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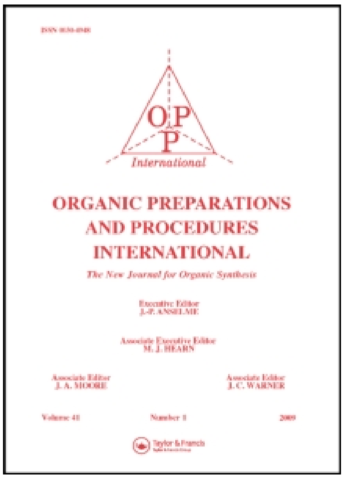

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REACTIVITY OF ACETYLMETHYLENE TRIPHENYLARSORANE

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ORGANIC PREPARATIONS AND PROCEDURES INT. 14(6), 373-380 (1982)

REACTIVITY OF ACETYLMETHYLENE TRIPHENYLARSORANE†

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Phosphorus ylides which bear an electron-withdrawing substituent(CO_2R, COPh, CN, etc.) in the alkylidene moiety show considerably reduced nucleophilicity and in many cases will not react with ketones.[1] Therefore the stabilized phosphorus ylides are of little value as reagents in Wittig reactions. However, the corresponding arsenic ylides are more reactive than phosphorus ylides; this greater reactivity is attributed to their greater polarity resulting from less effective $d\pi$-$p\pi$ bonding to arsenic.[2] Stabilized phosphorus ylides either do not react at all[1,3] or react with α,β-unsaturated esters or α,β-unsaturated ketones to give other ylides. In contrast, the corresponding arsenic ylides react with both α,β-unsaturated ketones and esters to furnish 1,2,3-trisubstituted cyclopropanes.[2] The superiority of arsenic ylides in these reactions is due to the fact that triphenylarsine is a good leaving group.[2]

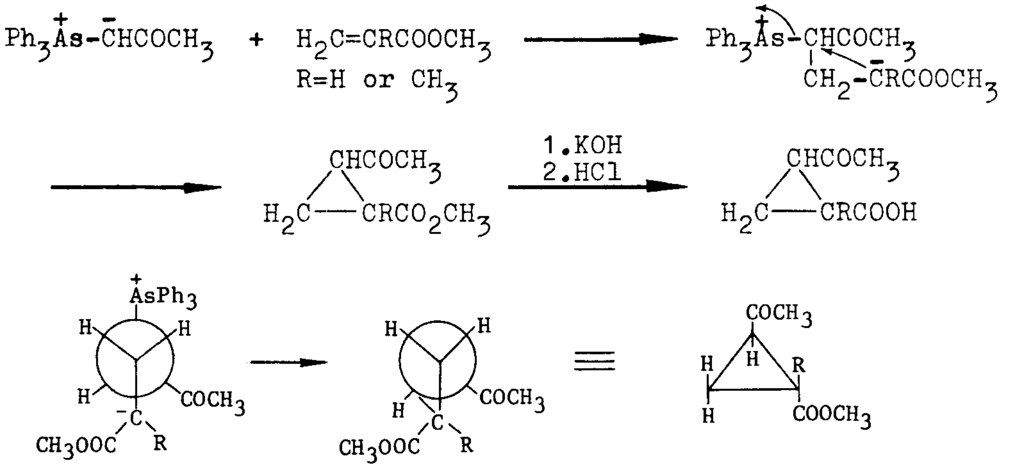
In contrast to acetylmethylene triphenylphosphorane which reacts with benzaldehyde at reflux in benzene after three days,[1] the corresponding arsorane reacted with substituted benzaldehydes and ketones under mild conditions (for aldehydes, 4-6 hrs. at 60° in benzene and for ketones, 5-8 hrs. at 80-110°) to afford good yields for aldehydes (80-95%) and for ketones (65-70%). Though Nesmeyanov[4] reported that acetylmethylene triphenylarsorane reacted with benzaldehyde to give the olefinic product, no reaction with ketones was reported. It should be noted that while the products from acetylmethylene triphenylarsorane with ketones have been synthesized by somewhat roundabout methods,[5] our route is instead a one-step reaction. The yields and physical constants of these olefinic products are shown in Table 1.

$$\mathrm{Ph_3\overset{+}{As}-\overset{-}{C}HCOCH_3} + \underset{R'}{\overset{R}{>}}\mathrm{C=O} \longrightarrow \underset{R'}{\overset{R}{>}}\mathrm{C=CHCOCH_3} + \mathrm{Ph_3AsO}$$

R = H, R' = *p*-$NO_2C_6H_4$, *p*-$Me_2NC_6H_4$, piperonyl, *p*-HOC_6H_4
R = CH_3, R' = C_6H_5 R,R' = $-(CH_2)_5-$

It has been reported that stabilized phosphorus ylides react with α,β-unsaturated esters or α,β-unsaturated ketones to form other ylides or did not react at all.[1,3] However, acetylmethylene triphenylarsorane reacted with methyl acrylate and methyl methacrylate to form substituted cyclopropanes, as we have shown in the cases of carbomethoxymethylene and benzoylmethylene triphenylarsorane previously.[2] The reaction is initiated by nucleophilic attack on the β-carbon of the double bond, forming an intermediate and the preferred conformation in transition state undergoes subsequent cyclization to give *trans*-substituted derivatives of cyclopropanes.

