Synthesis of Chloropyrimidinylmethylenephosphoranes and their Wittig Reactions with Aldehydes (1)

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Methylpyrimidines were treated with phosphorus pentachloride in phosphorus oxychloride to give trichloromethylpyrimidines, which reacted with two equivalent amounts of triphenylphosphine to yield chloropyrimidinylmethylenetriphenylphosphoranes as stable ylides in one step. These phosphorus ylides were subjected to the Wittig reaction with a variety of aldehydes to afford chloropyrimidinylolefins.

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It is well known that reaction of alkyl halides with triphenylphosphine gives the phosphonium salt, which, on treatment with base, is transformed into the phosphorus ylide or the Wittig reagent. However, only a few references are available concerning such reactions of *gem*-polyhalides with triphenylphosphine to afford triphenylphosphinehalomethylenes, which serve as reagents for the synthesis of halo-olefins and acetylenes. The reaction of methylene chloride with triphenylphosphine in the presence of *n*-butyllithium was reported to yield triphenylphosphinechloromethylene, which reacted with benzophenone to give 1,1-diphenyl-2,2-dichloromethylene in 46% yield (2). Similarly, such expansion of the Wittig reaction was carried out using carbon tetrabromide (3,4) and chloroiodomethane (5) as starting halides giving good yields of the corresponding ylides.

Previously, we reported that methylpyrimidones reacted with phosphorus pentachloride in phosphorus oxychloride to give trichloromethylpyrimidines (6). In the present paper we wish to report the continuation of our investigation concerning the synthesis of trichloromethylpyrimidines and their reaction with triphenylphosphine.

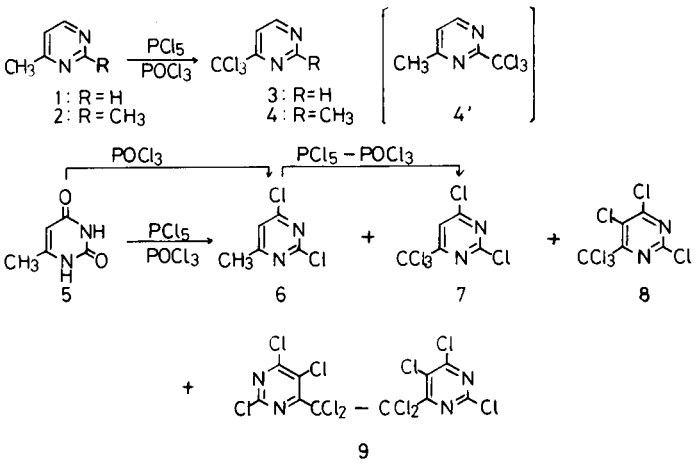
Synthesis of Trichloromethylpyrimidines.

Refluxing of a solution of 4-methylpyrimidine (**1**) and phosphorus pentachloride in phosphorus oxychloride gave 4-trichloromethylpyrimidine (**3**) in 51% yield. A similar reaction of 2,4-dimethylpyrimidine (**2**) afforded 2-methyl-4-trichloromethylpyrimidine (**4**) in 53% yield. In this case, 4-methyl-2-trichloromethylpyrimidine (**4'**) was not detected.

Chlorination of 6-methyluracil (**5**) under the similar conditions gave 2,6-dichloro-4-methylpyrimidine (**6**), 2,6-dichloro-4-trichloromethylpyrimidine (**7**), 2,5,6-trichloro-4-trichloromethylpyrimidine (**8**), and 4,4'-(1,1,2,2-tetrachloro-1,2-ethanediyl)-bis-2,5,6-trichloropyrimidine (**9**) in 7, 5, 11, and 5% yields, respectively. Structural assignment of these products was made on the basis of comparison with authentic samples (compound **6** and **7**), elemental analyses and spectral data detailed in the experimental section.

Heating of compound **5** in phosphorus oxychloride gave compound **6** in 84% yield, which was chlorinated with phosphorus pentachloride in phosphorus oxychloride to give the trichloromethylpyrimidine (**7**) in 25% yield.

