND DISCUSSION

We have found that the reaction of two moles of (2-oxovinylidene)triphenylphosphorane (**7a**) with one mole of tetrachloro-1,2-benzoquinone (**8**) or tetrachloro-1,4-benzoquinone (**18**) proceeds in tetrahydrofuran at room temperature to give triphenylphosphine oxide with the corresponding phosphoranylidene-cyclobutanedione derivative (**11a**) or (**19a**), respectively. Carrying out the reactions using four moles of the active phosphorane (**7a**) instead of two, against one mole of the quinone (**8** or **18**), led to the formation of the same cyclobutanedione derivatives, (**11a** or **19a**) along with some unchanged phosphorane (**7a**). Structural support for compound **11a** was based upon the following evidences: (a) Correct elementary analysis and molecular weight determination (MS) were recorded. (b) The IR spectrum showed strong absorption bands at 1720, 1705 (C=O), 1620 (C=P) and 1440 (P-phenyl).[6]

TABLE I

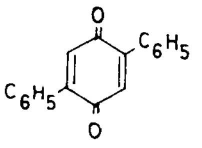
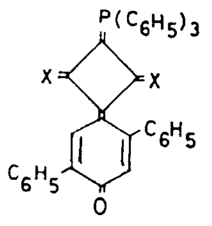
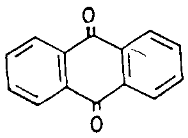
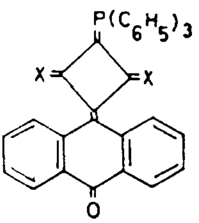
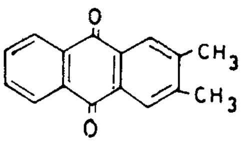
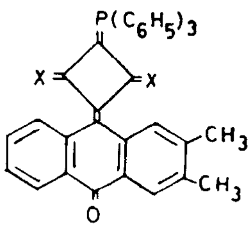
Phosphoranylidene-cyclobutanediones (**13a**, **15a**, **17a**, **19a**, **21a**, **23a**, **25a**) and Dithioxocyclobutylidenes (**13b**, **15b**, **17b**, **19b**, **21b**, **23b**, **25b**) resulted from the reaction of *o*- and *p*-quinones with the active phosphacumulenes

o -and p- Quinones	Phosphoranylidenecyclobutane Derivatives
 12	 13 a, X = O b, X = S
 14	 15a, X = O b, X = S
 16	 17a, X = O b, X = S
 18	 19a, X = O b, X = S

A signal at δ 22.55 was observed in the ^{31}P NMR of (**11a**) which fits with phosphorane with a four membered ring.[7] On the other hand, the IR, spectrum of the *p*-chloranil phosphoranylidene-cyclobutanedione derivative (**19a**) showed strong absorption bands at 1670, 1640 (C═O), 1620 (C═P) and 1440 (P-phenyl). Moreover, a signal at δ 23.7 was observed in its ^{31}P NMR.

(2-Thioxovinylidene)triphenylphosphorane (**7b**) was found to react with tetrachloro-1,2-benzoquinone (**8**) or tetrachloro-1,4-benzoquinone (**18**), in boiling toluene, to give triphenylphosphine oxide along with the corresponding phosphoranylidene-dithioxocyclobutylidenes (**11b**) or (**19b**). Elemental analysis and molecular weight determination (MS) of compound (**11b**) agreed with the molecular formula $C_{28}H_{15}Cl_4OPS_2$. Its IR revealed the presence of strong absorption bands at 1730

TABLE I (*Continued*)

 20	 21a, X = O b, X = S
 22	 23a, X = O b, X = S
 24	 25a, X = O b, X = S

(C=O), 1660 (C=P), 1440 (P-phenyl) and 1250 (C=S).[6] The distinguishing features of the ^{13}C NMR spectrum of (**11b**) were the presence of signals at δ 174 (C=S) and 170 (C=O), and the ^{31}P NMR shift recorded was δ + 22.16. On the other hand, the structure of the dithioxocyclobutylidene derivative (**19b**) was verified through spectroscopic results. Its ^{13}C NMR spectrum showed signals at δ 193 (C=S) and 180.5 (C=O). The ^{31}P NMR signal appears at δ 23.82 and the IR spectrum revealed the presence of strong absorption bands at 1680 (C=O), 1580 (C=P), 1440 (P-phenyl) and 1250 (C=S).

