Reaction of Tris(hydroxymethyl)phosphine with Substituted Ureas[1]

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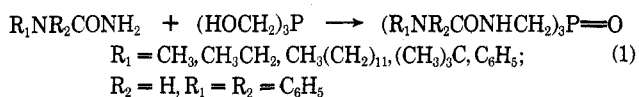*Southern Regional Research Center,[2a] New Orleans, Louisiana 70179*

The reaction of tris(hydroxymethyl)phosphine with monosubstituted and unsymmetrically disubstituted ureas has been shown to produce tris(4-substituted ureidomethyl)phosphine oxides. The products were characterized by ir spectra, NMR spectra, and elemental analyses. The NMR spectrum for tris(4-phenylureidomethyl)phosphine oxide showed a triplet for the NH attached to the phosphorus methylene, appearing at a higher field than the NH attached to the phenyl ring, which demonstrated that the reactive nitrogen of the urea was the unsubstituted nitrogen. Reactions of several monosubstituted ureas with tris(hydroxymethyl)phosphine oxide failed to give any of the tris(4-substituted ureidomethyl)phosphine oxides, indicating that oxidation of phosphorus occurred after formation of the P–C–N bond.

Hydroxymethylphosphorus compounds condense readily with amines, amides, ureas, and other nitrogen-containing compounds to yield linear and branched polymers which are useful in flame-retarding cotton cellulose.[3-6] Monomeric products have been obtained when secondary amines were allowed to react with hydroxymethylphosphonium salts or tris(hydroxymethyl)phosphine.[7-10] Our general interest in flame retardants and hydroxyalkylphosphorus chemistry, coupled with recent interest in reactions of phosphorus compounds with ureas in the presence of aldehydes,[11-13] has prompted us to report on the reactions of tris(hydroxymethyl)phosphine with partially substituted ureas.

Results and Discussion

Monomeric products have been obtained from the reaction of tris(hydroxymethyl)phosphine (THP) with several monosubstituted ureas according to eq 1.

$$R_1NR_2CONH_2 \ + \ (HOCH_2)_3P \ \longrightarrow \ (R_1NR_2CONHCH_2)_3P{=}O$$
$$R_1 = CH_3, CH_3CH_2, CH_3(CH_2)_{11}, (CH_3)_3C, C_6H_5; \qquad (1)$$
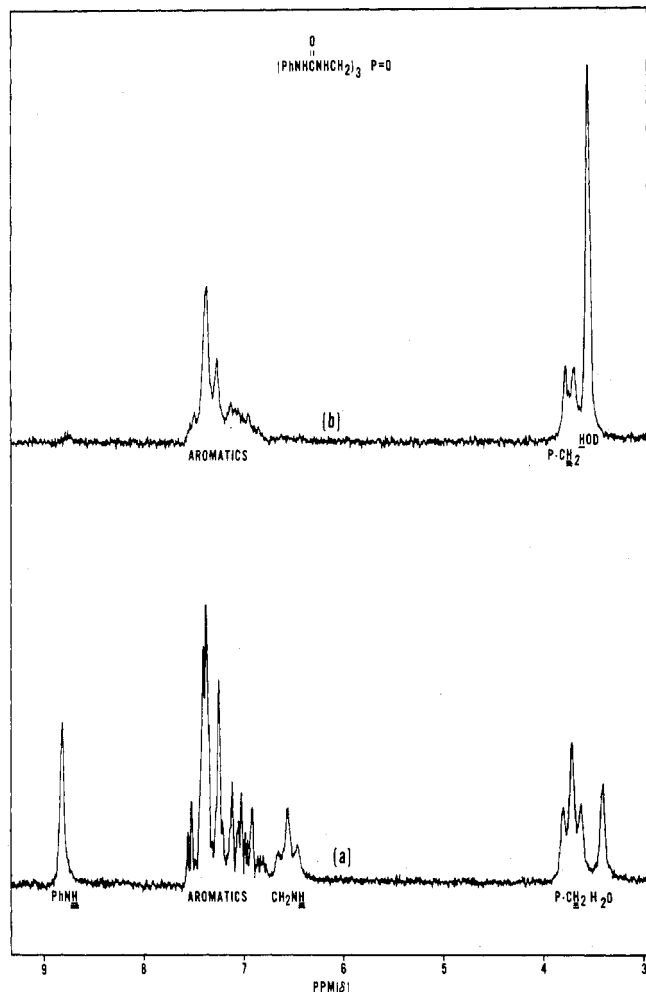$$R_2 = H, R_1 = R_2 = C_6H_5$$

