EXPERIMENTAL

General Procedure. In a typical experiment 2.0 grams of the phenol was dissolved in 10.0 ml. of dimethylformamide (reagent grade), 2.0 grams of anhydrous potassium carbonate was added, in addition to 5.0 ml. of reagent grade methyl iodide. The solution was refluxed for 20 hours. The reaction mixture was then poured into 150 ml. of cold water, and extracted twice with 100-ml. portions of ether. The combined ether extracts were washed twice with 10% NaOH solution and twice with distilled water. The ether extract was then dried over anhydrous potassium carbonate, filtered, and concentrated. The crude product was analyzed by gas chromatography using either a 10-foot × ¼-inch column packed with 20% DEGS/60- to 80-mesh Chrom W or a 5-foot × ¼-inch column, containing 20% Apiezon L/60- to 80-mesh Chrom W. The products were also analyzed by infrared spectroscopy.

Preparative Procedure. *p,p′*-Biphenol (62.0 grams, 0.33 mole) was dissolved in 500 ml. of reagent grade dimethylformamide. Anhydrous potassium carbonate, 125.0 grams, and 150.0 grams (1.06 moles) of methyl iodide were added. The mixture was refluxed for 26 hours. The hot solution was then poured into 2 liters of cold water and the product collected by filtration. After washing with water, the product was partially air-dried, then recrystallized once from DMF-methanol to give 48.0 grams (75% yield) of 4,4′-dimethoxybiphenyl, m.p. 177–78° C. [reported 173° C. (*3*)].

LITERATURE CITED

(1) Brieger, G., Pelletier, W.M., *Tetrahedron Letters* **40**, 3555 (1965).
(2) Claisen, L., *Ann.* **418**, 96 (1918).
(3) Hirsch, O., *Chem. Ber.* **22**, 335 (1889).
(4) Parker, A.J., "Advances in Organic Chemistry: Methods and Results," Vol. **5**, R.A. Raphael, E.C. Taylor, and H. Wynberg, Eds., Wiley, New York, 1965.
(5) Wagner, R.B., Zook, H.D., "Synthetic Organic Chemistry," Wiley, New York, 1953.

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Reaction of *N*-Pentachlorophenyl Ethylenediamine with Phosgene

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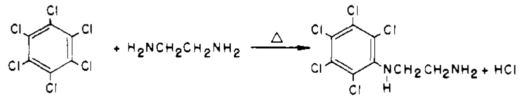
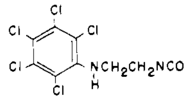
N-Pentachlorophenyl ethylenediamine was converted by treatment with phosgene to the novel cyclic allophanoyl chloride, 1-pentachlorophenyl-3-chlorocarbonyl-2-imidazolidinone. The desired acyclic product, 2-(pentachlorophenylanilino)-ethyl isocyanate, apparently formed as a reaction intermediate, but was not isolable. The fact that this phosgenation proceeded with ring closure despite the feeble basicity of the amino group attached to the polychlorinated aromatic ring attests to the importance of intramolecular proximity effects in governing the course of reactions wherein 5-membered ring formation is possible.

N-Pentachlorophenyl ethylenediamine, I, is available in a virtually quantitative yield from the condensation of hexachlorobenzene with ethylenediamine (*2*). The powerful electron withdrawing character of the pentachlorophenyl group, in combination possibly with a steric hindrance effect, so drastically reduces the basicity of the secondary amino group in I that the compound behaves in many respects as though it were a monoamine. Thus, although three amine hydrogens are present in I, only the two attached to the primary amine function will react with 1) 1,2-alkylene oxides at temperatures as high as 175° C.; 2) acetic anhydride in refluxing pyridine; and 3) epichlorohydrin in the presence of caustic soda (*1*). Furthermore, I analyzes as a monoamine when titrated with either sulfuric acid in aqueous methanol or with perchloric acid in glacial acetic acid. Finally, treatment of I with an excess of the highly reactive phenyl isocyanate in toluene solution for 30 minutes followed by quenching with an excess of di-*n*-butylamine and back-titration with standard hydrochloric acid solution yields an equivalent weight for I closely approximating its molecular weight, indicating again that reaction occurs with one amino group only.



I

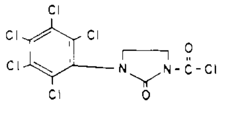
The marked tendency for I to behave as a monoamine suggested the possibility of converting this intermediate via phosgenation into 2-(pentachlorophenylanilino)-ethyl isocyanate, II, a molecule which would be unique from the standpoint of containing an isocyanate function and a secondary amine function in a state of stable coexistence. Our interests in II were both academic and commercial in nature, since in addition to possessing sheer novelty value, II represented a potentially interesting biological intermediate and special-purpose component for certain flame-proof polymer systems.



