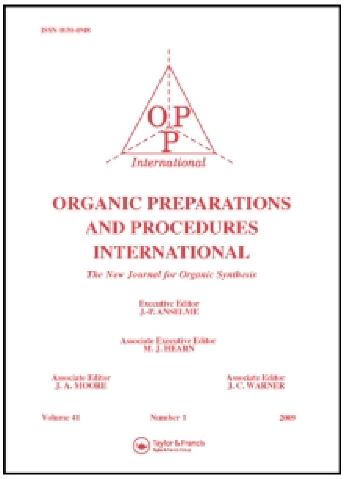

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NEW HYDRAZONOYL BROMIDES AND AZOMETHYLENE PHOSPHORANES

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NEW HYDRAZONOYL BROMIDES AND AZOMETHYLENE PHOSPHORANES

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Highly crystalline, stable azomethylene triphenylphosphoranes II (Table 2) are obtained from the reaction of equimolar amounts of hydrazonoyl bromide (I) and triphenylphosphine in the presence of a slight excess of triethylamine in benzene or

Table 1. New Hydrazonoyl Bromides

Cmpd.	Yield (%)	mp. (°C)	Analysis (%) Calcd. (Found)		
			C	H	Br
Ia,c	90	86-89	43.85(43.71)	4.31(4.70)	26.58(26.41)
Ib	76	100-102	46.31(46.24)	4.56(4.41)	28.07(28.12)
Id	80	92-94	52.34(52.10)	4.05(4.21)	24.92(24.90)
Ie	75	128-130	47.06(46.98)	4.31(4.20)	31.37(31.41)
If	70	60-62	47.06(47.12)	4.31(4.10)	31.37(31.20)
Ig	88	140-142	44.28(44.49)	4.05(4.10)	29.52(29.50)
Ih	85	130-131	44.28(44.18)	4.05(4.02)	29.52(29.51)
Ii	70	95-96	53.60(53.28)	3.78(3.79)	27.49(27.50)
Ij	72	222-224	39.04(38.84)	2.00(2.31)	20.03(20.14)
Ik	75	240-243	42.53(42.69)	2.78(3.01)	20.39(20.41)
Il	79	258-260	40.95(41.08)	2.36(2.52)	21.00(21.41)
Im	80	293-294	42.35(42.30)	3.06(3.20)	18.82(18.64)

Table 2. Azomethylene Triphenylphosphoranes

Cmpd.[a]	Yield (%)	mp. (°C)	Analysis (%) Calcd. (Found)		
			C	H	N
IIa[b]	90	190-191	72.19(72.25)	5.60(5.70)	5.80(5.70)
IIb[c]	80	200-203	72.16(72.24)	5.53(5.24)	6.19(6.20)
IIc[c]	84	176-178	71.79(71.82)	5.34(5.42)	5.98(5.79)
IId[c]	80	76-78	76.22(76.23)	5.12(5.20)	5.73(5.69)
IIe	91	146-148	77.06(77.21)	5.73(5.49)	6.42(6.40)
IIf	84	150-152	77.06(77.21)	5.75(5.62)	6.42(6.34)
IIg	74	118-120	74.33(74.11)	5.53(5.28)	6.19(6.20)
IIh	78	170-173	74.33(74.08)	5.53(5.73)	6.19(6.40)
IIi	62	123-125	78.81(78.91)	5.29(5.50)	5.93(5.58)
IIj	64	250-252	64.08(64.16)	3.79(3.70)	9.64(9.80)
IIk	70	231-234	70.07(70.23)	4.56(4.82)	5.10(5.21)
IIl	64	232-233	66.17(66.20)	4.09(4.21)	9.96(10.01)
IIm	72	208-210	65.34(65.42)	4.45(4.29)	9.24(9.32)

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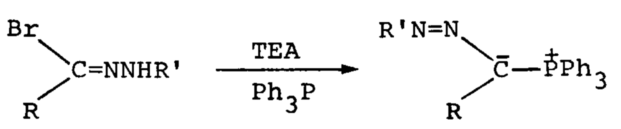
a) IIb-m were crystallized from chloroform-methanol unless otherwise noted; the colour of the compounds varies from yellow to red.

b) From benzene-hexane.

c) R = MeO_2C (An ester interchange occurs during crystalization).

chloroform at reflux.[1] All the phosphoranes displayed a P=C band at 1380-1310 cm^{-1} and a weak N=N band at 1590-1570 cm^{-1}.



I II

f. R = MeOC, R' = 2-MeC_6H_4
g. R = MeOC, R' = 2-$MeOC_6H_4$
h. R = MeOC, R' = 4-$MeOC_6H_4$

a. R = EtO_2C, R' = 4-$MeOC_6H_4$
b. R = MeO_2C, R' = 2-MeC_6H_4
c. R = MeO_2C, R' = 4-$MeOC_6H_4$
d. R = MeO_2C, R' = 2-$C_{10}H_7$
e. R = MeOC, R' = 3-MeC_6H_4

i. R = MeOC, R' = 2-$C_{10}H_7$
j. R = 4-ClC_6H_4, R' = 2,4-$(NO_2)_2C_6H_3$
k. R = 2-$MeOC_6H_4$, R' = 2,4-$(NO_2)_2C_6H_3$
l. R = 2-OHC_6H_4, R' = 2,4-$(NO_2)_2C_6H_3$

m. R = 3,4-$(OCH_3)_2C_6H_3$, R' = 2,4-$(NO_2)_2C_6H_3$

EXPERIMENTAL SECTION

All melting points are uncorrected. ^{1}H-NMR spectra were recorded on a Varian A-60 spectrometer with TMS as internal standard. IR spectra were determined on a Perkin-Elmer-298 spectrophotometer as nujol mulls.

Hydrazonoyl bromides were obtained according to literature procedures (Table 1).[2] Azomethylene phosphoranes were prepared from 0.05 mole of each component in 60 ml. of solvent (2-6 hrs reflux). The precipitated triethylamine hydrobromide was collected or extracted with hot water. The dried organic layer was evaporated *in vacuo* and recrystallized twice.

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