Only the phosphine oxides were isolated as oxidation of the phosphorus occurred at some stage of reaction or work-up. A similar reaction occurred when 1,1-diphenylurea was combined with THP. Yields of crude product varied widely and are summarized in Table I (see Experimental Section). No products were isolated from the reactions of THP with acetylurea, benzoylurea, 1,3-dibenzylurea, and 1,1-dimethylurea; rather, 75, 100, 45, and 75% of the starting ureas, respectively, were recovered. If the concentration of the reactants (THP plus substituted urea) was too low in the refluxing ethanol, then the starting urea was recovered in the dodecylurea (88%) and 1,1-diphenylurea (95%) examples. In both examples, concentrations of 16–20% of reactants were necessary before any product could be isolated. A similar dependence on concentration was noted in the *tert*-butylurea reaction, where, with only 4% of reactants, a dark yellow, intractable oil resulted, whereas raising the reactants concentration to 17% caused product to precipitate after refluxing for 16 h. However, even at the higher concentration, several other substituted ureas produced intractable oils from which no solid material could be recovered; among these were 1,3-dimethylurea, 1,3-diethylurea, allylthiourea, and *N*-methylethyleneurea.

The purified products were characterized by ir spectroscopy, NMR spectroscopy, and elemental analysis. The bonding in tris(4-phenylureidomethyl)phosphine oxide (**5**) was readily deduced from its NMR spectrum (Figure 1), which shows a triplet at 6.56 ppm which is assigned to the CH$_2$NH and integrates for three protons. The singlet at 8.81 ppm is assigned to the C$_6$H$_5$NH proton because of the deshielding effect of the phenyl group and integrates for three protons. The triplet for the higher field signal shows that the NH group bonded to the phosphorus methylene is the unsubstituted nitrogen, rather than the phenyl-substituted nitrogen. Such bonding obviously must exist in tris(4,4-diphenylureidomethyl)phosphine oxide (**6**), since one of the nitrogens is fully substituted. Based on steric considerations, one would expect tris(4-dodecylureidomethyl)phosphine oxide (**3**) and tris(4-*tert*-butylureidomethyl)phosphine oxide (**4**) to show similar bonding, since both *tert*-butyl and dodecyl are larger than phenyl. However, the steric bulk of methyl and ethyl is such that one cannot rule out the possibility of reaction occurring at either nitrogen. In fact, it may well occur at both nitrogens, but the products isolated indicate the presence of only one isomer. Clear-cut evidence for which nitrogen is involved in bonding to the methylene was not possible for all samples because the NMR spectra were obtained in D$_2$O, but bonding similar to **5** would be expected.