Scheme 1



Reaction of Triphenylphosphine with Trichloromethylpyrimidines.

Reaction of 4-chloro-2-methyl-6-trichloromethylpyrimidine (**11**) (6) with an equivalent amount of triphenylphosphine at room temperature yielded α-chloro-α-(6-chloro-2-methyl-4-pyrimidinyl)methylenetriphenylphosphorane (**15**) in 35% yield besides the formation of triphenylphosphine oxide. When two equivalent amounts of triphenylphosphine were used, the phosphorane (**15**) was obtained in 81% yield.

Similarly, 4-trichloromethylpyrimidine (**3**) and 4-chloro-6-trichloromethylpyrimidine (**10**) were allowed to react with two molar amounts of triphenylphosphine to give α-chloro-α-(4-pyrimidinyl)methylenetriphenylphosphorane (**13**) and α-chloro-α-(6-chloro-4-pyrimidinyl)methylenetriphenylphosphorane (**14**) in 41 and 40% yields, respec-

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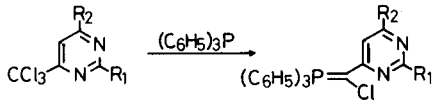
tively.

Reaction with 2,6-dichloro-4-trichloromethylpyrimidine (**7**) under similar conditions gave an unexpected product, whose structural assignment is under the investigation.

Similar reactions with 2-methyl-4-trichloromethylpyrimidine (**4**) and 4-chloro-2-phenyl-6-trichloromethylpyrimidine (**12**) (6) resulted in the recovery of the starting trichloromethylpyrimidines (**4** and **12**).

Scheme 2



3 : $R_1=R_2=H$
4 : $R_1=CH_3$, $R_2=H$
7 : $R_1=R_2=Cl$
10 : $R_1=H$, $R_2=Cl$
11 : $R_1=CH_3$, $R_2=Cl$
12 : $R_1=C_6H_5$, $R_2=Cl$

13 : $R_1=R_2=H$
14 : $R_1=H$, $R_2=Cl$
15 : $R_1=CH_3$, $R_2=Cl$

Reaction of Phosphoranes (**13,15**) with Aldehydes.

Heating of **15** and benzaldehyde in benzene gave a 42% yield of *Z*-4-chloro-6-(2-chlorostyryl)-2-methylpyrimidine (**17**) and a trace (1%) of *E*-4-chloro-2-methyl-6-styrylpyrimidine (**23**). Elemental analyses and spectroscopic data were consistent with these structures. The stereochemical structure of compound **17** was characterized as the *Z*-form on the basis of nmr study. A 5% nuclear Overhauser effect was observed between the pyrimidine ring proton (7.70 ppm) and the olefinic proton (8.46 ppm) of compound **17**. The assignment of the *E*-form to compound **23** was made on the basis of the coupling constants of the olefinic protons (6.94 ppm, 1H, d, J = 16 Hz and 7.86 ppm, 1H, d, J = 16 Hz). Similarly, reaction of the phosphorane (**15**) with anisaldehyde and cinnamaldehyde gave 4-chloro-6-(2-chloro-4′-methoxystyryl)-2-methylpyrimidine (**18**) and 4-chloro-6-(4-chlorocinnamylidene)-2-methylpyrimidine (**19**) in 53 and 50% yields, respectively.

Aliphatic aldehydes were allowed to react with the phosphorane giving the corresponding products. Thus, the phosphorane (**15**) reacted with propionaldehyde to yield 1-chloro-1-(6-chloro-2-methyl-4-pyrimidinyl)-(1,*Z*)-1-butene (**20**) and 1-(6-chloro-2-methyl-4-pyrimidinyl)-(1,*E*)-1-butene (**24**) in 25 and 34% yields, respectively. Structural assignments were made on the basis of elemental analyses and spectral data detailed in the experimental section.