When acenaphthenequinone (**12**) 9,10-phenanthraquinone (**14**), 3,4-diphenylcyclobutenedione (**16**), 2,5-diphenyl-*p*-benzoquinone (**20**), 9,10-anthraquinone (**22**) and/or 2,3-dimethyl-9,10-anthraquinone (**24**) were allowed to react with the active phosphacumulenes (**7a,b**) under the same previous experimental conditions, the new phosphoranylidenecyclobutanediones (**13a**, **15a**, **17a**, **21a**, **23a**, **25a**) and dithioxocyclobutylidenes (**13b**, **15b**, **17b**, **21b**, **23b**, **25b**) were isolated.

CONCLUSION

The reaction of active phosphacumulenes (**7a,b**) with *o*- and *p*-quinones represents an interesting approach for the preparation of cyclobutane derivatives. For example,

TABLE II

Physical and analytical data for phosphoranylidene-cyclobutanediones and dithioxocyclobutylidenes (**11**, **13**, **15**, **17**, **19**, **21**, **23** and **25**)

Compound	**Yield**	**m.p.**	**Mol. Form.**	**Anal. Calcd / found %**				
	in %	**°C**	**(M.Wt.)**	**C**	**H**	**Cl**	**P**	**S**
11_a	70	198^a	$C_{28}H_{15}O_3Cl_4P$	58.74	2.62	24.82	5.42	-
			(572)	58.96	2.59	24.00	5.87	-
13_a	55	183^b	$C_{34}H_{21}O_3P$	80.31	4.13	-	6.10	-
			(508)	79.94	4.24	-	6.20	-
15_a	60	295^c	$C_{36}H_{23}O_3P$	80.89	4.30	-	5.80	-
			(534)	80.64	4.35	-	5.94	-
17_a	60	173^c	$C_{38}H_{25}O_3P$	81.43	4.46	-	5.53	-
			(560)	81.10	4.34	-	5.29	-
19_a	75	178^c	$C_{28}H_{15}O_3Cl_4P$	58.74	2.62	24.82	5.42	-
			(572)	59.03	2.81	24.61	5.80	-
21_a	65	227^b	$C_{40}H_{27}O_3P$	81.91	4.60	-	5.29	-
			(586)	81.69	4.74	-	5.50	-
23_a	60	164^c	$C_{36}H_{23}O_3P$	80.89	4.30	-	5. 80	-
			(534)	80.48	4.50	-	5.90	-
25_a	60	122^c	$C_{38}H_{27}O_3P$	81.14	4.80	-	5.52	
			(562)	81.24	4.77	-	5.81	
11_b	65	240^b	$C_{28}H_{15}OCl_4PS_2$	55.63	2.48	23.63	5.13	10.50
			(604)	55.70	2.70	23.50	5.30	11.70
13_b	62	262^c	$C_{34}H_{21}OPS_2$	75.55	3.88	-	5.74	11.85
			(540)	75.30	3.77	-	5.85	11.90
15_b	65	272^b	$C_{36}H_{23}OPS_2$	76.32	4.06	-	5.48	11.30
			(566)	76.50	4.15	-	5.67	11.38
17_b	70	195^b	$C_{38}H_{25}OPS_2$	77.02	4.22	-	5.23	10.59
			(592)	77.21	4.35	-	5.30	10.70
19_b	50	248^b	$C_{28}H_{15}OCl_4PS_2$	55.63	2.48	23.63	5.13	10.50
			(604)	55.80	2.70	23.89	5.40	10.70
21_b	50	264^c	$C_{40}H_{27}OPS_2$	77.67	4.36	-	5.02	10.35
			(618)	77.80	4.40	-	5.27	10.40
23_b	50	190^c	$C_{36}H_{23}OPS_2$	76.32	4.06	-	5.48	11.30
			(566)	76.40	4.21	-	5.40	11.37
25_b	52	186^b	$C_{38}H_{27}OPS_2$	76.76	4.54	-	5.22	10.77
			(594)	76.72	4.60	-	5.40	11.00