The reaction of THP with secondary amines yields the tris(aminomethyl)phosphines,[7-10] but the reactions of THP with substituted ureas yields the tris(ureidomethyl)phosphine oxides. Monitoring of the THP–urea reactions by NMR indicated that some oxidation of THP was occurring, because the doublet due to the methylene protons of THP (D$_2$O, δ 4.1, $J = 5$ Hz) was overlapped by another doublet (D$_2$O, δ 4.2, $J = 3$ Hz) which we believed resulted from tris(hydroxymethyl)phosphine oxide (THPO). The use of ^{31}P NMR also indicated the presence of THPO; thus the reaction pathway might consist of oxidation of THP to THPO and subsequent reaction of THPO with the urea to form the tris(ureidomethyl)phosphine oxide. This mechanism would involve loss of formaldehyde from THPO by a
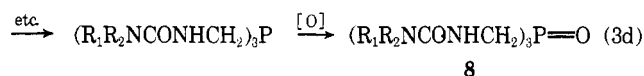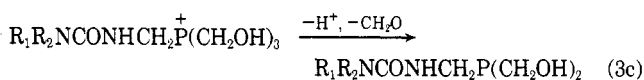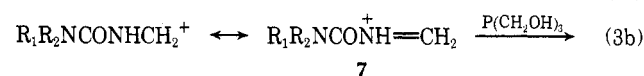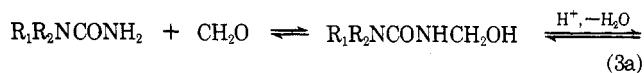
$$R_1R_2NCONH_2 \; + \; CH_2O \; \rightleftharpoons \; R_1R_2NCONHCH_2OH \xrightarrow{\; H^+, -H_2O \;}$$
(3a)

$$R_1R_2NCONHCH_2^+ \; \longleftrightarrow \; R_1R_2NCO\overset{+}{N}H\!=\!CH_2 \xrightarrow{\; P(CH_2OH)_3 \;}$$
(3b)

7

$$R_1R_2NCONHCH_2\overset{+}{P}(CH_2OH)_3 \xrightarrow{\; -H^+, -CH_2O \;}$$

$$R_1R_2NCONHCH_2P(CH_2OH)_2 \quad (3c)$$

$$\xrightarrow{etc.} \; (R_1R_2NCONHCH_2)_3P \xrightarrow{[O]} (R_1R_2NCONHCH_2)_3P\!=\!O \quad (3d)$$

8

Figure 1. NMR spectrum of tris(4-phenylureidomethyl)phosphine oxide: (a) in Me₂SO-d₆; (b) after D₂O exchange.

mechanism similar to that recently proposed for the reaction of benzylbis(α-hydroxybenzyl)phosphine oxide with primary amines through loss of benzaldehyde.[14] THPO was prepared and refluxed in ethanol with methylurea, phenylurea, or *tert*-butylurea, respectively. No tris(ureidomethyl)phosphine oxide was obtained in any of these reactions. The starting ureas were recovered in 50–65% yield, the remainder of the reaction mixture being an intractable oil.

$$(HOCH_2)_3P\!=\!O \; + \; R_1R_2NCONH_2 \; \xrightarrow{\; \times \;}$$
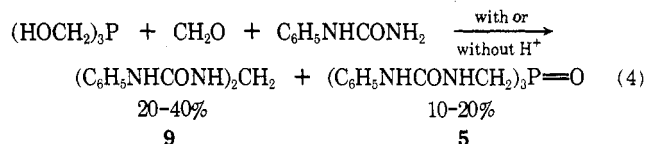
$$(R_1R_2NCONHCH_2)_3P\!=\!O \quad (2)$$
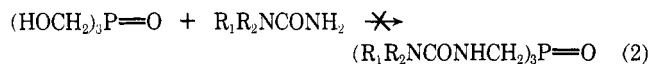
This oil was water soluble in all three examples, whereas compounds 4 and 6 were water insoluble. Addition of acid or base and more vigorous reaction conditions (refluxing toluene) did not produce evidence that THPO reacted with the substituted ureas. Oxidation of THP to THPO prior to reaction with the urea is thus effectively eliminated as a possible mechanism for production of tris(ureidomethyl)phosphine oxides, as shown in eq 2. A likely mechanism for the reaction of THP with substituted ureas may involve nucleophilic attack by THP on the carbonium–immonium ion 7, which is formed by reaction of the urea with formaldehyde and subsequent acid-catalyzed loss of water,[15] as shown in eq 3. Formaldehyde and traces of acid (a 1% solution of THP has a pH of 5.6–6.0) are present in the commercially supplied THP.