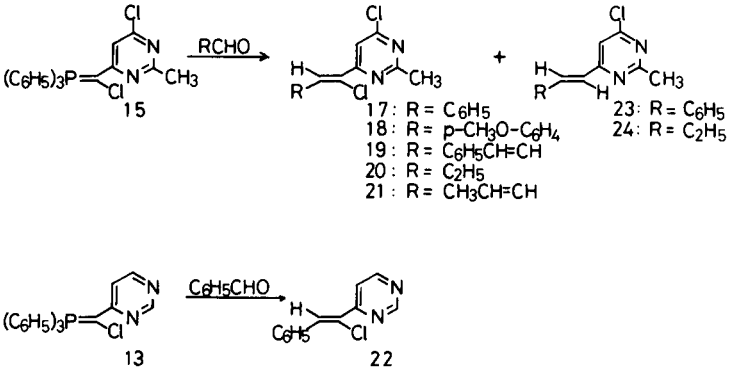
Similarly, crotonaldehyde reacted with the phosphorane (**15**) to give 1-chloro-1-(6-chloro-2-methyl-4-pyrimidinyl)-1,3-pentadiene (**21**) in 45% yield.

The phosphorane (**13**) also reacted with benzaldehyde to afford 4-(2-chlorostyryl)pyrimidine (**22**) in 21% yield.

Reaction of 4-Chloro-6-(2-chlorostyryl)-2-methylpyrimidine (**17**).

Compound **17** was not so stable, *e.g.*, a solution of **17** in chloroform was allowed to stand at room temperature for several days to yield colorless prisms (**25**), m.p. 237° dec. When the reaction was carried out under irradiation, compound **25** was obtained in 75% yield. Elemental analyses and mass spectroscopy indicated product (**25**) to be a dimer of **17**. Uv and nmr spectra suggested the structure to be 1,3-dichloro-1,3-di-(6-chloro-2-methyl-4-pyrimidinyl)-2,4-diphenylcyclobutane (**25**). Such a reaction had to be considered in view of the reported formation of the cyclobutane, 1,3-(*trans*)-di-(3-methyl-4-nitro-5-isoxazyl)-2,4-(*trans*)-diphenylcyclobutane (**30**) by the photolysis of 3-methyl-4-nitro-5-styrylisoxazole (**29**) (7).

Scheme 3



15

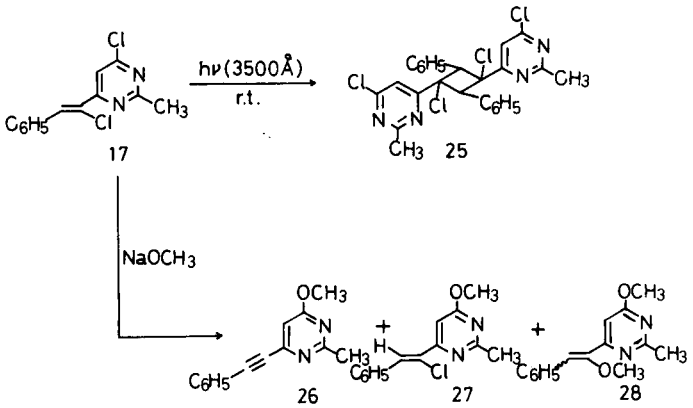
17 : R = C_6H_5
18 : R = p-CH_3O-C_6H_4
19 : R = C_6H_5CH=CH
20 : R = C_2H_5
21 : R = CH_3CH=CH

23 : R = C_6H_5
24 : R = C_2H_5

13 22

Lastly, treatment of **17** with sodium methoxide in methanol yielded 2-methyl-4-methoxy-6-phenylethynylpyrimidine (**26**), 4-(2-chlorostyryl)-6-methoxy-2-methylpyrimidine (**27**), 4-methoxy-6-(2-methoxystyryl)-2-methylpyrimidine (**28**) in 10, 20, and 30% yields, respectively. Configuration of compound **28** was not determined.

