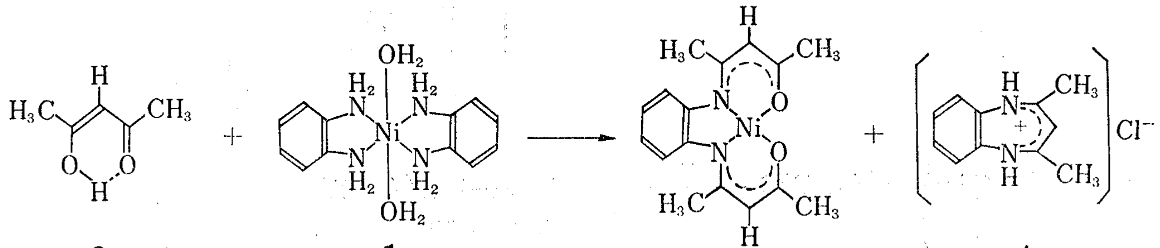
nickel(II) complex, and C–H in-plane bending vibration bands appear at 760 and 772 cm^{-1}, giving sharpmedium lines.

The nuclear magnetic resonance spectrum of this diamagnetic complex (3) shows A_2B_2 type resonance lines of phenylene ring at δ 6.65 and 6.95 and methine proton singlet line at δ 5.53 and two methyl proton singlet lines at δ 2.25 and 1.90.



2 1 3 4

Experimental

Reaction of Bis(*o*-phenylenediamine)nickel(II) Chloride and Acetylacetone——Bis(*o*-phenylenediamine)-nickel(II) chloride dihydrate (1.8 g; 0.003 mol) and acetylacetone (1.2 g; 0.012 mol) were allowed to react in EtOH (100 ml) at room temperature with stirring. After stirring for 4 hr, the resulting bis(acetylacetonato)-nickel(II) dihydrate was filtered off, and the violet filtrate was evaporated to dryness and extracted with hot benzene. The wine red extract was evaporated and the residue was recrystallized from benzene–hexane. Bis(acetylacetonato)(*o*-phenylenediamine)nickel(II) complex (3) was obtained as deep-purple needles, mp 218.5—219° (0.13 g; 13% yield). *Anal.* Calcd. for $C_{16}H_{18}O_2N_2Ni$: C, 58.41; H, 5.48, N, 8.73. Found: C, 58.49; H, 5.53; N, 8.73.

A violet product (1.1 g) was obtained from the insoluble part of the above benzene extraction. It was probably a nickel complex. Treatment of this nickel complex with 10% NaOH gave 2,4-dimethyl-1,5-benzodiazepinium chloride, mp 131—132°. This violet product seems to be a mixture of the nickel complex of 2,4-dimethyl-1,5-benzodiazepinium chloride[3] and 2,4-dimethyl-1,5-benzodiazepinium chloride but its purification failed.

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Reaction of Schiff Bases with Trichloroacetyl Chloride in the Presence of Triphenylphosphine

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It has now been found that trichloroacetyl chloride is capable to react with Schiff bases in the presence of triphenylphosphine to give 3,3-dichloro-2-azetidinones. Mechanistically the reaction appears to involve the chlorine cation extraction from the initially formed adduct by triphenylphosphine.

In an earlier paper[2] we have reported the 3,3-dichloro-2-azetidinone synthesis by the reaction of Schiff bases of N-benzylideneamine type with trichloroacetic anhydride. It was revealed that this reaction proceeds through the adduct intermediate, N-(α-trichloroacetoxy-