All the reactions of ureas with THP were complicated by formation of other products, probably some mono- and disubstituted ureidomethyl phosphine oxides and phosphorus-free products, such as methylenebisureas. Methylene-

bisureas were the predominant product when formaldehyde was added at an equimolar ratio to THP in the THP–urea reactions.

The reaction of THP with formaldehyde and phenylurea was conducted, both at reflux and at ambient temperature, in ethanol with or without added acid. Yields of solid ranged from 30 to 60% (based on phenylurea) and were separated into two components, 20–40% of 1,1'-methylenebis(3-phenylurea) (9) and 10–20% of 5.

$$(HOCH_2)_3P \; + \; CH_2O \; + \; C_6H_5NHCONH_2 \; \xrightarrow[\text{without } H^+]{\text{with or}}$$

$$(C_6H_5NHCONH)_2CH_2 \; + \; (C_6H_5NHCONHCH_2)_3P\!=\!O \quad (4)$$

20–40%   10–20%

9   **5**

A similar reaction occurred when tetrakis(hydroxymethyl)phosphonium chloride (Thpc), neutralized with sodium hydroxide, was mixed with phenylurea to produce 9 in 26% yield. The neutralization of Thpc by sodium hydroxide has been shown by Vullo[16] to yield a mixture of THP, THPO, formaldehyde, and hemiacetals of THP and THPO. This complex mixture is referred to as THPOH.

$$THPOH \; + \; C_6H_5NHCONH_2 \; \longrightarrow \; (C_6H_5NHCONH)_2CH_2 \quad (5)$$

26%

9
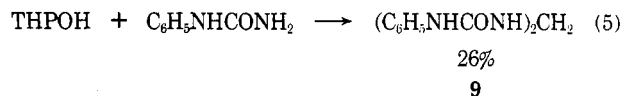
The reaction of 1,1-diphenylurea with Thpc in refluxing ethanol led to formation of 1,1'-methylenebis(3,3-diphenylurea) (10) in a 31% yield.

$$(HOCH_2)_4P^+Cl^- \; + \; (C_6H_5)_2NCONH_2 \; \longrightarrow$$

$$[(C_6H_5)_2NCONH]_2CH_2 \quad (6)$$

31%

10
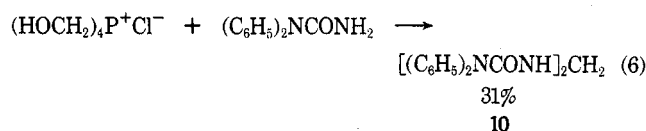
When an equimolar (or greater) amount of formaldehyde is present, formation of the methylenebisureas is favored over formation of the tris(ureidomethyl)phosphine oxides.

Coupling of the ureas also occurred when sodium hydroxide equimolar to THPO was added during the reaction of THPO with phenylurea. Formation of the methylenebisurea (9) in 22% yield indicated that some decomposition of THPO occurred, yielding free formaldehyde.

$$(HOCH_2)_3PO \; + \; C_6H_5NHCONH_2 \xrightarrow{\text{NaOH}} (C_6H_5NHCONH)_2CH_2$$

9

(7)
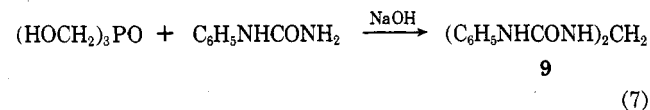
All of the reactions discussed above were conducted in a completely homogeneous system, because both the ureas and THP were readily soluble in hot ethanol. It was of interest to determine what course the reaction might take in another solvent system. THP has only a limited solubility in hot toluene (1–3%), whereas the substituted ureas vary from slightly soluble to soluble. The reactions of *tert*-butylurea, methylurea, dodecylurea, ethylurea, and phenyl-