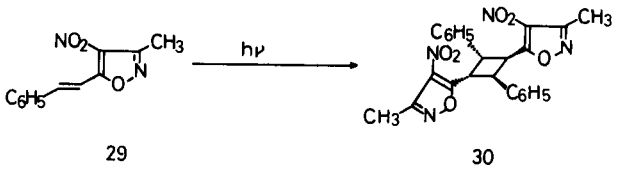
Scheme 4



17 25

26 27 28

Scheme 5



29 30

EXPERIMENTAL

All melting points were uncorrected. Uv and ir spectra were measured with Beckman DB-G and JASCO IR-S spectrometers, respectively. Nmr spectra were measured on a Hitachi-Perkin Elmer R-20 spectrometer and reported as δ value (ppm) relative to tetramethylsilane as an internal standard. Mass spectra were obtained on a Hitachi RMU-7L double focusing mass spectrometer.

4-Trichloromethylpyrimidine (**3**).

A mixture of 4-methylpyrimidine (**1**) (8) (1.3 g., 0.014 mole) and phosphorus pentachloride (15.3 g., 0.07 mole) in phoshporus oxychloride (10.8 g., 0.07 mole) was refluxed in an oil bath (125°) for 5 hours. The reaction mixture was poured into ice-water, and the mixture was extracted with chloroform. The chloroform solution was washed with 1% sodium bicarbonate solution. After being dried over potassium carbonate, the chloroform solution was condensed. The residue was distilled under reduced pressure to give 1.23 g. (51%) of **3** as a crystalline substance, b.p. 99-100°/12 mmHg, m.p. 24-26°; ir (chloroform): ν max cm^{-1} 1580, 1400; nmr (deuteriochloroform): δ 7.95 (1H, d, J = 6 Hz), 8.95 (1H, d, J = 6 Hz), 9.37 (1H, s).

Anal. Calcd. for $C_5H_3Cl_3N_2$ (**3**): C, 30.38; H, 1.52; N, 14.18; Cl, 53.92. Found: C, 30.51; H, 1.43; N, 14.42; Cl, 53.46.

2-Methyl-4-trichloromethylpyrimidine (**4**).

Following the same procedure described above, refluxing of 2,4-dimethylpyrimidine (**2**) (9) (1.5 g., 0.014 mole) and phosphorus pentachloride (15.3 g., 0.07 mole) in phosphorus oxychloride (10.7 g., 0.07 mole) afforded 1.44 g. (53%) of the product (**4**) as colorless prisms, m.p. 39-40°, b.p. 111-112/25 mmHg; ir (chloroform): ν max cm^{-1} 1560, 1400; nmr (deuteriochloroform): δ 2.86 (3H, s), 7.80 (1H, d, J = 6 Hz), 8.90 (1H, d, J = 6 Hz).

Anal. Calcd. for $C_6H_3Cl_3N_2$ (**4**): C, 34.04; H, 2.36; N, 13.24; Cl, 50.35. Found: C, 33.64; H, 2.53; N, 12.87; Cl, 50.56.

Chlorination of 4-Methyluracil (**5**).

According to the procedure (**6**) reported previously, a mixture of **5** (3 g., 0.024 mole) and phosphorus pentachloride (27 g., 0.13 mole) in phosphorus oxychloride (12 ml., 0.13 mole) was refluxed for 1.5 hours. The mixture was poured into ice-water, and extracted with chloroform. The chloroform solution was washed with 5% sodium bicarbonate solution. After removal of the solvent, the residue was purified by silica gel (150 g.) column chromatography. Elution with *n*-hexane yielded an oily substance, which was purified by distillation to give 0.3 g. (11%) of 2,5,6-trichloro-4-trichloromethylpyrimidine (**8**) as a colorless oil, b.p. 100°/2 mm Hg; ir (chloroform): ν max cm^{-1} 1520, 1490; ms: m/e 298 (M^+), 263 (M^+-Cl), 228 (M^+-2Cl).

Anal. Calcd. for $C_5Cl_6N_2$ (**8**): C, 19.95; N, 9.31. Found: C, 20.19; N, 9.16.

Subsequent elution with *n*-hexane afforded a crystalline substance, which was recrystallized from petroleum benzine to give 0.5 g. (5%) of 4,4'-(1,1,2,2-tetrachloro-1,2-ethanediyl)-bis-2,5,6-trichloropyrimidine (**9**) as colorless prisms, m.p. 181-183°; ir (chloroform): ν max cm^{-1} 1526, 1495; ms: m/e 491 (M^+-Cl), 456 (M^+-2Cl).

