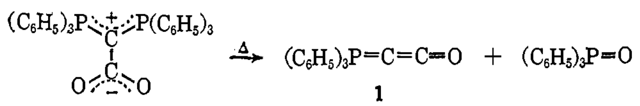
Cycloaddition Reactions of Triphenylphosphoranylideneketene

Gail H. Birum and Clifford N. Matthews

Contribution from the Monsanto Company, Central Research Department, St. Louis, Missouri 63166. *Received December 26, 1967*

Abstract: Stable, ylide-substituted 1,3-cyclobutanediones **4** were synthesized from triphenylphosphoranylideneketene, $Ph_3P{=}C{=}C{=}O$ (**1**), and aldehydes or active ketones, presumably through formation of unusual methyleneketene intermediates, $RR'C{=}C{=}C{=}O$ (**3**). Related cyclobutanediones **5** were formed directly from **1** and ketenes in a one-step reaction. Structure identifications were made principally by nmr and mass spectra. Although the symmetrical dimer of **1** has not been obtained, a methyl iodide adduct **9a** of the hypothetical dimer resulted from treatment of **1** with methyl iodide. Analogous methyl iodide adducts **10** of dimers of triphenylphosphoranylideneketenimines, $Ph_3P{=}C{=}C{=}NR$ (**11**), were also synthesized. Phenyl isocyanates and **1** gave stable 2:1 adducts having six-membered ring structures **14**. A four-membered ring is postulated as an intermediate in the conversion of **1** by carbon disulfide to triphenylphosphoranylidenethioketene (**15**).

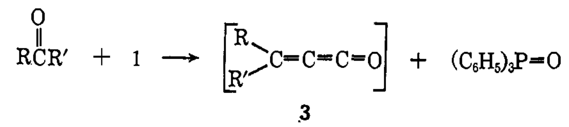
Triphenylphosphoranylideneketene (**1**) is a surprisingly stable compound (mp 172–173.5°) obtained by thermal cleavage of [(carboxy)(triphenylphosphoranylidene)methyl]triphenylphosphonium inner salt **2**. Ready reaction of **1** with active hydrogen compounds has been reported.[1] The present paper describes cycloaddition reactions leading to the formation of new cyclic organophosphorus compounds from this versatile heterocumulene.



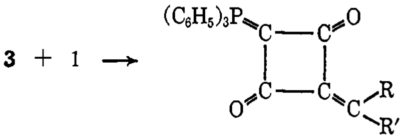
2 **1**

Structurally, triphenylphosphoranylideneketene can be regarded as both an ylide and a ketene. It was, therefore, of particular interest to investigate the course of its reaction with aldehydes and ketones since these carbonyl compounds react readily with ketenes to give β-lactones[2] and with phosphorus ylides to give olefinic products and phosphine oxides.[3] Experiments yielding ylide-substituted 1,3-cyclobutanediones as final products indicate that **1** reacted in successive steps first as an ylide and then as a ketene. The initial step, presumably, was a Wittig reaction leading to previously unknown methyleneketenes **3**. These reactive intermediates then added rapidly to **1** to give the final cyclobutane products **4**. The over-all reaction proceeded readily at room temperature with aldehydes and active ketones. No reaction occurred, however, with less active ketones such as acetone and fluorenone.

The proposed structural assignments for **4a–4f** are supported by elemental analyses, molecular weight measurements, and nmr, infrared, and mass spectra.[4] The mass spectra showed the parent ions and a characteristic fragmentation pattern that may be interpreted according to Scheme I. The ion fragments frequently contained one less hydrogen atom than expected. This was true also for the mass spectrum of **1** where an M − 1 [301] peak was larger than the parent ion [M^+ = 302] peak.

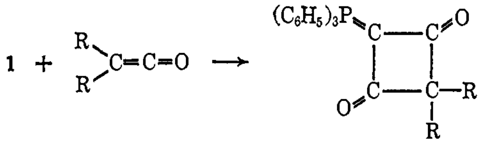


3



4a, R = H; R′ = C_6H_4CN-*p*
b, R = H; R′ = $C_6H_4NO_2$-*p*
c, R = H; R′ = C_6H_4CHO-*p*
d, R = CN; R′ = C_6H_5
e, R = CF_3; R′ = CF_3
f, R = CF_3; R′ = C_6H_4Cl-*p*

Additional evidence favoring structures **4a–4f** was provided by the marked similarity of their spectra to those of the products formed from **1** and ketenes. In these cases, direct cycloaddition[5] evidently occurred to give the 1,3-cyclobutanedione structures **5a** and **5b**.



5a, R = H
b, R = C_6H_5

With the exception of a fragment ion indicating the loss of carbon dioxide from **5b**, the mass spectra of **5a** and **5b** have similar fragmentation patterns that are consistent with Scheme II. The loss of carbon dioxide from **5b** probably occurred after rearrangement to a propiolactone ion.

Both **4** and **5** have infrared absorption bands at 5.7 (w), 6.1 (s), and 7.7–7.8 μ (s). The ^{31}P nmr chemical shifts of **4** were at −2 to 0 ppm, and those of **5** were at +3 to +4 ppm. Both **4a** and **5b** were recovered unchanged from solutions in concentrated trifluoroacetic acid. Compound **4b** was recovered unchanged

---

[1] C. N. Matthews and G. H. Birum, *Tetrahedron Letters*, 5707 (1966).

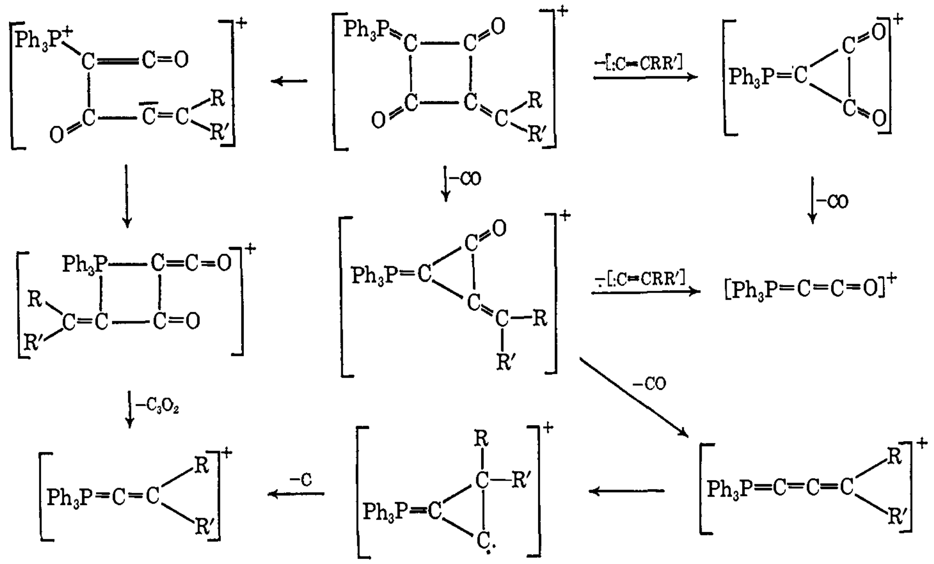
[2] H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press Inc., New York, N. Y., 1967.