Table I
Tris(4-substituted)ureidomethyl Phosphine Oxides $(R_1R_2NCONHCH_2)_3P{=}O$

Compd	R_1	R_2	Method	Crude yield, %	Recrystallizing solvent	Mp, °C
1	CH_3	H	A	15	Ethanol	233–234
			B	54		
2	C_2H_5	H	A	14	Ethanol–ethyl acetate	244
			B	97		
3	$CH_3(CH_2)_{11}$	H	A	94	Ethanol–ethyl acetate	170
			B	67		
4	$(CH_3)_3C$	H	A	61	Ethanol–water	220
			B	82		
5	C_6H_5	H	A	53	Dimethyl sulfoxide–water	263–264
			B	37		
6	C_6H_5	C_6H_5	A	38	Acetone	147–148

urea with THP in refluxing toluene proceeded readily, with water evolution being quantitative in 6–8 hr. The crude products were identified by ir spectroscopy as tris(ureidomethyl)phosphine oxides. Yields (37–97%) were generally better in the reactions conducted in toluene.

In contrast to reactions carried out in ethanol, the reaction of 1,1-diphenylurea with Thpc in refluxing toluene did not give either methylenebisurea or THPO. The ir spectra indicated a phosphonium salt, and the elemental analyses indicate that the product is tetrakis(4,4-diphenylureidomethyl)phosphonium chloride (11).

$$(HOCH_2)_4P^+Cl^- + (C_6H_5)_2NCONH_2 \xrightarrow{\text{toluene}}$$

$$[(C_6H_5)_2NCONHCH_2]_4P^+Cl^- \quad (8)$$

14
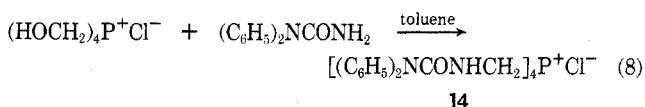
A similar product has been found in the reactions of N-substituted carbamates with Thpc in refluxing toluene.[17] Reactions of Thpc with 1,1-dimethylurea, ethylurea, and phenylurea, however, all yielded intractable oils. Thus the reaction of THP with substituted ureas appear to be general, giving tris(ureidomethyl)phosphine oxides in two quite different solvents, ethanol and toluene. The reactions of Thpc with substituted ureas are not general and give mixtures of products under the different solvent conditions.

Experimental Section

Reagent grade chemicals were used without further purification. THP, supplied by American Cyanamid Co.,[2b] was shown by NMR to contain small amounts of THPO, methanol, formaldehyde, and other impurities. These contaminants were negligible in a freshly opened container of the solid, but increased on standing for 6 months to 5–10%. The formaldehyde used was a 37.4% aqueous solution from Fisher Scientific Co. The ir spectra were obtained on a Perkin-Elmer 137 with sodium chloride optics. Solid samples were run as KBr pellets containing about 0.3% of the sample. The ^1H NMR spectra were taken on a Varian A-60A and the ^{31}P NMR spectra were obtained on a JEOLCO CH-60. Elemental analyses and molecular weight determinations were performed by Enviro Analytical Laboratory,[2b] Knoxville, Tenn. All melting points are uncorrected.

Reaction of THP with Substituted Ureas. Method A consisted of mixing tris(hydroxymethyl)phosphine (0.015–0.1 mol) with the substituted urea (0.045–0.3 mol) in a 1:3 molar ratio in sufficient ethanol (75–200 ml) to produce a 16–20% weight concentration of reactants. The mixture was heated to reflux, and the water formed in the condensation reaction was removed by drying the distillate in a Soxhlet tube containing a corundum thimble filled with Linde molecular sieve 4A. Reaction was allowed to proceed for 1 week, or until a large amount of precipitate had formed. Work-up varied, depending on the original urea.