Anal. Calcd. for $C_{10}Cl_{10}N_4$ (**9**): C, 22.62; N, 10.56; Cl, 66.80. Found: C, 22.70; N, 10.49; Cl, 67.01.

Elution was continued with benzene to give 0.23 g. (5%) of 2,4-dichloro-6-trichloromethylpyrimidine (**7**) as colorless needles (petroleum ether), m.p. 82-83° (lit. (6) m.p. 85-86°), and 0.5 g. (7%) of 2,4-dichloro-6-methylpyrimidine (**6**) as colorless needles (from petroleum ether), m.p. 47-48° (lit. (10) m.p. 45-46°).

2,4-Dichloro-6-trichloromethylpyrimidine (**7**).

A mixture of 2,4-dichloro-6-methylpyrimidine (**6**) (10) (7.6 g., 0.047 mole) and phosphorus pentachloride (48.6 g., 0.24 mole) in phosphorus oxychloride (36.3 g., 0.24 mole) was refluxed in an oil bath (120-130°) for 3 hours. After cooling to room temperature, the reaction mixture was poured into ice-water, and the mixture was extracted with chloroform. The chloroform solution was washed with 5% sodium bicarbonate solution. After being dried over potassium carbonate, the chloroform solution was condensed. The residue was subjected to silica gel (300 g.) column chromatography. Elution with *n*-hexane yielded a crystalline substance, which was purified by sublimation to give 3 g. (25%) of **7** as colorless needles.

α-Chloro-α-(4-pyrimidinyl)methylenetriphenylphosphorane (**13**).

To a solution of 4-trichloromethylpyrimidine (**3**) (1.97 g., 0.01 mole) in dry benzene (20 ml.), was added dropwise a benzene (30 ml.) solution of triphenylphosphine (5.2 g., 0.02 mole) under ice-cooling over a period of 20 minutes. After being stirred for 10 hours, the mixture was poured into water. The aqueous solution was made alkaline with potassium carbonate, and extracted with chloroform. The chloroform solution was evaporated and the residue was crystallized from ether to give 1.6 g. (41%) of **13** as pale yellow prisms, m.p. 167-169° dec.; ir (chloroform): ν max cm^{-1} 1590, 1470; nmr (deuteriobenzene): δ 6.80-7.80 (18H, m); ms: m/e (388 (M^+), 353 (M^+-Cl).

Anal. Calcd. for $C_{23}H_{18}ClN_2P$ (**13**): C, 71.05; H, 4.63; N, 7.21. Found: C, 71.35; H, 5.03; N, 7.48.

α-Chloro-α-(6-chloro-4-pyrimidinyl)methylenetriphenylphosphorane (**14**).

To a benzene (10 ml.) solution of 4-chloro-6-trichloromethylpyrimidine (**10**) (6) (1 g., 0.004 mole), was added dropwise a solution of triphenylphosphine (2.26 g., 0.08 mole) in benzene (10 ml.) under ice-cooling over a period of 10 minutes. After stirring for 2 hours, the mixture was poured into water. The aqueous layer was made alkaline with potassium carbonate, and extracted with chloroform. The chloroform fraction gave a crystalline substance. Recrystallization from ether gave 0.63 g. (40%) of **14** as yellow prisms, m.p. 130-131° dec.; ir (chloroform): ν max cm^{-1} 1570, 1470; nmr (deuteriobenzene): δ 6.70-7.70 (16H, m), 7.82 (1H, s); ms: m/e 422 (M^+), 387 (M^+-Cl).

Anal. Calcd. for $C_{23}H_{17}Cl_2N_2P \cdot \frac{1}{3}H_2O$ (**14**): C, 64.35; H, 4.12; N, 6.50. Found: C, 64.41; H, 4.65; N, 6.31.

α-Chloro-α-(6-chloro-2-methyl-4-pyrimidinyl)methylenetriphenylphosphorane (**15**).