The configuration of these products was ascertained by ^{1}H-NMR spectroscopy.



In a similar manner, the acetylmethylene triphenylarsorane reacted with phenyl styrylketone and phenyl propenylketone to give 1,2,3-trisubstituted cyclopropanes; their configuration was assigned on the basis that the chemical shift of the proton of the cyclopropane ring is affected mainly by the *gem*-substitutent and that the coupling constant between *cis*-protons is greater than that of *trans*-protons.[6] The yields and physical constants of cyclopropane derivatives are shown in Table 2.

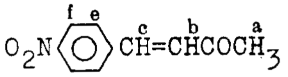
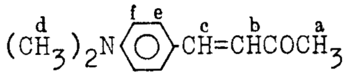
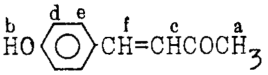
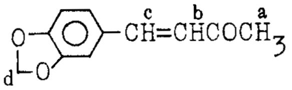
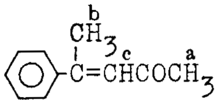
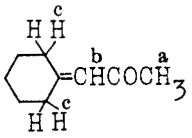
EXPERIMENTAL SECTION

All boiling points and melting points are uncorrected. ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer with TMS as internal standard.

Bromoacetone was prepared in 40% yield according to the method reported by Levene,[7] bp. 39-44°/13 mm, lit.[7] 40-42°/13 mm.

Acetylmethyl Triphenyl Arsonium Bromide. - To a well stirred

TABLE 1. **Yields** and Physical Constants of the Products From **Acetylmethylene** Triphenylarsorane with Aldehydes and Ketones

Product*	m.p(°C) or b.p(°C/mm)	Yield (%)	^{1}H-NMR (CDCl$_3$)	J (Hz)
	107-108[1]	95	2.45(3H^a,s) 6.90(1H^b,d) 7.45(1H^c,d) 7.80(2H^e,d) 8.35(2H^f,d)	J_{bc} 17.1 J_{ef} 9
	134-135[2]	80	2.36(3H^a,s) 3.05(6H^d,s) 6.61(1H^b,d) 7.42(2H^f,d) 7.50(1H^c,d) 7.75(2H^e,d)	J_{bc} 16.2 J_{ef} 9
	105-107[3]	91	2.35(3H^a,s) 6.50(1H^b,s) 6.53(1H^c,d) 6.85(1H^d,d) 7.42(1H^e,d) 7.48(1H^f,d)	J_{cf} 16.8 J_{de} 8
	107-108[4]	94	2.36(3H^a,s) 6.61(1H^b,d) 7.51(1H^c,d) 6.05(2H^d,s) 7.00(3H, m)	J_{bc} 16.2
	124-127/11[5]	70	2.24(3H^b,s) 2.54(3H^a,s) 6.48(1H^c,s) 7.40(5H, m)	
	49- 52/1[6]	65	2.15(3H^a,s) 2.80(2H^c,br.) 5.93(1H^b,s) 1.60(8H, br.)	

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*All compounds showed satisfactory analytical and IR data.
1. R. J. W. LeFèvre, P. J. Markham and J. Pearson, J. Chem. Soc. 344 (1933). 2. F. Sacks and W. Lewin, Ber. 39 3785 (1906). 3. T. H. Zinke and G. Mühlhausen, Ber. 36, 134(1903). 4. F. Haben, Ber. 24, 618(1891). 5. J. D. A. Johnson and G. A. R. Kon, J. Chem. Soc. 2757(1926). 6. A. H. Dickins, W. E. Hugh and G. A. R. Kon, ibid, 1636(1928).

solution of triphenylarsine (30.6g, 0.1 mole) in dry benzene (30 ml) was added bromoacetone (13.7g, 0.1 mole) dropwise under a N_2 atmosphere. The mixture was stirred and refluxed for 3 hrs. The precipitate was collected, washed with benzene and dried under vacuum to yield 47g (84%) of acetylmethylene triphenylarsonium bromide. After recrystallization from nitromethane-THF, it melted at 165-165.5°.[4]

IR 1700 cm^{-1} (C=O).