Method B consisted of mixing tris(hydroxymethyl)phosphine (0.004–0.02 mol) with the substituted urea (0.012–0.06 mol) in a 1:3 molar ratio in 50–75 ml of toluene. The heterogeneous mixture was heated to reflux, and the water formed in the condensation was collected in a Dean-Stark trap. Reflux was allowed to proceed until the evolution of water ceased or until theoretical water was collected (<8 h). The solid precipitated from the reaction mixture

on cooling and was recrystallized from an appropriate solvent. Yields, recrystallizing solvents, and melting points of the compounds are summarized in Table I.

Tris(4-methylureidomethyl)phosphine Oxide (1). Method A afforded a 15% yield of white solid after a refluxing acetone trituration of the oil which remained after ethanol was removed from the reaction mixture.

Method B gave a 54% yield of white solid after a similar work-up. One recrystallization from ethanol gave the analytical sample, 1: ir (KBr) 3.02 (NH), 3.3–3.5 (aliphatic CH), 6.1 and 6.32 (amide bands), 8.68 μ (P=O); NMR (D_2O) δ 2.7 (s, 9 H, CH_3), 3.77 (d, J = 4 Hz, 6 H, PCH_2).

Anal. Calcd for $C_9H_{21}N_6O_4P$: C, 35.06; H, 6.87; N, 27.26; P, 10.05. Found: C, 35.16; H, 6.96; N, 26.80; P, 9.91.

^1H and ^{31}P NMR Evidence for Oxidation of THP to THPO. A 10-ml aliquot of the reaction mixture of THP with methylurea was taken after 1 h reflux in ethanol. The solvent was removed by heating under vacuum, and the ^1H and ^{31}P NMR spectra were taken of the residual oil. Integration of the ^1H NMR spectrum was impossible because the signals of interest overlapped. However, in the ^{31}P NMR, there is a wide separation of signals due to phosphorus in different oxidation states since THP absorbs at +25 ppm relative to H_3PO_4, while THPO absorbs at −50 ppm. The ^{31}P NMR spectrum (D_2O, H_3PO_4 external reference) of the reaction mixture showed a signal at +25 ppm (THP, 62% of the integration) and one at −50 ppm (THPO, 32% of the integration). Thus considerable oxidation does occur, at least in the methylurea example.

Tris(4-ethylureidomethyl)phosphine Oxide (2). Method A gave a 14% yield of white solid after a refluxing acetone trituration of the oil which remained after removal of ethanol from the reaction mixture.

Method B gave a 97% yield of white solid. One recrystallization from an acetone–ethanol mixture, followed by a recrystallization from ethanol, yielded the analytical sample, 2: ir (KBr) 2.98 (NH), 3.31–3.4 (aliphatic CH), 6.08 and 6.38 (amide bands), 8.64 μ (P=O); NMR (D_2O) δ 1.1 (t, J = 7 Hz, 9 H, CH_3CH_2), 3.2 (q, J = 7 Hz, 6 H, CH_3CH_2), 3.8 (d, J = 5 Hz, 6 H, PCH_2).

Anal. Calcd for $C_{12}H_{27}N_6O_4P$: C, 41.10; H, 7.77; N, 24.00; P, 8.84. Found: C, 41.24; H, 7.63; N, 24.18; P, 8.84.

Tris(4-dodecylureidomethyl)phosphine Oxide (3). Method A yielded 94% of white solid.

Method B gave a 67% yield of solid. The product proved difficult to recrystallize; only powders formed from a variety of solvents and solvent pairs. The analytical sample, 3, was obtained after two recrystallizations from ethyl acetate–ethanol: ir (KBr) 2.99 (NH), 3.4 and 3.49 (aliphatic CH), 6.12 and 6.32 (amide bands), 8.7 μ (P=O). The solubility of 3 in common NMR solvents was too low to provide an interpretable spectrum.

Anal. Calcd for $C_{39}H_{87}N_6O_4P$: C, 64.25; H, 11.20; N, 11.53; P, 4.25. Found: C, 64.07; H, 10.97; N, 11.28; P, 4.10.