To an ice-cold solution of 4-chloro-2-methyl-6-trichloromethylpyrimidine (**11**) (6) (10 g., 0.04 mole) in dry benzene (100 ml.), was added dropwise a solution of triphenylphosphine (21 g., 0.08 mole) in dry benzene (100 ml.) under ice-cooling over a period of 30 minutes. After stirring at room temperature for 3 hours, the mixture was poured into water. The aqueous layer was made alkaline with potassium carbonate to yield a yellow crystalline solid, which was collected by suction. Recrystallization from ether gave 12.6 g. (72%) of **15** as pale yellow prisms, m.p. 200-201° dec.; ir (potassium bromide): ν max cm^{-1} 1565, 1490; nmr (deuteriobenzene): δ 1.9 (3H, s), 6.70-7.70 (16H, m); ms: m/e 436 (M^+), 401 (M^+-Cl).

Anal. Calcd. for $C_{24}H_{19}Cl_2N_2P$ (**15**): C, 65.92; H, 4.35; N, 6.41; Cl, 16.22. Found: C, 65.60; H, 4.25; N, 6.72; Cl, 16.57.

Z-4-Chloro-6-(2-chlorostyryl)-2-methylpyrimidine (**17**) and *E*-4-Chloro-6-styryl-2-methylpyrimidine (**23**).

The phosphorane (**15**) (4.37 g., 0.01 mole) was added by portions to a solution of benzaldehyde (1 g., 0.01 mole) in dry benzene (10 ml.) with stirring at room temperature. After refluxing on a steam bath for 4.5 hours, the reaction mixture was condensed *in vacuo*. The residue was extracted with ether. The ether solution was evaporated, and the residue was purified by silica gel (100 g.) column chromatography using benzene as an eluent to give 1.1 g. (42%) of **17** as colorless needles (ethanol), m.p. 89°; ir (chloroform): ν max cm^{-1} 1620 (C=C); nmr (deuteriochloroform): δ 2.75 (3H, s), 7.39-7.62 (3H, m), 7.70 (1H, s), 7.83-8.10 (2H, m), 8.46 (1H, s).

Anal. Calcd. for $C_{13}H_{10}Cl_2N_2$ (**17**): C, 58.87; H, 3.77; N, 10.57; Cl, 26.79. Found: C, 59.19; H, 3.94; N, 10.55; Cl, 26.99.

Subsequent elution with benzene afforded 0.03 g. (1%) of **23** as colorless needles (petroleum ether), m.p. 83-84°; ir (potassium bromide): ν

max cm^{-1} 1630 (C=C); nmr (deuteriochloroform): δ 2.68 (3H, s), 6.94 (1H, d, J = 16 Hz), 7.12 (1H, s), 7.20-7.70 (5H, m), 7.86 (1H, d, J = 16 Hz); ms: m/e 230 (M$^+$).

Anal. Calcd. for $C_{13}H_{11}ClN_2$ (**23**): C, 67.69; H, 4.77; N, 12.15. Found: C, 67.40; H, 4.74; N, 12.13.

4-Chloro-6-(2-chloro-4′-methoxystyryl)-2-methylpyrimidine (**18**).

Following the procedure given for compound **17**, anisaldehyde (0.28 g., 0.002 mole) was allowed to react with **15** (0.88 g., 0.002 mole) in benzene (10 ml.) for 8.5 hours. Purification by silica gel (18 g.) column chromatography gave 0.32 g. (53%) of **18** as pale yellow needles (ethanol), m.p. 99-101°; ir (chloroform): ν max cm^{-1} 1605 (C=C); nmr (deuteriochloroform): δ 2.72 (3H, s), 3.85 (3H, s), 6.95 (2H, d, J = 9 Hz), 7.61 (1H, s), 7.90 (2H, d, J = 9 Hz), 8.35 (1H, s).

Anal. Calcd. for $C_{14}H_{12}Cl_2N_2O$ (**18**): C, 56.95; H, 4.07; N, 9.49; Cl, 24.07. Found: C, 56.95; H, 3.95; N, 9.46; Cl, 24.07.

4-Chloro-6-(4-chlorocinnamylidene)-2-methylpyrimdine (**19**).