[3] A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966.

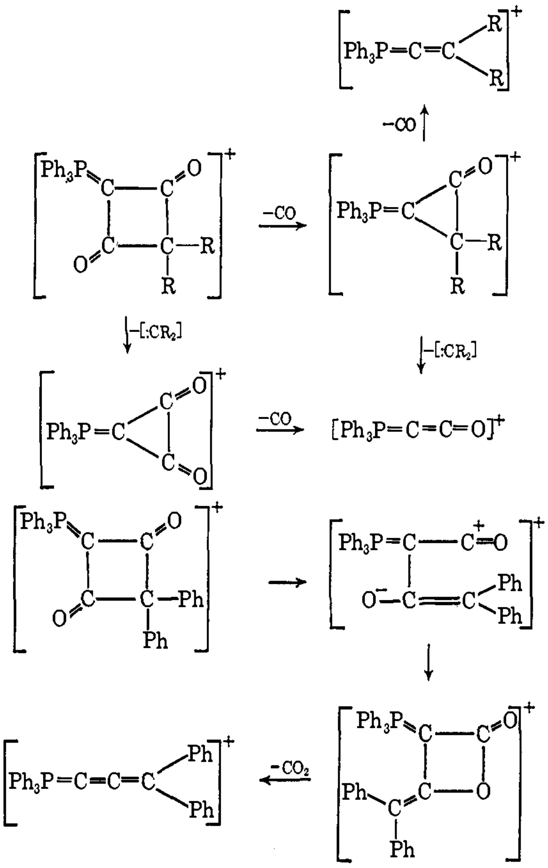
[4] We thank Professor W. H. Urry of the University of Chicago for obtaining some of the mass spectra and for helpful suggestions on interpretations of data.

[5] The question of whether addition proceeds stepwise or in a concerted manner is still open. A referee has helpfully pointed out that a naive application of the Woodward–Hoffman rules would lead one to expect stepwise addition, whereas recent reconsiderations seem to indicate that ketenes and heterocumulenes containing second-row elements are theoretically justifiable exceptions to the rule.

Scheme I

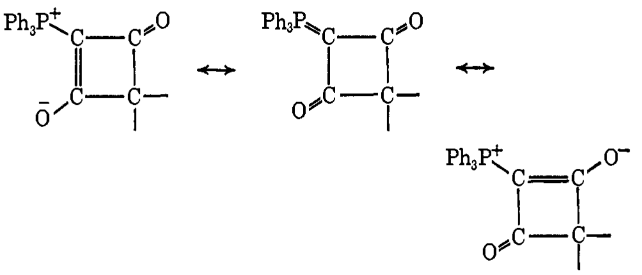


Scheme II

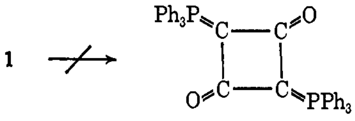


after treatment with aniline in boiling benzene and after warming in acidified methanol. Likewise, **5b** was recovered from a methanol–chloroform solution acidified with trifluoroacetic acid. Inertness to these reagents is believed to rule out lactone-type structures.[6]

The stability of the cyclobutanedione structures discussed above can be accounted for by resonance between conjugated cyclobutane and cyclobutene forms.[7]



Although the symmetrical cyclic dimer **8** would also



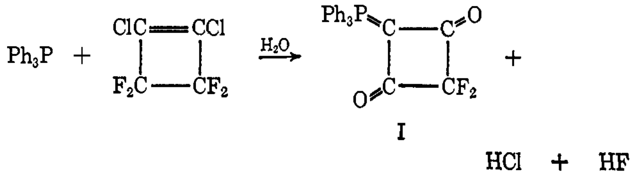
8

be expected to be stable, direct synthesis from **1** by uv irradiation, heating, and treatment with acids and bases under various conditions has, so far, been unsuccessful. However, a methyl iodide adduct **9a** of the hypothetical dimer was prepared by treating **1** with methyl iodide. This phosphonium salt is apparently the end product of a reaction sequence involving ylide formation from **1** and methyl iodide followed by further reaction of the ylide with more **1** and then ring closure. Metathesis of **9a** with fluoroboric acid and potassium hexafluorophosphate gave the corresponding tetrafluoroborate **9b** and hexafluorophosphate **9c**. There was no evidence for reaction of **9a** with excess methyl iodide or fluoroboric acid. The ^{1}H nmr spectrum of

---

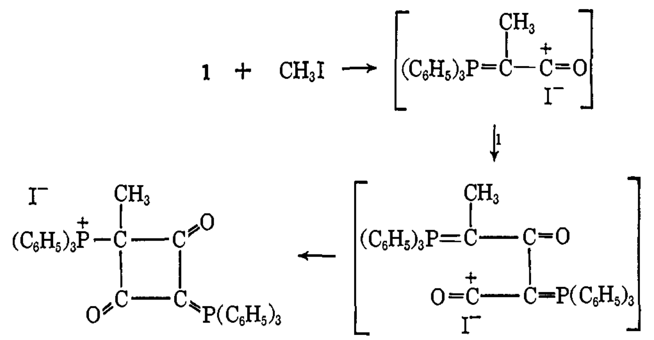
This synthesis was repeated and spectral measurements were obtained with the following characteristics: ir: 5.61 (w), 5.98 (s), and 8.00 μ (s); ^{31}P nmr: -3.0 ppm; mass spectrum: 380 [M$^+$], 351 [M − (CO + H)], 329 [M − (CF$_2$ + H)], 323 [M − (2CO + H)], 302 [M − (CO + CF$_2$)], and 301 [M − (CO + CF$_2$ + H)]. The similarity of these spectra to those of **5** provides additional evidence for the proposed structures. The ^{31}P nmr chemical shifts at -3.0 ppm for I, at -2 to 0 ppm for **4**, at $+3$ to $+4$ ppm for **5**, and at 0 ppm for **9** are at unusually high fields for resonance-stabilized ylides, indicating that the cyclobutane structure has a significant effect on the shielding of phosphorus in these compounds.

(6) After the completion of this manuscript, our attention was called to the disclosure of S. E. Elzey, Jr., U. S. Patent 3,359,321 (Dec 19, 1967), describing the synthesis of compound I.



I

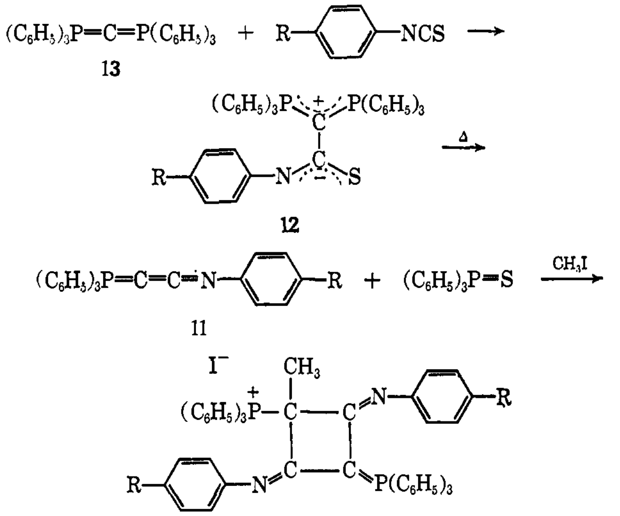
(7) For convenience we have represented the above compounds as cyclobutanediones rather than ionic cyclobutenones. A growing body of evidence, both chemical and spectroscopic, suggests that betaine structures more accurately describe the electron distribution for β-carbonyl-stabilized ylides.