a- solvent of crystallization is chloroform/light petroleum.
b- solvent of crystallization is benzene / light petroleum.
c- crystallized from : chloroform/ n-hexane.

TABLE III

^{31}P NMR, ^{1}H NMR and IR spectral data for phosphoranylidene-cyclobutanediones and dithioxocyclobutylidenes (**13**, **15**, **17**, **21**, **23** and **25**)

Compound	^{31}P NMR	IR
13_a	13.47	1700 broad (C=O), 1620 (C=P) and 1440 (P-phenyl)
15_a	23.92	1720 ,1680 (C=O), 1660 (C=P) and 1440 (P-phenyl)
17_a	22.34	1740 ,1680 (C=O), 1640 (C=P) and 1440 (P-phenyl)
19_a	23.70	1670 ,1640 (C=O), 1620 (C=P) and 1440 (P-phenyl)
21_a	22.38	1730 ,1700 (C=O), 1660 (C=P) and 1440 (P-phenyl)
23_a	29.69	1720 ,1690 (C=O), 1660 (C=P) and 1440 (P-phenyl)
25_{ai}	23.78	1730 ,1680 (C=O), 1640 (C=P) and 1440 (P-phenyl)
13_b	22.68	1720 (C=O), 1670 (C=P) and 1440 (P-phenyl) and 1250 (C=S)
15_b	21.84	1720 (C=O), 1630 (C=P) and 1440 (P-phenyl) and 1250 (C=S)
17_b	21.89	1740 (C=O), 1640 (C=P) and 1440 (P-phenyl) and 1250 (C=S)
19_b	23.82	1680 (C=O), 1640 (C=P) and 1440 (P-phenyl) and 1250 (C=S)
21_b	22.43	1700 (C=O), 1640 (C=P) and 1440 (P-phenyl) and 1250 (C=S)
23_b	-7.57	1680 (C=O), 1620 (C=P) and 1440 (P-phenyl) and 1250 (C=S)
25_{bii}	22.19	1730 (C=O), 1640 (C=P) and 1440 (P-phenyl) and 1250 (C=S)

i) ^{1}H NMR : δ 2.45 (s, CH3), 7.90 (m, aromatics).

ii) ^{1}H NMR : δ 2.22 (s, CH3), 7.70 (m, aromatics).

formation of phosphoranylidene-cyclobutanes (**11**) by the reaction of (2-oxovinylidene)- (**7a**) and/or (2-thioxovinylidene)triphenylphosphorane (**7b**) with tetrachloro-1,2-benzoquinone (**8**) occurs by the [2+2]-cycloaddition of one carbonyl group in the quinone (**8**) to the ylidic C—P bond of the phosphacumulenes (**7**) to give the oxaphosphetanes (**9**) as intermediates.[8] Triphenylphosphine oxide is eliminated with the formation of the unstable ketene (**10**),[9] which add a second molecule of the active ylide (**7**) by a [2+2]-cycloaddition to give the phosphoranylidene-cyclobutanes (**11**). Moreover, the difference in the nucleophilic character of (2-oxovinylidene)- (**7a**) and (2-thioxovinylidene)triphenylphosphorane (**7b**) can be noticed, too, (**7a** > **7b**),[5] since (**7b**) reacts less rapidly than (**7a**) (Scheme II). On the other hand, the stabilized phosphoranes (**1**) behave differently towards *o*- and *p*-quinones, affording the coumarins (**3**), furans (**4**) and/or complicated phosphonium ylide (**6**), respectively (Scheme I). This new trend supplements the wide utilization of active phosphacumulenes in preparative work.[10]