Anal. Calcd. for $C_{21}H_{20}AsBrO$: C, 57.11 H, 4.57 Br, 18.03
Found: C, 57.15 H, 4.28 Br, 18.37

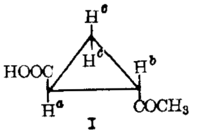
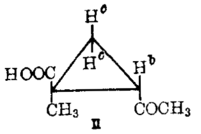
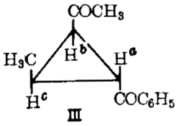
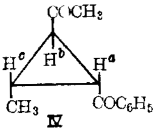
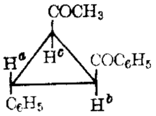
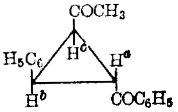
Acetylmethylene Triphenylarsorane. – To a well stirred solution of sodium methoxide in methanol prepared from sodium (0.92g, 0.04 mole) and dry methanol (14 ml) was added a solution of acetylmethyl triphenyl arsonium bromide (17.8g, 0.04 mole) in methanol under a N_2 atmosphere. The mixture was allowed to react at 40° for 10 min. and then at 15° for 30 min. After evaporation of the solvent at reduced pressure, the residue was triturated with ice-water, filtered and dried under vacuum to give 13.5g (93%) of acetylmethylene triphenylarsorane. After recrystallization from benzene, it melted at 160-162° (dec.).[4]

IR 1510 cm^{-1} (As$\cdots$C$\cdots$C$\cdots$O).

Anal. Calcd. for $C_{21}H_{19}AsO$: C, 69.44 H, 5.29.
Found: C, 69.46 H, 5.16.

Reaction of Acetylmethylene Triphenylarsorane with Aldehydes and Ketones. General Procedure. – A solution of acetylmethylene triphenylarsorane (10 ml) was stirred under a N_2 atmosphere (for aldehyde, 4-6 hrs. at 60° in benzene solution and for ketones, 5-8 hrs. at 80-110°). After cooling and addition of ether, it was washed with 5% HCl and then water, dried over

TABLE 2. Yields and Physical Constants of Substituted Cyclopropanes

Products[a]	mp(°C) or bp(°C/mm)	Yield (%)	^{1}H-NMR ($CDCl_3$)
 I	121-123/3 (lit.[b] 160-165/17)	63	1.46(m,2H^c),2.15(m,H^a) 2.30(s,3H,$COCH_3$) 2.52(m,H^b),9.60(br.H,COOH)
 II	75- 76	42	1.28(s,3H,CH_3),1.50(m,2H^c) 2.30(s,3H,$COCH_3$) 2.70(m,H^b)
 III  IV	oil	65	1.10+1.16(2d,6H,CH_3) 2.10(m,2H^c) 2.25+2.26(2s,6H,$COCH_3$) 2.80(m,2H^b),5.26(m,2H^a) 7.70(m,10H)
	102-103	45	2.08(s,3H,$COCH_3$) 2.80(d-d,H^c),3.20(d-d,H^b) 3.37(d-d,H^a),7.60(m,10H) J_{ab}6.3,J_{ac}6.3,J_{cb}9.0
	oil		2.12(s,3H,$COCH_3$) 3.14(d-d,H^c),3.46(d-d,H^b) 4.00(d-d,H^a),7.60(m,10H) J_{ab}6.2,J_{ac}5.0,J_{bc}10.0

a) All compounds gave satisfactory analytical and IR data.

b) H. Staudinger, O. Muntoyler, L. Ruzicka and S. Seibt, Helv. Chim. Acta, 7, 390 (1924).

anhyd. Na_2SO_4. Removal of the solvent yielded the crude product, which was purified either by recrystallization or distillation under reduced pressure.

Reaction of Acetylmethylene Triphenylarsorane with Methyl Acrylate. – A solution of acetylmethylene triphenyl arsorane (10.9g, 0.03 mole), methyl acrylate (8 ml) and anhyd. benzene (30 ml) was refluxed under a N_2 atmosphere for 4 hrs. After removal of the solvent and of excess methyl acrylate under reduced pressure, the residue was hydrolyzed with 10% aqueous methanolic KOH solution at room temp. overnight. The reaction mixture was extracted with ether and the aqueous layer was separated and acidified with conc. hydrochloric acid. Extraction with ether and removal of solvent from the ethereal extract, followed by distillation at reduced pressure yielded 2.4g(63%) of the cyclopropane as a colorless liquid, bp. 121-123°/3 mm.

Reaction of Acetylmethylene Triphenylarsorane with 1-Benzoyl-1-propene. – A solution of acetylmethylene triphenylarsorane (3.62, 0.01 mole) and 1-benzoyl-1-propene (1.46g, 0.01 mole) in anhyd. benzene (15 ml) was refluxed under a N_2 atmosphere and purified by column chromatography on alumina to yield 1.4g (65%) of a mixture of III and IV (Table 2).

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†This paper is the 21st report on the studies of the application of elementoorganic compounds of the fifth and sixth groups in organic syntheses.

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