9a

9a contained a doublet of doublets for the methyl group at -1.99 ppm ($J_{HP} = 16.6$ cps; $J_{HP'} = 1.0$ cps) in the theoretical 1:10 area ratio with respect to the six phenyl groups. The ^{31}P nmr spectrum had moderately broad peaks of equal areas at -25.8 ppm for the phosphonium substituent and at 0.0 ppm for the phosphorus ylide substituent, the latter's ^{31}P chemical shift and the infrared spectrum being markedly similar to those of **4** and **5**.

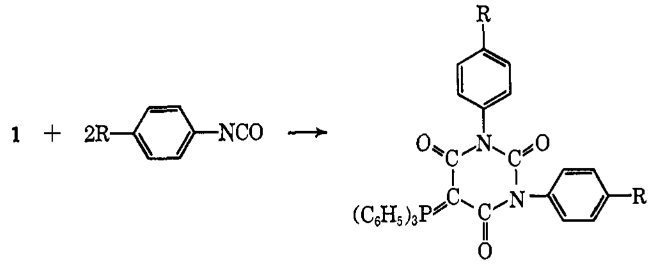
Additional support for the 1,3-cyclobutanedione structure **9a**, as well as for **4** and **5**, was provided by the similarity of their nmr spectra to those of the methyl iodide adducts **10a–c** of the dimers of triphenylphosphoranylideneketenimines **11**.[8] The ketenimines were prepared by thermal cleavage of mesomeric phosphonium inner salts **12** obtained by addition of aryl isothiocyanates to hexaphenylcarbodiphosphorane (**13**).



10a, R = H
b, R = CH_3
c, R = NO_2

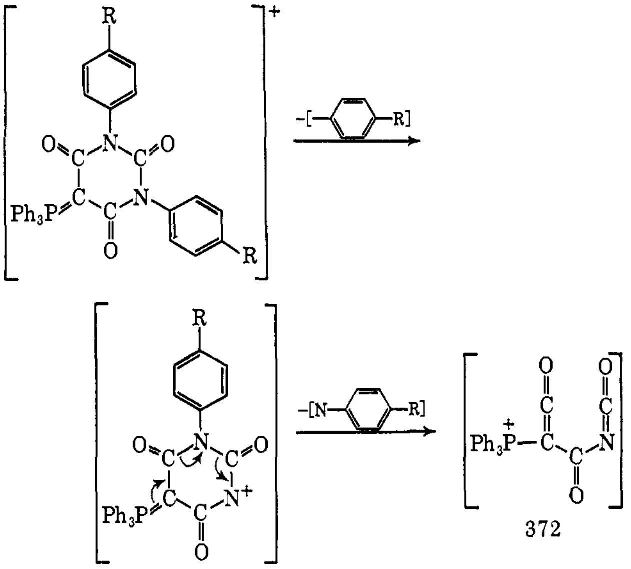
The ^{31}P nmr spectrum of **10b** had moderately broad peaks of equal areas at -28.3 ppm for the phosphonium substituent and at $+4.0$ ppm for the phosphorus ylide; the ^1H spectrum had aryl multiplets at -7.0 to -8.4 ppm (30 H), a well-resolved four-peak system at -6.18 (8 H) with the characteristic A_2B_2 pattern of *para*-disubstituted phenyl groups, a doublet at -2.60 ppm (3 H) ($J_{HP} = 17$ cps), and a singlet at -2.02 ppm (6 H). The well-resolved four-peak system for the eight ring-bonded tolyl hydrogen atoms and the single peak for the two tolyl methyl groups indicate equivalent environments for the two tolyl groups, as would be expected for the cyclic structure.

Other types of stable adducts can also be formed from **1**. Aromatic isocyanates, for example, react readily, but in this case the products isolated have six-membered rings and contain two molecules of isocyanate for each molecule of **1**. A single ^1H nmr peak for the two tolyl methyl groups of **14b**, prepared from tolyl isocyanate and **1**, show that the two tolyl groups have equivalent environments as would be the case for the proposed cyclic structure. The mass spectra of compounds

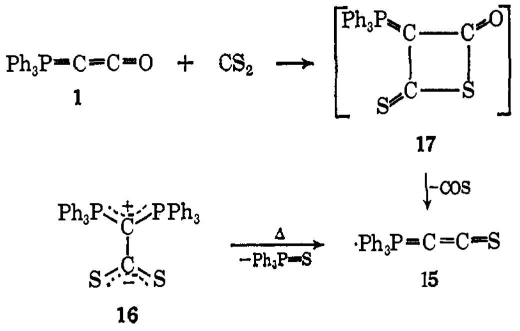


14a, R = H
b, R = CH_3
c, R = F
d, R = CN
e. R = NO_2

14a–d contained, in addition to parent ion peaks, ion fragments from loss of one and two isocyanate groups, indicating that there were no skeletal rearrangements during formation of the parent compounds. An ion fragment (*m/e* 372) observed in the spectra of all members of this class could have evolved by the following route.



Another instance of cycloaddition may have occurred in the reaction of **1** with carbon disulfide. In this case the product isolated was triphenylphosphoranylidenethioketene (**15**), synthesized also by thermal cleavage of



---

(8) G. H. Birum and C. N. Matthews, to be published.

[(dithiocarboxy)(triphenylphosphoranylidene)methyl]triphenylphosphonium inner salt **16**.[1] The conversion of **1** to **15** presumably took place *via* the cyclic intermediate **17**.

The ketene and thioketene groups of **1** and **15** are isoelectronic with the functional groups of isocyanates and isothiocyanates.

$$Ph_3\overset{+}{P}{-}\overset{-}{C}{=}C{=}O \qquad Ph_3\overset{+}{P}{-}\overset{-}{C}{=}C{=}S$$

$$R{-}\ddot{N}{=}C{=}O \qquad R{-}\ddot{N}{=}C{=}S$$

This parallel is reflected in the fact that just as isothiocyanates are less reactive than isocyanates,[2] triphenylphosphoranylidenethioketene undergoes addition reactions less readily than triphenylphosphoranylideneketene.[8]

Experimental Section

Melting points were obtained in a Thomas-Hoover Unimelt instrument and are corrected. Infrared spectra were determined in potassium bromide disks (unless otherwise noted) on a Beckman IR4 spectrophotometer. Proton nuclear magnetic resonance (nmr) spectra were obtained at 60.0 or 100.0 Mc on Varian A-60 or HR-100 spectrometers with tetramethylsilane as an internal standard. Phosphorus nmr spectra were determined at 24.3 or 40.5 Mc on Varian HR-60 or HR-100 instruments and are reported with respect to 85% H_3PO_4 contained in a capillary. Fluorine nmr spectra were measured at 56.4 Mc on a Varian A-56/60 instrument and are reported with respect to trichlorofluoromethane. The nmr measurements were generally made on saturated solutions. Mass spectra were obtained on a Consolidated Engineering Corp. Type 21-104 spectrometer fitted with a probe for direct introduction of solids. Elemental analyses and molecular weights were determined by Galbraith Laboratories, Knoxville, Tenn.