EXPERIMENTAL

All melting points are uncorrected. The solvents were dried and distilled by usual techniques. Reactions were carried out under, nitrogen atmosphere. Elemental analyses were carried out at the "Microanalysis Department," National Research Centre. The IR spectra were measured in KBr, on a Perkin-Elmer infracord Spectrometer Model 157 (Grating). The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Spectrometer 90 MHZ, using TMS as an internal reference. ^{31}P NMR spectra were run, relative to external H_3PO_4 (85%), with a Varian FT-80 Spectrometer. Mass spectra were obtained on a Varian MAT CH-4B instrument.

The reaction of tetrachloro-1,2-benzoquinone (**8**) *and/or tetrachloro-1,4-benzoquinone* (**18**) *with (2-oxovinylidene)triphenylphosphorane* (**7a**). *Preparation of the new phosphoranylidenecyclobutanedione derivatives* (**11a** *and* **19a**). To a solution of tetrachloro-1,2-benzoquinone (**8**),[11] or tetrachloro-1,4-benzoquinone (**18**)[12] (0.01 mole) in 20 ml of tetrahydrofuran was added dropwise, with stirring at room temperature, a solution of (2-oxovinylidene)triphenylphosphorane (**7a**)[13] (0.02 mole) in 30 ml THF. The reaction mixture was left for six hours, during which the colour was changed from orange to brown. After THF had been distilled off under reduced pressure the residue was dissolved in 20 ml of chloroform followed by addition of 20 ml of *n*-hexane and the new solution was left overnight in the refrigerator. The precipitate that formed was filtered off and crystallized from an appropriate solvent to give the phosphoranylidene cyclobutanedione derivatives (**11a** and **19a**). The chloroform/*n*-hexane filtrate was chromatographed on alumina, affording triphenylphosphine oxide, m.p. and mixed m.p., 151°C.[14]

When the reaction was performed using four moles of the phosphorane (**7a**) against one mole of the quinone (**8** or **18**) the phosphorane reacted with only one carbonyl group in the quinone and the same cyclobutanedione derivatives (**11a** or **19a**) together with same unchanged phosphorane (**7a**) were obtained.

Yields, analytical and physical data of compounds (**11a**) and (**19a**) are shown in Table II.

Reaction of (2-thioxovinylidene) triphenylphosphorane (**7b**) *with the o-benzoquinone* (**8**) *and/or the p-benzoquinone* (**18**). *Synthesis of phosphoranylidene dithioxocyclobutylidenes* (**11b** *and* **19b**). A mixture of the thiophosphorane (**7b**)[13] (0.02 mole) and toluene (40 ml) was refluxed for eight hours. Toluene was distilled off and the residue that left behind was crystallized from benzene to give the dithioxocyclobutylidene (**11b**) and or (**19b**) respectively (Tables I and II). The benzene filtrate, afforded upon concentration and addition of hexane, triphenylphosphine oxide.

In a similar manner, the phosphoranylidene cyclobutanediones (**13a**, **15a**, **17a**, **21a**, **23a**, **25a**) and the dithioxocyclobutylidenes (**13b**, **15b**, **17b**, **21b**, **23b**, **25b**) were obtained from the reaction of (2-oxovinylidene)-(**7a**) and/or (2-thioxovinylidene)triphenylphosphorane (**7b**), with acenapthenequinone (**12**),[15] 9,10-phenanthraquinone (**14**),[16] 3,4-diphenylcyclobutenedione (**16**),[17] 2,5-diphenyl-*p*-benzoquinone (**20**),[18] 9,10-anthraquinone (**22**),[19] and/or 2,3-dimethyl-9,10-anthraquinone (**24**),[20] in boiling toluene (Tables I and II). The spectral data are collected in Table III.

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