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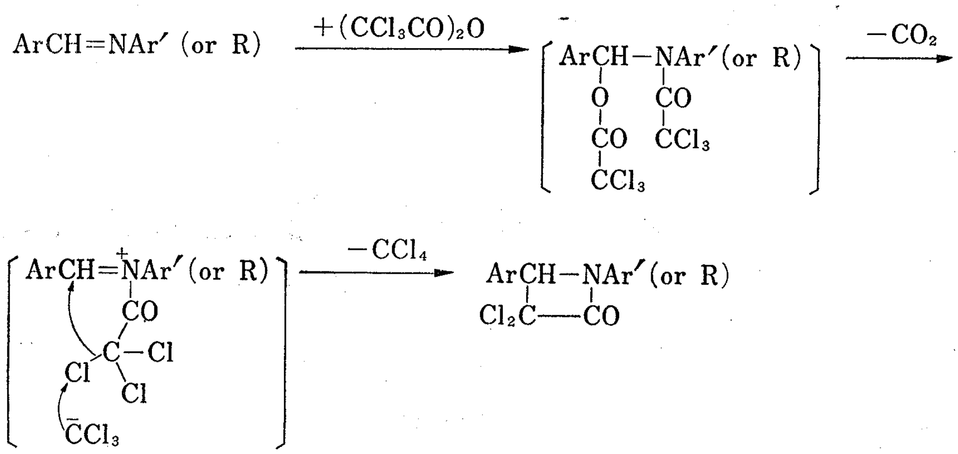
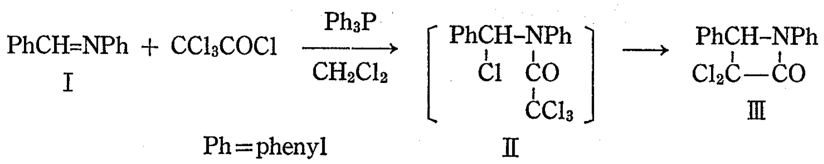
1) Location: *2-2-1, Oshika, Shizuoka.*
2) M. Sekiya and T. Morimoto, *Chem. Pharm. Bull.* (Tokyo), 23, 2353 (1975).

benzyl)trichloroacetamide, and is unique in the chlorine cation extraction from N-trichloroacetyl group by trichloromethyl anion derived through the decarboxylation of trichloroacetate anion, as in the following.



As previously known with acyl halides,[3] trichloroacetyl chloride exhibited an adduct formation when mixed with N-benzylideneaniline (I) in solution at room temperature. A chloroform solution of I and trichloroacetyl chloride in 1:1 molar proportion exhibited an existence of the adduct, N-(α-chlorobenzyl)trichloroacetanilide (II), which was evidenced by the following spectral assignment. A >C=O stretching absorption in its infrared (IR) spectrum appeared at 1695 cm^{-1} is well agreement with that (1697 cm^{-1}) of trichloroacetanilide and in its nuclear magnetic resonance (NMR) spectrum the methine proton signal at δ 7.68 ppm showed a reasonable shift to higher magnetic field when compared with that (δ 8.32 ppm) of the starting I. Therefore, if the chlorine cation extraction from N-trichloroacetyl group of this adduct could be possible, 3,3-dichloro-2-azetidinone formation might occur similarly to the case of using trichloroacetic anhydride. In the literature[4] the reaction of trichloroacetamides induced by trivalent phosphorous compounds has been stated to involve the chlorine cation extraction, yielding trichlorovinylamines. We succeeded in obtaining 3,3-dichloro-2-azetidinone, when triphenylphosphine was added to a dichloromethane solution of the adduct, II, at room temperature. On standing a dichloromethane solution of I, trichloroacetyl chloride and triphenylphosphine in 1:1:1.2 molar proportion 3,3-dichloro-1,4-diphenyl-2-azetidinone (III) was obtained in 62% yield.