Triphenylphosphoranylideneketene (1). Hexaphenylcarbodiphosphorane[9-11] (16.0 g, 0.03 mol) and dry diglyme (50 g) were stirred under N_2 in a 100-ml flask as gaseous CO_2 was introduced below the surface at room temperature. A white solid formed as the yellow color gradually disappeared. After 1.5 hr the temperature was raised to 65°. Carbon dioxide addition was then stopped and the reaction mixture allowed to cool under N_2. Filtration under N_2, washing with diglyme and then with ethyl ether, and drying under N_2 gave 17.2 g (96.5% yield) of white powder, **2**, mp 140–141°.

Anal. Calcd for $C_{38}H_{30}O_2P_2$: C, 78.60; H, 5.22; P, 10.68. Found: C, 78.58; H, 5.36; P, 10.51.

A mixture of the hexaphenylcarbodiphosphorane–carbon dioxide adduct (15.8 g) and dry diglyme (30 g) was stirred under N_2 and warmed at 140–145° for 0.25 hr, giving a clear yellow solution having ^{31}P nmr signals at −23.4 and −3.6 ppm (an authentic sample of triphenylphosphine oxide had a ^{31}P signal at −24.0 ppm in diglyme). The reaction mixture was cooled for 4 hr to induce crystallization and filtered under N_2 and the product washed with diglyme and with ether to give 6.3 g of white powder, mp 130–160°, having strong infrared bands at 4.74 and 8.38 μ. Repeated recrystallization from diglyme resulted in diminishing infrared absorption at 8.38 μ (P=O) and higher melting points. After five recrystallizations, 1.6 g (19.5% yield) of white needles, **1**, was obtained, mp 172–173.5°, having essentially no infrared absorption at 8.38 μ but a very strong band at 4.74 μ. The ^{31}P nmr spectrum showed a signal at −2.6 ppm (in benzene at 40.5 Mc); molecular weight in $CHCl_3$, 298 (calcd: 302.3). The mass spectrum had peaks at 302 [M^+], 301 [M − H], 278 [$(C_6H_5)_3P{=}O$], 277 [$(C_6H_5)_3P{=}O$ − H], 274 [$C{=}P(C_6H_5)_3$], 273 [$C{=}P(C_6H_5)_3$ − H], 262 [$P(C_6H_5)_3$], 225 [M − C_6H_5], 201 [$(C_6H_5)_2P{=}O$], 185 [$(C_6H_5)_2P$], and 183.

Anal. Calcd for $C_{20}H_{15}OP$: C, 79.44; H, 5.00; P, 10.24. Found: C, 79.51; H, 4.93; P, 10.20.

An additional 1.1 g of slightly less pure product was isolated from the filtrates. Concentration of the combined filtrates to dryness, extraction of the residue with hot heptane, and repeated recrystallization of the heptane-soluble material gave 5.3 g of a white solid, mp 156–157°, having a ^{31}P nmr signal at −29.1 ppm in $CDCl_3$ (an authentic sample of triphenylphosphine oxide melted at 156–158° and had a ^{31}P signal at −28.5 ppm). The infrared spectrum contained no band at 4.74 μ and was identical with that of an authentic sample of triphenylphosphine oxide.

Infrared spectra of the various recrystallization mixtures and filtrate residues contained only bands that are characteristic of the two isolated compounds, indicating that these are the only two products produced in significant quantities under the decomposition conditions used. It was frequently found convenient to use the crude reaction solution in the preparation of derivatives of **1**.

2-(*p*-Cyanobenzylidene)-4-(triphenylphosphoranylidene)-1,3-cyclobutanedione (4a). A 3.0-g (0.01 mol) portion of **1** and 0.7 g (0.005 mol) of *p*-cyanobenzaldehyde were stirred in 10 g of benzene under N_2. The initially insoluble **1** gradually dissolved as the color of the reaction mixture changed from light yellow to orange, and another solid separated after about 1 hr. Stirring was continued at room temperature for 20 hr. Filtration under N_2 and washing with benzene and ether gave 1.8 g (78% yield) of light yellow solid, **4a**, mp 248–250° (melting point unchanged after recrystallization from benzene–acetonitrile). Triphenylphosphine oxide, 1.3 g (86% yield), having ^{31}P nmr and infrared spectra identical with an authentic sample, was isolated from the filtrate. The ^{31}P nmr spectrum of **4a** had a peak at 0.0 ppm (in $CDCl_3$); the ^1H spectrum contained aryl multiplets at −7.2 to −8.3 ppm and a singlet at −6.46 ppm, the areas approximating the theoretical 19:1 ratio. The infrared spectrum had bands at 4.49 (w), 5.70 (w), 6.11 (s), and 7.7–7.8 μ (s); molecular weight in acetone, 467 (calcd: 457.4). The mass spectrum had peaks at 457 [M^+], 428 [M − (CO + H)], 401 [M − 2CO], 388 [M − (2CO + C + H)], 355 [M − C_6H_4CN], 329 [M − $C{=}CHC_6H_4CN$ + H)], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], and 301.

Anal. Calcd for $C_{30}H_{20}NO_2P$: C, 78.73; H, 4.40; N, 3.06; P, 6.77. Found: C, 78.55; H, 4.52; N, 3.04; P, 6.93.

The ^{31}P nmr spectrum of **4a** in concentrated trifluoroacetic acid had a peak at −3.4 ppm; the ^1H spectrum had an aryl multiplet at −7.58 to −8.33 ppm and a singlet at −6.91 ppm. Evaporation of the trifluoroacetic acid left a light yellow solid having an infrared spectrum essentially identical with that of the starting material **4a**.

2-(*p*-Nitrobenzylidene)-4-(triphenylphosphoranylidene)-1,3-cyclobutanedione (4b). A 2.2-g portion of a 4:1 mixture of **1** and triphenylphosphine oxide was stirred in benzene under N_2 as 1.5 g of *p*-nitrobenzaldehyde was added. The mixture was warmed to reflux, cooled at 5° overnight, and filtered under N_2 to give a yellow-brown solid which was recrystallized twice from benzene–acetonitrile to give 0.7 g of yellow solid, **4b**, mp 258–259°. The ^{31}P nmr spectrum had a singlet at −1.2 ppm (in $CDCl_3$); the ^1H spectrum contained an aryl singlet at −8.26 ppm, an aryl multiplet at −7.4 to −8.1 ppm, and a singlet at −6.53 ppm, the areas approximating a 4:15:1 ratio. The infrared spectrum had bands at 5.68 (w), 6.08 (s), 7.43 (s), and 7.7–7.8 μ (s); molecular weight in $CHCl_3$, 463 (calcd: 477.4). The mass spectrum had peaks at 477 [M^+], 449 [M − CO], 421 [M − 2CO], 409 [M − (2CO + C)], 329 [M − ($C{=}CHC_6H_4NO_2$ + H)], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], and 301.

