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NEW HYDRAZONOYL BROMIDES AND AZOMETHYLENE PHOSPHORANES

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- Abs., 85, 15357a (1976).
2. W. G. Brouwer, E. J. MacPherson, R. B. Ames, and R. W. Neidermyer, Canadian Patent 966,490; U.S. Patent 3,882,138; Chem. Abs., 83, 114415h (1975).
 3. Photolysis of 3,5-diphenylisoxazole to 2,5-diphenyloxazole has been reported by B. Singh and E. F. Ullman, J. Am. Chem. Soc., 89, 6911 (1967).
 4. R. L. N. Harris and J. L. Huppertz, Aust. J. Chem., 30, 2225 (1977).
 5. J. Nadelson, U.S. Patent 4,032,644; Chem. Abs., 87, 102314u (1977).
 6. R. K. Howe and F. M. Schleppek, J. Heterocyclic Chem., 19, 721 (1982).
 7. C. Goedeckemeyer, Ber., 21, 2684 (1888).
 8. W. T. Caldwell and G. C. Schweiker, J. Am. Chem. Soc., 75, 5884 (1953).

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 hydrazonyl bromide (I) and triphenylphosphine in the presence of a slight excess of triethylamine in benzene or

Table 1. New Hydrazoneoyl Bromides

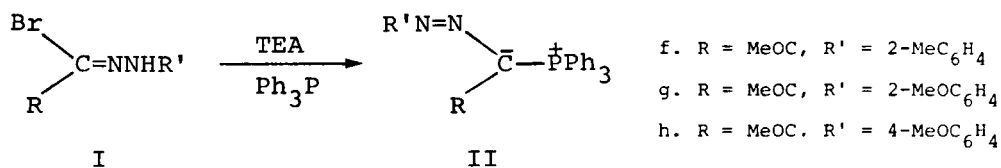
Cmpd.	Yield (%)	mp. (°C)	Analysis (%)		Calcd. (Found)
			C	H	Br
Ia,c	90	86-89	43.85 (43.71)	4.31 (4.70)	26.58 (26.41)
Ib	76	100-102	46.31 (46.24)	4.56 (4.41)	28.07 (28.12)
Id	80	92-94	52.34 (52.10)	4.05 (4.21)	24.92 (24.90)
Ie	75	128-130	47.06 (46.98)	4.31 (4.20)	31.37 (31.41)
If	70	60-62	47.06 (47.12)	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)

- 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 = MeO₂C (An ester interchange occurs during crystallization).

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.



- a. R = EtO₂C, R' = 4-MeOC₆H₄ i. R = MeOC, R' = 2-C₁₀H₇
 b. R = MeO₂C, R' = 2-MeC₆H₄ j. R = 4-ClC₆H₄, R' = 2,4-(NO₂)₂C₆H₃
 c. R = MeO₂C, R' = 4-MeOC₆H₄ k. R = 2-MeOC₆H₄, R' = 2,4-(NO₂)₂C₆H₃
 d. R = MeO₂C, R' = 2-C₁₀H₇ l. R = 2-OHC₆H₄, R' = 2,4-(NO₂)₂C₆H₃
 e. R = MeOC, R' = 3-MeC₆H₄
 m. R = 3,4-(OCH₃)₂C₆H₃, R' = 2,4-(NO₂)₂C₆H₃

EXPERIMENTAL SECTION

All melting points are uncorrected. ¹H-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.

REFERENCES

1. S. P. Konotopova, V. N. Chistokletov and A. A. Petrov, Zh. Obshch. Khim., 42, 2412 (1972); L. A. Tamm, V. N. Chistokletov and A. A. Petrov, *ibid.*, 42, 1926 (1972); 43, 2178 (1973).
2. G. M. Burgess and M. S. Gibson, J. Chem. Soc., 1500 (1964); D. B. Sharp and C. S. Hamilton, J. Am. Chem. Soc. 68, 586 (1946).