Employing the procedure described above, cinnamaldehyde (0.27 g., 0.002 mole) was allowed to react with **15** (0.88 g., 0.02 mole) in benzene (10 ml.) for 5.5 hours. Purification by silica gel (18 g.) column chromatography using petroleum benzine as a eluent gave 0.29 g. (50%) of **19** as pale yellow needles (petroleum ether), m.p. 121-123°; ir (chloroform): ν max cm^{-1} 1615, 1515 (C=C); nmr (deuteriochloroform): δ 2.68 (3H, s), 7.1-7.6 (8H, m), 8.14 (1H, dd, J = 6 Hz, J = 1 Hz).

Anal. Calcd. for $C_{15}H_{12}Cl_2N_2$ (**19**): C, 61.86; H, 4.12; N, 9.62; Cl, 24.40. Found: C, 61.98; H, 4.13; N, 9.60; Cl, 24.63.

1-Chloro-1-(6-chloro-2-methyl-4-pyrimidinyl)-(1,*Z*)-1-butene (**20**) and 1-(6-Chloro-2-methyl-4-pyrimidinyl)-(1,*E*)-1-butene (**24**).

According to the procedure described above, propionaldehyde (0.18 g., 0.003 mole) was allowed to react with **15** (1.32 g., 0.003 mole) in benzene (10 ml.) for 8 hours. The reaction mixture was condensed, and the residue was extracted with ether. The ether extract was subjected to silica gel (18 g.) column chromatography. *n*-Hexane elution gave 0.16 g. (25%) of oily product (**20**), b.p. 77°/20 mm Hg; ir (chloroform): ν max cm^{-1} 1620 (C=C); nmr (deuteriochloroform): δ 1.22 (3H, t, J = 8.3 Hz), 2.20-2.93 (2H, m), 2.80 (3H, s), 7.45 (1H, s), 7.62 (1H, t, J = 6 Hz).

Anal. Calcd. for $C_9H_{10}Cl_2N_2$ (**20**): C, 49.77; H, 4.61; N, 12.90. Found: C, 49.98; H, 4.55; N, 12.77.

Subsequent elution with *n*-hexane-benzene (1:1) gave 0.185 g. (34%) of pale yellowish oil (**24**), b.p. 75°/16 mm Hg; ir (chloroform): ν max cm^{-1} 1655 (C=C); nmr (deuteriochloroform): δ 1.09 (3H, t, J = 8.3 Hz), 2.02-2.68 (2H, m), 2.63 (3H, s), 6.10-6.40 (1H, dt, J = 15 Hz, J = 1.5 Hz), 6.86-7.31 (2H, m).

Anal. Calcd. for $C_9H_{11}ClN_2$ (**24**): C, 59.18; H, 6.03; N, 15.34. Found: C, 59.24; H, 6.03; N, 14.92.

1-Chloro-1-(6-chloro-2-methyl-4-pyrimidinyl)-1,3-pentadiene (**21**).

According to the procedure described above, reaction of crotonaldehyde (0.56 g., 0.008 mole) in benzene (5 ml.) afforded 0.82 g. (42%) of **21** as colorless needles (ether-petroleum ether), m.p. 72-73°; ir (chloroform): ν max cm^{-1} 1630 (C=C); nmr (carbon tetrachloride): δ 2.00 (3H, d, J = 8 Hz), 2.64 (3H, s), 6.02-6.82 (2H, m), 7.42 (1H, s), 7.82 (1H, d, J = 10 Hz).

Anal. Calcd. for $C_{10}H_{10}Cl_2N_2$ (**21**): C, 52.40; H, 4.34; N, 12.23. Found: C, 52.44; H, 4.34; N, 12.04.

4-(2-Chlorostyryl)pyrimidine (**22**).