Anal. Calcd for $C_{29}H_{20}NO_4P$: C, 72.94; H, 4.22; N, 2.93; P, 6.49. Found: C, 72.76; H, 4.26; N, 2.81; P, 6.50.

Compound **4b** was recovered unchanged after stirring at room temperature for 2 days in diglyme containing water, after treatment with aniline in boiling benzene, and after a dispersion in methanol acidified with sulfuric acid was warmed at reflux for 2 hr.

2-(*p*-Formylbenzylidene)-4-(triphenylphosphoranylidene)-1,3-cyclobutanedione (4c). A mixture of triphenylphosphine oxide and about 2.0 g of **1** in diglyme was stirred under N_2 as 0.7 g of terephthalaldehyde was added. After 20 hr the reaction mixture was diluted with ether, causing 0.9 g of yellow solid to precipitate. Recrystallization from acetonitrile–chloroform gave 0.4 g of yellow crystals, **4c**, mp 265–268°. The ^1H nmr spectrum (in $CDCl_3$) had singlets at −9.98 and −6.53 ppm and aryl multiplets at −7.25 to −8.33 ppm, the areas approximating the theoretical 1:1:19 ratio. The infrared spectrum had bands at 5.72 (w), 5.91 (m), 6.12 (s), and 7.76 μ (s); molecular weight in acetone, 449 (calcd: 460.4). The mass spectrum had peaks at 460 [M^+], 432 [M − CO], 404 [M − 2CO], 392 [M − (2CO + C)], 329 [M − ($C{=}CHC_6H_4CHO$ + H)], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], and 301.

Anal. Calcd for $C_{30}H_{21}O_3P$: C, 78.23; H, 4.60; P, 6.72. Found: C, 77.30; H, 4.69; P, 6.83.

2-[(Cyano)(phenyl)methylene]-4-(triphenylphosphoranylidene)-1,3-cyclobutanedione (4d). A 1.0-g portion of **1** and 0.3 g of benzoyl cyanide were stirred in benzene under N_2 at room temperature.

---

(9) F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Am. Chem. Soc.*, **83**, 3539 (1961).

(10) (a) C. N. Matthews, J. S. Driscoll, J. E. Harris, and R. J. Wineman, *ibid.*, **84**, 4349 (1962); (b) C. N. Matthews, U. S. Patent 3,262, 971 (July 26, 1966).

(11) G. H. Birum and C. N. Matthews, *J. Am. Chem. Soc.*, **88**, 4198 (1966).

The initially insoluble **1** gradually dissolved and another solid separated on further stirring. Recrystallization from benzene–acetonitrile gave 0.4 g of off-white solid, **4d**, mp 227–229°, having infrared bands at 4.51 (w), 5.68 (w), 6.07 (s), and 7.78 μ (s); molecular weight in acetone, 470 (calcd: 457.4). The mass spectrum had peaks at 457 [M^+], 430 [M − (CN + H)], 429 [M − CO], 401 [M − 2CO], 389 [M − (2CO + C)], 380 [M − C_6H_5], 329 [M − ($C{=}CCNC_6H_5$ + H)], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], and 301.

Anal. Calcd for $C_{30}H_{20}NO_2P$: C, 78.73; H, 4.40; N, 3.06; P, 6.77. Found: C, 78.77; H, 4.54; N, 2.94; P, 6.50.

2-[Bis(trifluoromethyl)methylene]-4-(triphenylphosphoranylidene)-1,3-cyclobutanedione (4e). A suspension of 1.2 g of **1** in 7 g of benzene was stirred under N_2 as gaseous hexafluoroacetone was dispersed over the surface. The solid **1** gradually dissolved as the treatment with hexafluoroacetone was continued for 0.5 hr. Evaporation of the solvent gave a solid mixture having ^{31}P nmr peaks of approximately equal areas at −24.9 ppm for triphenylphosphine oxide and at −1.9 ppm for **4e** (in benzene), and the ^{19}F spectrum had a doublet at +57.1 ppm, J_{FP} = 1.1 cps. The infrared spectrum in benzene had bands at 5.63 (w), 6.01 (s), 7.47 (s), 8.04 (s), 8.32 (m), and 8.60 μ (s). The mass spectrum of the mixture had peaks at 492 [M^+ of **4e**], 473 [M − F], 463 [M − (CO + H)], 436 [M − 2CO], 435 [M − (2CO + H)], 424 [M − (2CO + C)], 423 [M − CF_3], 395 [M − (CF_3 + CO)], 367 [M − (CF_3 + 2CO)], 355 [M − (2CF_3 − H)], 329 [M − ($C{=}C(CF_3)_2$ + H)], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], 301, and 278 [M^+ of $(C_6H_5)_3P{=}O$].

2-[(*p*-Chlorophenyl)(trifluoromethyl)methylene]-4-(triphenylphosphoranylidene)-1,3-cyclobutanedione (4f). A 0.5-g portion of **1** and 0.3 g of *p*-chlorophenyl trifluoromethyl ketone were stirred in benzene under N_2 for several hours, and the reaction mixture was evaporated to dryness. The residue was recrystallized from benzene, yielding 0.2 g of white solid, **4f**, mp 246–247°. The ^{31}P nmr spectrum (in $CDCl_3$) had a moderately broad peak at −1.9 ppm, and the ^{19}F spectrum had a peak at +57.8 ppm. The infrared spectrum had bands at 5.67 (w), 6.07 (s), and 7.75 μ (s); molecular weight in benzene, 542 (calcd: 534.9). The mass spectrum had peaks at 534 [M^+], 515 [M − F], 505 [M − (CO + H)], 478 [M − 2CO], 466 [M − (2CO + C)], 465 [M − CF_3], 329 [M − ($C{=}C$-$CF_3C_6H_4Cl$ + H)], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], and 301.

Anal. Calcd for $C_{30}H_{19}ClF_3O_2P$: C, 67.35; H, 3.58; Cl, 6.63; P, 5.79. Found: C, 66.95; H, 3.52; Cl, 7.17; P, 5.96.

2-Triphenylphosphoranylidene-1,3-cyclobutanedione (5a). A dispersion of 1.5 g of **1** in 15 g of benzene was stirred under N_2 and treated with ketene generated from acetone by the method of Williams and Hurd.[12] Undissolved **1** gradually disappeared, and after a few minutes another solid separated. Ketene treatment was continued for 0.1 hr more, and the reaction mixture was filtered under N_2 and washed with benzene and ether to give 1.1 g of crude **5a**. Recrystallization twice from benzene–acetonitrile gave 0.7 g of white crystals, mp 219–221° dec. It had a ^{31}P nmr chemical shift at +4.4 ppm (in $CDCl_3$), and an ^{1}H nmr doublet at −3.48 ppm, J_{HP} = 3.1 cps, in a 2:15 area ratio with an aryl multiplet at −7.33 to −8.08 ppm. The infrared spectrum had bands at 5.67 (m), 5.77 (m), 6.12 (s), and 7.6–7.7 μ (s); molecular weight in $CHCl_3$, 340 (calcd: 344.3). The mass spectrum had peaks at 344 [M^+], 330 [M − CH_2], 329 [M − (CH_2 + H)], 316 [M − CO], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], 301, and 287 [M − (2CO + H)]; in some samples a small peak was observed at 368 [M + 2C].