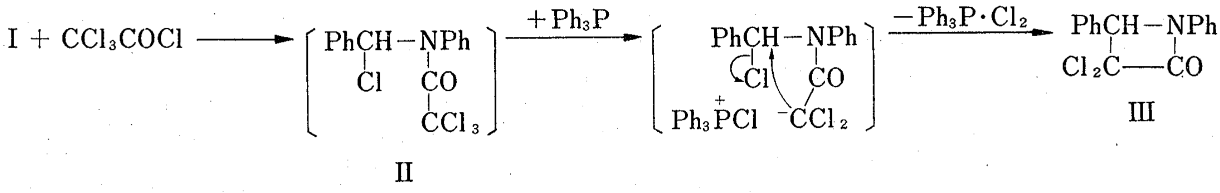


Ph=phenyl

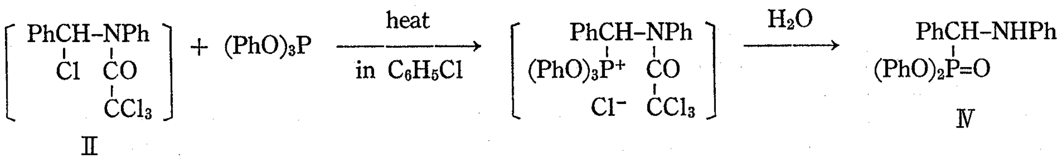
In comparison the use of hexamethylphosphorous triamide in place of triphenylphosphine under the same conditions gave III (26% yield) and that of triphenylphosphite resulted in no formation of the product. However the latter reacted in chlorobenzene on refluxing to give a product, mp 152—152.5° (24% yield), after hydrolysis, in addition to III (8% yield). This product was assigned as α-anilinobenzylphosphonic acid diphenyl ester (IV) mostly on the basis of NMR evidence where a large size of the coupling (J=12.8 Hz) arising at the methine proton was indicative of the carbon-phosphorous bond.

3) T.C. James and C.W. Judd, *J. Chem. Soc.*, **105**, 1427 (1941); H. Böhme and K. Hartke, *Chem. Ber.*, **96**, 600 (1963); H. Böhme, S. Ebel and K. Hartke, *ibid.*, **98**, 1463 (1965); H. Breederveld, *Rec. trav. chim.*, **79**, 401 (1960).
4) A.J. Speziale and L.R. Smith, *J. Am. Chem. Soc.*, **84**, 1868 (1962).

When we speculate on a mechanism for the 3,3-dichloro-2-azetidinone formation, the reaction may involve the chlorine cation extraction by triphenylphosphine from trichloroacetyl group of the adduct followed by an intramolecular nucleophilic substitution by the resultant carbanion, as shown in the following. The leaving triphenylphosphine dichloride in the above path was isolated as triphenylphosphine oxide from the reaction mixture through hydrolysis.



The formation of IV by the use of triphenylphosphite may be brought about by the following mechanistic path.



By the use of triphenylphosphine the reaction of trichloroacetyl chloride was extensively examined with a number of Schiff bases of the type ArCH=NAr′ (or R) under standardized conditions standing their dichloromethane solutions at room temperature. As summarized in Table I the corresponding 3,3-dichloro-2-azetidinones were successfully synthesized by the reaction in fair yields. Thus 3,3-dichloro-2-azetidinone analogs were generally synthesized from Schiff bases by the reaction with trichloroacetyl chloride in the presence of triphenylphosphine as well as by the previously reported reaction with trichloroacetic anhydride.

TABLE I

ArCH=NAr′ (or R) —(CCl_3COCl, Ph_3P; at room temperature)→ ArCH–NAr′ (or R) / Cl_2C—CO

Ar	Ar′ (or R)	Yield (%)
C_6H_5	C_6H_5	62
p-$CH_3OC_6H_4$	C_6H_5	87
p-$O_2NC_6H_4$	C_6H_5	42
C_6H_5	$C_6H_4OCH_3$-p	62
C_6H_5	⟨H⟩	60
C_6H_5	CH_3	37

molar ratio: Schiff base (0.02 mole): trichloroacetyl chloride: triphenylphosphine=1:1:1.2
solvent: dichloromethane (30 ml)

Experimental[5]

General Procedure for Reaction of Schiff Bases with Trichloroacetyl Chloride in the Presence of Triphenylphosphine——The examined runs shown in Table I were carried out by the following general procedures. To a solution of each 0.02 mole of the Schiff bases in 20 ml of dry CH_2Cl_2 was added 0.02 mole of trichloroacetyl chloride on cooling. To this solution a solution of 0.024 mole of triphenylphosphine in 10 ml of CH_2Cl_2 was added on cooling for 1 hr, and the reaction mixture was allowed to stand at room temperature overnight. In

5) All melting points are uncorrected. IR spectra were determined on a Hitachi EPI-G2 spectrophotometer. NMR spectra were taken at 60 MHz with a Hitachi R-24 spectrometer using tetramethylsilane as an internal standard.

the use of N-(*p*-methoxybenzylidene)aniline most of the product, 3,3-dichloro-4-(*p*-methoxyphenyl)-1-phenyl-2-azetidinone, was deposited in the reaction mixture. After washed with sulfuric acid, aqueous $NaHCO_3$ and then water, the dichloromethane solution was dried over $MgSO_4$ and concentrated to give crystals of the 3,3-dichloro-2-azetidinone product, which were recrystallized from an appropriate solvent.