Tris(4-tert-butylureidomethyl)phosphine Oxide (4). Method A yielded 61% of white solid that precipitated after 3 days of reflux in ethanol.

Method B gave 82% of white solid. Recrystallization four times from ethanol–water gave a white, crystalline solid which softened at 132–138°, then resolidified and melted at 220–222°. The elemental analysis of this solid indicated a dihydrate of 4.

After further recrystallization, some of this solid was dried in a vacuum oven at 140° until it had softened and resolidified. The melting point of the dried solid (4d) was 220°, whereas the undried solid (4u) exhibited both a low and a high melting point. The ir spectra of the two solids were identical, but the NMR spectra of 4u

showed four protons from the water at δ 3.6, which **4d** did not. After D_2O exchange, the spectra were identical: ir (KBr) 2.96 (NH), 3.3–3.35 (aliphatic CH), 6.00 and 6.40 (amide bands), 8.6 μ (P=O); NMR (mixture of $CDCl_3$–Me_2SO-d_6) δ 1.3 [s, 27 H, $(CH_3)_3C$], 3.6 (**4u**, m, 10 H, PCH_2, 2 H_2O), 3.6 (**4d**, m, 6 H, PCH_2), 5.8 (broad s, 3 H, NH), 6.4 (broad s, 3 H, NH); after D_2O exchange δ 1.3 [s, 27 H, $(CH_3)_3C$], 3.65 (m, 6 H, PCH_2). The elemental analyses of **4d** and **4u** indicated that 2 mol of water was lost on drying.

Anal. Calcd for $C_{18}H_{39}N_6O_4P$: C, 49.75; H, 9.05; N, 19.34; P, 7.13. Found for **4d**: C, 49.71; H, 8.86; N, 19.17; P, 7.19.

Anal. Calcd for $C_{18}H_{39}N_6O_4P \cdot 2H_2O$: C, 45.94; H, 9.21; N, 17.86; P, 6.58. Found for **4u**: C, 45.86; H, 9.12; N, 17.55; P, 6.57.

Tris(4-phenylureidomethyl)phosphine Oxide (5). Method A gave a 53% yield of white solid after only 48 h in refluxing ethanol.

Method B afforded a 37% yield of solid. Recrystallization from dimethyl sulfoxide–water gave the analytical sample, **5**: ir (KBr) 2.99 (NH), 3.25 (aromatic CH), 3.4 (aliphatic CH), 6.03, 6.24, 6.5, and 6.7 (overlapping amide bands and aromatic C=C), 8.59 μ (P=O); NMR (Me_2SO-d_6, 80°) δ 3.7 (d of d, J_{PCH} = J_{NHCH} = 5 Hz, 6 H, PCH_2), 6.56 (t, J = 5 Hz, 3 H, CH_2NH), 6.7–7.65 (m, 15 H, aromatics), 8.81 (s, 3 H, PhNH); after D_2O exchange, δ 3.74 (d, J_{PCH} = 5 Hz, 6 H, PCH_2), 6.7–7.65 (m, 15 H, aromatics).

Anal. Calcd for $C_{24}H_{27}N_6O_4P$: C, 58.29; H, 5.50; N, 17.00; P, 6.27. Found: C, 58.34; H, 5.60; N, 16.99; P, 6.28.

Tris(4,4-diphenylureidomethyl)phosphine Oxide (6). Method A yielded 38% of white solid after 10 days reflux. However, on cooling to ambient temperature, the first solid collected from the reaction mixture was diphenylurea. Addition of water to the ethanolic reaction mixture was necessary to precipitate **6**, which was recrystallized from acetone–ethanol and then from ethyl acetate–ethanol to yield the analytical sample, **6**: ir (KBr) 2.98 (NH), 3.24 (aromatic CH), 3.39 (aliphatic CH), 5.98 and 6.7 (amide bands), 8.65 μ (P=O); NMR ($CDCl_3$) δ 3.67 (m, 6 H, PCH_2), 5.6 (m, 3 H, NH), 7.23 (m, 30 H, aromatics); after D_2O exchange δ 3.73 (d, J = 5 Hz, 6 H, PCH_2), 7.23 (m, 30 H, aromatics). The elemental analysis indicated a dihydrate.