Employing the procedure described above, benzaldehyde (0.27 g., 0.0026 mole) was allowed to react with the phosphorane (**13**) (1 g., 0.0026 mole) in benzene (20 ml.) for 12 hours. The reaction mixture was condensed and the residue was extracted with ether. The ether solution was condensed to give a semi-solid (0.5 g.), which was purified by silica gel (20 g.) column chromatography. Elution with *n*-hexane-ether (4:1) gave 0.12 g. (21%) of **22** as colorless needles (*n*-hexane), m.p. 51-53°; ir (chloroform): ν max cm^{-1} 1618 (C=C); nmr (deuteriochloroform): δ 7.15-7.66 (3H, m), 7.76-8.08 (3H, m), 8.43 (1H, s), 8.87 (1H, d, J = 5 Hz), 9.25 (1H, s).

Anal. Calcd. for $C_{12}H_9ClN_2$ (**22**): C, 66.53; H, 4.16; N, 12.94. Found: C, 66.40; H, 4.14; N, 12.96.

1,3-(*trans*)-Dichloro-1,3-(*trans*)-di-(6-chloro-2-methyl-4-pyrimidinyl)-2,4-(*trans*)-diphenylcyclobutane (**25**).

A conc. solution of compound **17** (30 mg.) in chloroform (0.5 ml.) was applied on the inner wall of a quartz glass tube and the solvent was evaporated. After being irradiated (3500 Å) for 1 hour, crystals attached were collected and purified by recrystallization from petroleum benzine to give 22.5 mg. (75%) of **25** as colorless prisms, m.p. 237° dec; uv (methanol): λ max nm (log ε) 261 (4.24); nmr (deuteriochloroform): δ 2.74 (6H, s), 6.16 (2H, s), 6.89 (2H, s), 7.23 (10H, s); ms: m/e 528 (M$^+$).

Anal. Calcd. for $C_{26}H_{20}Cl_4N_4$ (**25**): C, 58.86; H, 3.77; N, 10.56. Found: C, 58.99; H, 3.67; N, 10.54.

Reaction of Compound **17** with Sodium Methoxide.

To a solution of sodium methoxide in methanol prepared from 0.1 g. (0.0043 atom) of Na and abs. methanol (10 ml.), was added compound **17** (0.5 g., 0.0019 mole). The mixture was refluxed for 32 hours and condensed *in vacuo*. The residue was neutralized with dilute hydrochloric acid, and the mixture was extracted with chloroform. The chloroform solution was evaporated, and the residue was purified by silica gel (8 g.) column chromatography. Elution with *n*-hexane-ether (4:1) gave 42 mg. (10%) of **26** as colorless prisms (petroleum ether), m.p. 51-53°; ir (chloroform): ν max cm^{-1} 2200 (C≡C); nmr (deuteriochloroform): δ 2.53 (3H, s), 3.89 (3H, s), 6.58 (1H, s), 7.15-7.63 (5H, m).

Anal. Calcd. for $C_{14}H_{12}N_2O$ (**26**): C, 74.99; H, 5.38; N, 12.49. Found: C, 75.06; H, 5.49; N, 12.40.

Subsequent elution with ether-petroleum ether (1:4) gave 0.1 g. (20%) of **27** as colorless needles (ethanol), m.p. 56-57°; ir (chloroform): ν max cm^{-1} 1620 (C=C); nmr (deuteriochloroform): δ 2.62 (3H, s), 3.96 (3H, s), 7.01 (1H, s), 7.20-7.50 (3H, m), 7.73-7.95 (2H, m), 8.23 (1H, s).

Anal. Calcd. for $C_{14}H_{13}ClN_2O$ (**27**): C, 64.49; H, 4.99; N, 10.74. Found: C, 64.57; H, 4.99; N, 10.76.

Elution was continued with the same eluent to give 0.15 g. (30%) of **28** as an oil, b.p. 165°/4 mmHg; ir (chloroform): ν max cm^{-1} 1625 (C=C); nmr (deuteriochloroform): δ 2.58 (3H, s), 3.62 (3H, s), 3.94 (3H, s), 6.08 (1H, s), 7.25-7.67 (6H, m).

Anal. Calcd. for $C_{15}H_{16}N_2O_2$ (**28**): C, 70.29; H, 6.29; N, 10.93. Found: C, 70.06; H, 6.17; N, 10.73.

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