In the above the following procedures for the product isolation were also applicable instead. The reaction solution was washed with aqueous $NaHCO_3$, dried over $MgSO_4$ and concentrated. The resulting residue was triturated with EtOH, whereupon most of the 3,3-dichloro-2-azetidinone product remained undissolved. The residue obtained by concentration of the ethanolic solution was mostly composed of triphenylphosphine oxide.

The run with N-benzylidenemethylamine is an exception of the above procedure. The concentration residue of the washed and dried reaction solution was repeatedly washed with *n*-hexane under reflux, whereupon triphenylphosphine oxide remained undissolved. The combined *n*-hexane washings were concentrated and the resulting residue was fractionally distilled to give 3,3-dichloro-1-methyl-4-phenyl-2-azetidinone.

The following with their melting points are the obtained 3,3-dichloro-2-azetidinones, yields of which are listed in Table I; 3,3-dichloro-1,4-diphenyl-2-azetidinone (mp 161—162°, lit.[6] mp 164°, lit.[2] mp 161—162°), 3,3-dichloro-4-(*p*-methoxyphenyl)-1-phenyl-2-azetidinone (mp 156—157°, lit.[2] mp 154—155°), 3,3-dichloro-4-(*p*-nitrophenyl)-1-phenyl-2-azetidinone (mp 147.5—148°, lit.[6] mp 158°, lit.[2] mp 150—151°), 3,3-dichloro-1-(*p*-methoxyphenyl)-4-phenyl-2-azetidinone (mp 110—111°, lit.[6] mp 118°, lit.[2] mp 110.5—112°), 3,3-dichloro-1-cyclohexyl-4-phenyl-2-azetidinone (mp 97—98°, lit.[2] mp 98—98.5°), and 3,3-dichloro-1-methyl-4-phenyl-2-azetidinone (mp 88—89°, lit.[2] 88—89.5°). The melting points of these products were undepressed by admixture with authentic specimens obtained in our previous work. Their IR spectra were well consistent with those of authentic specimens.

Reaction of N-Benzylideneaniline with Trichloroacetyl Chloride in the Presence of Hexamethylphosphorous Triamide——By the use of hexamethylphosphorous triamide in place of triphenylphosphine a reaction of N-benzylideneaniline (I) with trichloroacetyl chloride was carried out by the same way as described in the above general procedure. After washed with aqueous $NaHCO_3$ the reaction solution was concentrated to give a pasty residue, which was triturated with a small amount of EtOH. As insoluble crystals, 3,3-dichloro-1,4-diphenyl-2-azetidinone (III), mp 159—160°, was obtained in 26% yield.

Reaction of N-Benzylideneaniline with Trichloroacetyl Chloride in the Presence of Triphenylphosphite——To a solution of 3.6 g of I and 3.6 g of trichloroacetyl chloride in 30 ml of chlorobenzene 6.2 g of triphenylphosphite was added and the mixture was refluxed for 5 hr. The reaction solution was concentrated under redued pressure. The resulting oily residue was diluted with 40 ml of wet ether and allowed to stand overnight. Deposited crystals were collected by filtration and recrystallized from EtOH to give 2.0 g (24%) of α-anilinobenzylphosphonic acid diphenyl ester (IV) as prisms, mp 152—152.5°. *Anal.* Calcd. for $C_{25}H_{22}O_3NP$: C, 72.28; H, 5.34; N, 3.37. Found: C, 71.77; H, 5.31; N, 3.27. IR ν_{max}^{KBr} 3345 cm^{-1} (NH). NMR δ (in $CDCl_3$): 4.50 (1H, broad, >NH), 5.06 (1H, doublet, $J=12.8$ Hz, >CH-), 6.45—7.7 (20H, multiplet, $4\times C_6H_5$). The ethereal filtrate was washed with aqueous K_2CO_3, dried over K_2CO_3 and concentrated. Distillation of the resulting residue under 0.2 mmHg at above 200° of bath temperature gave a viscous oil, which was triturated with ether to give crystals, 0.45 g (8%) of III, mp 156—158°.

Acknowledgement The authors are indebted to the members of Analysis Center of this college for microanalyses.

6) E. Ziegler, Th. Wimmer, and H. Mittelbach, *Monatsh. Chem.*, **99**, 2128 (1968).