Anal. Calcd for $C_{22}H_{17}O_2P$: C, 76.71; H, 4.97; P, 8.99. Found: C, 76.45; H, 5.04; P, 9.03.

2,2-Diphenyl-4-triphenylphosphoranylidene-1,3-cyclobutanedione (5b). A dispersion of 1.5 g of **1** in benzene was stirred under N_2 as 1.0 g of diphenylketene was added dropwise. Stirring was continued for 1 hr, and the reaction mixture was filtered, yielding 2.3 g of white solid. Recrystallization of a 1.4-g portion from benzene gave 1.1 g of white crystals, **5b**, mp 207–208°. The ^{31}P nmr spectrum (in $CDCl_3$) had a singlet at +3.4 ppm (~0 ppm in trifluoroacetic acid). The infrared spectrum contained bands at 5.71 (m), 6.11 (s), and 7.7 μ (s); molecular weight in $CHCl_3$, 510 (calcd: 496). The mass spectrum had peaks at 496 [M^+], 467 [M − (CO + H)], 452 [M − CO_2], 439 [M − (2CO + H)], 438 [M − (2CO + 2H)], 391 [M − (C_6H_5 + CO)], 363 [M − (C_6H_5 + 2CO)], 329 [M − ($C(C_6H_5)_2$ + H)], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], 301, 194 [$(C_6H_5)_2C{=}C{=}O$], and 165 [$C(C_6H_5)_2$ − H].

Anal. Calcd for $C_{34}H_{25}O_2P$: C, 82.21; H, 5.07; P, 6.24. Found: C, 81.91; H, 5.13; P, 6.18.

Compound **5b** was recovered unchanged from concentrated trifluoroacetic acid as shown by nmr spectra (^{31}P and ^{1}H in $CDCl_3$) and by infrared spectra. Likewise, **5b** was recovered unchanged after a warm solution in equal volumes of methanol and chloroform was acidified with trifluoroacetic acid.

2,4-Dioxo-1-methyl-3-triphenylphosphoranylidene-1-cyclobutyltriphenylphosphonium Iodide (9a). A methylene chloride solution of a mixture (2.0 g) of **1** and triphenylphosphine oxide was stirred under nitrogen as methyl iodide (3.0 g) was added. Stirring was continued for 2 hr, when the solvent and excess methyl iodide were evaporated. The residue was washed with benzene and ether to give 2.0 g of white powder. Recrystallization from diglyme–acetonitrile gave 1.1 g of **9a**, mp 241–242° dec. The ^{31}P nmr spectrum (in $CDCl_3$) contained moderately broad peaks of equal areas at −25.8 and 0.0 ppm (at −26.2 and 0.0 ppm in CF_3CO_2H). The ^{1}H spectrum contained aryl multiplets at −7.0 to −8.2 ppm and a doublet of doublets at −1.99 ppm (J_{HP} = 16.6 cps; $J_{HP'}$ = 1.0 cps), the areas of aryl multiplets to primary doublet having the ratio 10:1. The infrared spectrum contained absorption bands at 5.66 (m), 6.05 (s), and 7.69 μ (s).

Anal. Calcd for $C_{41}H_{33}IO_2P_2$: C, 65.94; H, 4.45; I, 16.99; P, 8.30. Found: C, 65.85; H, 4.42; I, 17.10; P, 8.29.

Tetrafluoroborate Salt of 9a (9b). A solution of **9a** (0.7 g) in methanol was stirred as excess 48% fluoroboric acid was added dropwise, causing a white solid to separate rapidly. The reaction mixture was warmed to reflux and filtered to give 0.5 g of white powder, **9b**, mp 241–242° dec. The ^{1}H nmr spectrum (in $CDCl_3$) contained aryl multiplets at −7.1 to −8.2 ppm and a doublet of doublets at −1.96 ppm (J_{HP} = 16.6 cps; $J_{HP'}$ = 1.0 cps), the area ratio of aryl multiplets to primary doublet being approximately 10:1. The infrared spectrum contained bands at 5.66 (m), 6.08 (s), 7.6–7.7 (s), and 9.4 μ (vs).

Anal. Calcd for $C_{41}H_{33}BF_4O_2P_2$: C, 69.68; H, 4.71; B, 1.53; F, 10.75; P, 8.77. Found: C, 69.39; H, 4.72; B, 1.55; F, 10.77; P, 8.85.

Hexafluorophosphate Salt of 9a (9c). A solution of **9a** (0.4 g) in methanol was stirred as KPF_6 (0.2 g) was added. A white solid separated rapidly. The mixture was warmed to reflux and filtered hot, and the product was washed several times with warm methanol, yielding 0.3 g of white solid, **9c**, mp 238–239° dec.

Anal. Calcd for $C_{41}H_{33}F_6O_2P_3$: C, 64.38; H, 4.35; F, 14.90; P, 12.15. Found: C, 63.99; H, 4.48; F, 14.94; P, 12.21.

1-Methyl-2,4-bis(phenylimino)-3-triphenylphosphoranylidene-1-cyclobutyltriphenylphosphonium Iodide (10a). A mixture of 21.4 g (0.04 mol) of hexaphenylcarbodiphosphorane and 110 g of diglyme was stirred under N_2 as 8.0 g (0.06 mol) of phenyl isothiocyanate was added dropwise. The reaction mixture was warmed at 50–60° for 1 hr, cooled, and then filtered. The solid product was washed with diglyme and ether and dried at 60° (0.1 mm) to give 25.9 g (96.5% yield) of light yellow powder, **12a**, mp 204–205° dec. A freshly prepared solution in CH_2Cl_2 showed a ^{31}P nmr singlet at −12.1 ppm; after 1 hr an additional singlet was observed at −21.6 ppm, and this became the only measurable peak after 20 hr, indicating complete reaction of **12a** with the solvent. The infrared spectrum of **12a** had bands at 6.67 (s) and 8.83 μ (s); molecular weight in $CHCl_3$, 669 (theoretical, 671.7).

Anal. Calcd for $C_{44}H_{35}NP_2S$: C, 78.64; H, 5.25; N, 2.08; P, 9.22; S, 4.77. Found: C, 78.43; H, 5.29; N, 2.09; P, 9.32; S, 5.03.

A mixture of 5.0 g of **12a** and 10 g of *o*-dichlorobenzene was stirred and warmed under N_2 to a maximum temperature of 178°. After 2 min at 177–178°, the reaction mixture was cooled, giving a dark red solution having a very strong infrared absorption band at 5.0 μ ($C{=}C{=}N$). The ^{31}P nmr spectrum of this solution contained singlets at −42.9 ppm for triphenylphosphine sulfide and at −2.4 ppm for **11a** in approximately a 3:2 area ratio.