Anal. Calcd for $C_{42}H_{39}N_6O_4P \cdot 2H_2O$: C, 66.48; H, 5.71; N, 11.08; P, 4.08. Found: C, 66.41; H, 5.61; N, 11.00; P, 4.17.

Tetrakis(4,4-diphenylureidomethyl)phosphonium Chloride (11). A mixture of 3.4 g (0.016 mol) of 1,1-diphenylurea, 0.76 g (0.004 mol) of Thpc, and 50 ml of toluene was refluxed for 4.5 h. The reaction mixture was allowed to cool, and the solid that formed was collected (2.0 g, 52% yield). This was recrystallized once from ethanol and twice from acetone–ethanol to yield the analytical sample, **11**: mp 246–247°; ir (KBr) 3.0 (NH), 3.25 (aromatic CH), 3.39 (aliphatic CH), 5.98, 6.27, and 6.7 μ (overlapping

amide bands and aromatic C=C); NMR (mixture of $CDCl_3$–Me_2SO-d_6) δ 4.27 (m, 8 H, PCH_2), 6.75 (m, 4 H, NH), 7.3 (m, 40 H, aromatics); after D_2O exchange δ 4.3 (d, J = 4 Hz, 8 H, PCH_2), 7.3 (m, 40 H, aromatics).

Anal. Calcd for $C_{56}H_{52}N_8O_4PCl$: C, 69.52; H, 5.42; N, 11.58; P, 3.20; Cl, 3.67.

However, the elemental analyses indicate a monohydrate of **11**.

Anal. Calcd for $C_{56}H_{52}N_8O_4PCl \cdot H_2O$: C, 68.25; H, 5.52, N, 11.37; P, 3.14; Cl, 3.60. Found: C, 68.13; H, 5.45; N, 11.24; P, 3.20; Cl, 3.95.

References and Notes

(1) Presented at the 26th Southeastern Regional Meeting of the American Chemical Society, Norfolk, Va., Oct 23–25, 1974.
(2) (a) One of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture. (b) Throughout this paper, the mention of trade names does not imply their endorsement by USDA over similar products not mentioned.
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Reaction of Picryl Azide with Aryloxyallenes[1]

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The reaction of aryloxyallenes with picryl azide gives two types of isolated adducts, **2** and **4**. The reaction is proposed to proceed via formation of the unisolated triazoline of type **5**. These compounds undergo an exceptionally facile Claisen rearrangement to yield the adducts of structure **4**, which unless blocked by a substituent at R_5 rapidly tautomerize to the isomeric adducts of type **2**.

As an extension of our work on allene oxides,[2] we have explored several potential synthetic routes to allenimines,[3] the nitrogen analogues of this strained small-ring heterocyclic system. One such approach[4] involves a 1,3-dipolar addition of organoazides to allenes, followed by photochemical expulsion of nitrogen from the adduct to give the desired allenimine (see eq 1). Bleiholder and Shechter[5] have earlier examined the reaction of several azides with alkyl-substituted allenes.[6] Although these authors were able to isolate the desired adducts in several instances,[7] these materials decomposed readily and the ring-contraction step of

$$ (1) $$
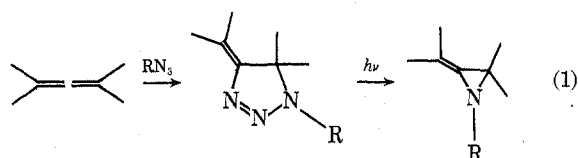
eq 1 was not achieved. In the present study we utilized aryloxyallenes as substrates with the idea that these electron-rich allenes might undergo more facile cycloaddition reactions with azides. In fact, the observed products result from