The dark red solution containing **11a** was stirred under N_2 as 1.0 g of methyl iodide was added dropwise. After being stirred for 20 hr at room temperature, the reaction mixture was diluted with 20 ml of benzene and then filtered to give 2.8 g of light yellow solid. Recrystallization from benzene–acetonitrile gave 1.7 g (51% yield) of light yellow solid, mp 199–201° dec.

An analytical sample was recrystallized twice from acetonitrile to give a white solid, **10a**, mp 199–201° dec. The ^{31}P nmr spectrum (in $CDCl_3$) contained moderately broad singlets of equal areas at −28.1 and +4.4 ppm; the ^{1}H spectrum contained aryl multiplets at −8.3 to −7.0 ppm (30 H), at −6.7 to −6.3 ppm (6 H), and at −6.3 to −5.9 ppm (4 H) and an alkyl doublet at −2.56 ppm (3 H), J_{HP} = 17 cps. The infrared spectrum had bands at 5.88 (w), 6.18 (s), 6.31 (s), and 7.85 μ (s).

Anal. Calcd for $C_{53}H_{43}IN_2P_2$: C, 70.98; H, 4.83; I, 14.15; N, 3.12; P, 6.91. Found: C, 70.22; H, 4.90; I, 13.93; N, 3.20; P, 6.77; S, 0.00.

---

(12) J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **4**, 122 (1939).

1-Methyl-2,4-bis(*p*-methylphenylimino)-3-triphenylphosphoranylidene-1-cyclobutyltriphenylphosphonium Iodide (10b). A suspension of hexaphenylcarbodiphosphorane (16.1 g, 0.03 mol) in 75 g of diglyme was stirred under N_2 as *p*-tolyl isothiocyanate (7.5 g, 0.05 mol) was added dropwise. The reaction mixture was warmed at 80–90° for 0.5 hr and then filtered hot and washed with diglyme and ether to give 19.2 g (93.4%) of yellow solid, **12b**, mp 205–207° dec.

A mixture of 5.0 g of **12b** and 10 g of *o*-dichlorobenzene was stirred and warmed under N_2 to 165°, giving a dark red solution having a strong infrared absorption band at 5.0 μ (C=C=N). The ^{31}P nmr spectrum contained singlets at −3.0 ppm for **11b** and at −42.3 ppm for triphenylphosphine sulfide in approximately a 2:3 area ratio. Methyl iodide (1.0 g) was added to the dark red solution, and after 2 hr, the solution was diluted with an equal volume of benzene. Stirring was continued at room temperature for 15 hr, and then the reaction mixture was filtered and the solid was washed with benzene and ether, giving 2.1 g of crude **10b**, mp 203–208° dec. Recrystallization of a portion from benzene–acetonitrile gave a yellow solid, mp 204–207° dec. The ^{31}P nmr spectrum (in $CDCl_3$) had moderately broad peaks of equal areas at −28.3 and +4.0 ppm; the ^1H spectrum had complex aryl multiplets at −7.0 to −8.4 ppm (30 H), a well-resolved, four-peak system centered at −6.18 ppm (8 H) with the A_2B_2 pattern characteristic of *para*-disubstituted phenyl systems, a doublet at −2.60 ppm (3 H) (J_{HP} = 17 cps), and a singlet at −2.02 ppm (6 H). The infrared spectrum had bands at 5.9 (w), 6.28 (s), and 7.87 μ (m).

Anal. Calcd for $C_{55}H_{47}IN_2P_2$: C, 71.41; H, 5.12; I, 13.72; N, 3.03; P, 6.70. Found: C, 71.29; H, 4.87; I, 13.72; N, 3.25; P, 6.51.

1-Methyl-2,4-bis(*p*-nitrophenylimino)-3-triphenylphosphoranylidene-1-cyclobutyltriphenylphosphonium Iodide (10c). A mixture of 10.8 g (0.02 mol) of hexaphenylcarbodiphosphorane in 50 g of diglyme was stirred as 6.0 g (0.033 mol) of *p*-nitrophenyl isothiocyanate was added in portions under N_2. A red color developed immediately. The reaction mixture was stirred for 0.5 hr at room temperature and then filtered to give 13.7 g (95.7%) of brick red powder, **12c**, mp 229–230° dec. The infrared spectrum had bands at 6.7 (m), 7.15 (m), 7.7–7.8 (s), and 8.6 μ (s). The red solid was too insoluble in the following solvents for molecular weight and nmr measurements: dimethylformamide, dimethylacetamide, dimethyl sulfoxide, methylene chloride, chloroform, acetone, acetonitrile, carbon tetrachloride, methanol, ethanol, ethyl acetate, tetrahydrofuran, and water.

Anal. Calcd for $C_{44}H_{34}N_2O_2P_2S$: C, 73.72; H, 4.78; N, 3.91; P, 8.64; S, 4.47. Found: C, 72.50; H, 4.99; N, 3.85; P, 8.42; S, 4.78.

A dispersion of 3.0 g of **12c** in 8 g of *o*-dichlorobenzene was warmed at 180° for 5 min, giving a dark red-brown solution having ^{31}P nmr peaks at −42.2 ppm for triphenylphosphine sulfide and at −1.6 ppm for **11c** (area ratio, ~4:3). The infrared spectrum had a strong absorption band at 4.9 μ (C=C=N).

The *o*-dichlorobenzene solution containing **11c** was stirred under nitrogen as 1.0 g of methyl iodide was added. After standing at room temperature for 8 days, the reaction mixture was diluted with ether, causing precipitation of 1.5 g of orange solid. Recrystallization from diglyme–acetonitrile gave 0.2 g of yellow solid, mp 230–233° dec. The ^{31}P nmr spectrum (in $CDCl_3$) had moderately broad peaks of about equal areas at −27.7 and +3.7 ppm; the ^1H spectrum contained a complex aryl region at −7.0 to −8.4 ppm (34 H), two peaks centered at −6.23 ppm (4 H) (probably half of a *para*-disubstituted aryl pattern, the other half being masked by the major aryl complex), and a methyl doublet at −2.76 ppm (3 H), J_{HP} = 16.5 cps. The infrared spectrum had bands at 5.85 (w), 6.18 (s), 6.35 (s), 6.60 (s), and 7.48 μ (s).

Anal. Calcd for $C_{53}H_{41}IN_4O_4P_2$: C, 64.49; H, 4.19; I, 12.86; N, 5.68; P, 6.28. Found: C, 64.21; H, 4.44; I, 12.76; N, 5.63; P, 6.06.

1,3-Diphenyl-2,4,6-trioxo-5-triphenylphosphoranylidene-1,3-diazacyclohexane (14a). A dispersion of **1** (1.2 g) in benzene was stirred under nitrogen as phenyl isocyanate (0.5 g) was added dropwise. A red color developed, and a solid separated while stirring was continued for 1 hr. Filtration and recrystallization of the solid from diglyme–acetonitrile gave 0.5 g of white solid, **14a**, mp 350–352°, having a ^{31}P nmr singlet at −17.1 ppm and ^1H aryl multiplets from −7.1 to −8.0 ppm. The infrared spectrum contained bands at 5.83 (m), 6.12 (s), 7.01 (m), and 7.34 μ (s). The mass spectrum had peaks at 540 [M^+], 421 [M − C_6H_5NCO], 372 [M − (C_6H_5 + C_6H_5N)], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], and 301.

Anal. Calcd for $C_{34}H_{25}N_2O_3P$: C, 75.51; H, 4.66; N, 5.18; P, 5.73. Found: C, 75.47; H, 4.73; N, 5.35; P, 5.84.

1,3-Di-*p*-tolyl-2,4,6-trioxo-5-triphenylphosphoranylidene-1,3-diazacyclohexane (14b). A diglyme solution of **1** (30 ml) and triphenylphosphine oxide was stirred under nitrogen at room temperature as *p*-tolyl isocyanate (3 ml) was added. Stirring was continued for 20 hr, and then ether was added, causing 0.8 g of yellow solid to separarate. Recrystallization from diglyme–acetonitrile yielded 0.3 g of light yellow solid, **14b**, mp 315–317°, having a ^{31}P nmr singlet at −17.4 ppm (in $CDCl_3$), an ^1H singlet at −2.23 ppm, and an aryl multiplet at −7.1 to −8.0 ppm, the areas being in the theoretical 6:23 ratio. The infrared spectrum contained absorption bands at 5.82 (m), 6.12 (s), 7.01 (m), and 7.36 μ (s); molecular weight in $CHCl_3$, 557 (theoretical, 568). The mass spectrum had peaks at 568 [M^+], 435 [M − $CH_3C_6H_4NCO$], 372 [M − ($CH_3C_6H_4$ + $CH_3C_6H_4N$)], 302 [$(C_6H_5)_3P{=}C{=}C{=}O$], and 301.

Anal. Calcd for $C_{36}H_{29}N_2O_3P$: C, 76.02; H, 5.14; N, 4.93; P, 5.45. Found: C, 76.06; H, 5.32; N, 4.97; P, 5.51.

1,3-Di(*p*-fluorophenyl)-2,4,6-trioxo-5-triphenylphosphoranylidene-1,3-diazacyclohexane (14c). A diglyme solution of **1** (20 ml) and triphenylphosphine oxide was stirred under nitrogen as *p*-fluorophenyl isocyanate (1 ml) was added. Stirring was continued for 2 hr, when the reaction mixture was diluted with ether and cooled at 5° for 5 hr. Filtration gave a white solid which was recrystallized by precipitation of a diglyme–acetonitrile solution with ether to give 0.4 g of white powder, **14c**, mp 296–299°, having a ^{31}P nmr singlet at −17.6 ppm (in $CDCl_3$). The ^{19}F spectrum contained a complex multiplet centered at +114.3 ppm, and the ^1H spectrum had complex multiplets from −6.8 to −7.9 ppm. The infrared spectrum had absorption bands at 6.12 (s), 5.81 (m), 6.99 (m), and 7.36 μ (s); molecular weight in acetone, 570 (theoretical, 576). The mass spectrum had peaks at 576 [M^+], 439 [M − FC_6H_4NCO], 372 [M − (FC_6H_4 + FC_6H_4N)], 302 [M − $2FC_6H_4NCO$], and 301.

Anal. Calcd for $C_{34}H_{23}F_2N_2O_3P$: C, 70.81; H, 4.02; F, 6.59; N, 4.86; P, 5.37. Found: C, 70.22; H, 3.90; F, 6.52; N, 4.77; P, 5.40.

1,3-Di(*p*-cyanophenyl)-2,4,6-trioxo-5-triphenylphosphoranylidene-1,3-diazacyclohexane (14d). A diglyme solution of **1** (30 ml) and triphenylphosphine oxide was stirred under nitrogen as *p*-cyanophenyl isocyanate (1.0 g) was added in portions. After 1 hr the reaction mixture was diluted with ether and filtered. Recrystallization of the solid product from diglyme–acetonitrile gave 1.0 g of white solid, **14d**, mp 325–327°. The ^{31}P nmr spectrum consisted of a singlet at −18.1 ppm (in $CDCl_3$), and the ^1H spectrum consisted of complex aryl multiplets from −7.0 to −8.3 ppm. The infrared spectrum had absorption bands at 4.47 (w), 5.82 (m), 6.99 (m), 6.13 (s), and 7.36 μ (s); molecular weight in $CHCl_3$, 592 (theoretical, 590). The mass spectrum had peaks at 590 [M^+], 446 [M − NCC_6H_4NCO], 372 [M − (NCC_6H_4 + NCC_6H_4N)], and 301.

Anal. Calcd for $C_{36}H_{23}N_4O_3P$: C, 73.20; H, 3.93; N, 9.49; P, 5.24. Found: C, 72.96; H, 4.08; N, 9.28; P, 5.24.

1,3-Bis(*p*-nitrophenyl)-2,4,6-trioxo-5-triphenylphosphoranylidene-1,3-diazacyclohexane (14e). A solution of 2.2 g of **1** and 2.5 g of *p*-nitrobenzaldehyde in 25 ml of benzene was warmed to reflux under N_2. Filtration of the reaction mixture after cooling to room temperature and then recrystallization of the solid product from benzene–acetonitrile gave 3.1 g of yellow powder, **14e**, mp 330–332°. It had a ^{31}P nmr peak at −17.6 ppm (in $CDCl_3$). The ^1H nmr spectrum had peaks at −8.38 and −8.21 ppm which appeared to represent the left half of an A_2B_2 pattern for the two *para*-disubstituted phenyl groups, the right half apparently being masked in an aryl multiplet at −8.08 to −7.33 ppm. The infrared spectrum had bands at 5.82 (w), 6.12 (s), 6.52 (m), 6.98 (m), and 7.39 μ (s); molecular weight in $CHCl_3$, 628 (calcd: 630.5). The mass spectrum had peaks at 630 [M^+], 466 [M − $O_2NC_6H_4NCO$], 372 [M − ($O_2NC_6H_4$ + $O_2NC_6H_4N$)], 302 [M − $2O_2NC_6H_4NCO$], and 301.

Anal. Calcd for $C_{34}H_{23}N_4O_7P$: C, 64.73; H, 3.67; N, 8.88; P, 4.91. Found: C, 64.39; H, 3.75; N, 8.84; P, 5.06.

Triphenylphosphoranylidenethioketene (15). A solution of a mixture (1.3 g) of **1** and triphenylphosphine oxide in benzene (15 ml) and carbon disulfide (0.5 g) was stirred for 40 hr at room temperature. A solid that separated during this time was recrystallized from benzene, yielding 0.5 g of tan crystals, mp 224–226° (no melting point depression with an authentic sample of **15**). The ^{31}P nmr and infrared spectra were also essentially identical with those of **15**.[1]

Anal. Calcd for $C_{20}H_{15}PS$: C, 75.43; H, 4.75; P, 9.73; S, 10.07. Found: C, 75.25; H, 4.71; P, 9.70; S, 10.10.

Acknowledgments. We thank R. F. Jansen for obtaining infrared, nmr, and mass spectra, and J. D. Wilson and M. J. S. Dewar for helpful suggestions.