II

Phosgenation of I in *o*-dichlorobenzene solution using the conventional cold-hot, two-stage technique (*4*) proceeded smoothly, hydrogen chloride being evolved vigorously at 130° C. Monitoring of the progress of the phosgenation by the strength of the —NCO absorption band at 4.4 microns in the infrared indicated, however, that although isocyanate functionality was being generated, the reaction was not stopping at the desired stage. This fact became even more apparent when a solid product precipitated from the hot solution during the solvent stripping phase of the workup procedure.

The establishment of a structure for this unexpected reaction product was relatively straightforward, based upon spectral data, physical properties, chemical reactivity, microanalysis, and derivative formation. The infrared spectrum of the crude product m.p. 171-175° C.) indicated the absence of isocyanate functionality and the presence of complex carbonyl functionality with an especially strong absorption at 5.55 microns indicative of an acyl- or carbamoyl-type halide. The absence of —NH absorption in the 3.0-micron region suggested the possibility of a cyclic structure, wherein the absorption at 5.55 microns could be attributable to a carbamoyl chloride derived from a tertiary nitrogen atom. The yield of the crude product was consistent with the addition of one —COCl moiety and its solubility characteristics and behavior toward amines (exothermic reaction with formation of a water-soluble salt) were all consistent with those expected for the novel cyclic allophanoyl chloride, 1-pentachlorophenyl-3-chlorocarbonyl-2-imidazolidinone, III. Microanalytical values on a sample of III purified by recrystallization from carbon tetrachloride provided confirmation for the validity of this structural assignment, as did subsequent derivative formation and characterization.



III

Some typical reactions of III are summarized in Figure 1, R being used throughout to denote the pentachlorophenyl radical. Generally speaking, III reacted with a variety of protonic species in the manner expected for a tertiary carbamoyl chloride. Thus, it hydrolyzed with loss of carbon dioxide to give 1-pentachlorophenyl-2-imidazolidinone, IV, and reacted with anhydrous alcohols to give carbamic acid esters such as VI which themselves hydrolyzed readily back to IV. With ammonia and amines, III reacted as expected to give the corresponding carbamic acid amides, which in turn hydrolyzed back to IV when treated with aqueous alkali in the presence of a coupling solvent. In refluxing carbon tetrachloride, III condensed with IV to afford the high-melting, very insoluble carbonylbis(1-pentachlorophenyl)-2-imidazolidinone VIII.

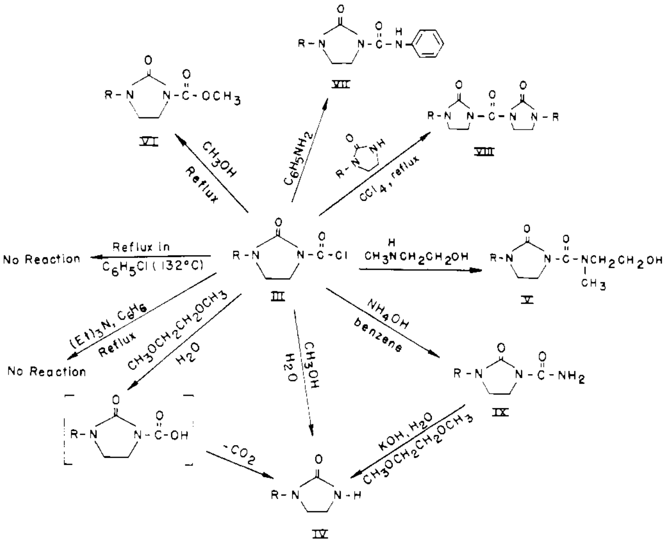
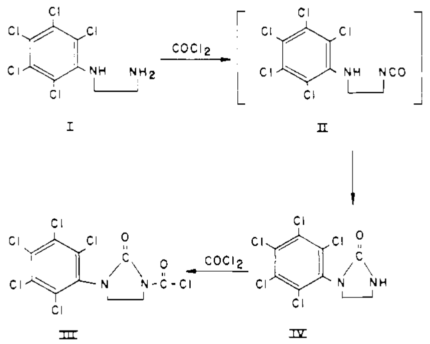


Figure 1. Typical reactions of 1-pentachlorophenyl-3-chlorocarbonyl-2-imidazolidinone

The chemistry of III is of interest primarily from the viewpoint that the compound represents a novel class of allophanoyl chlorides, the 1-unsubstituted (hydrogen in place of pentachlorophenyl) members of which are commercially important because their chemistry is intimately related to that of the ethylene diisocyanates (*3*). The absence of a hydrogen atom at the 1-position causes III to behave toward both heat and triethylamine in a manner markedly different from that of either the acyclic allophanoyl chlorides or the 1-unsubstituted cyclic allophanoyl chlorides studied by Sayigh and coworkers (*3*). Whereas these two latter species lose hydrogen chloride under such conditions to afford isocyanurates, linear polymers or ethylene diisocyanate derivatives via ring opening, III is recovered unchanged from comparable treatments.

The unexpected formation of III from the phosgenation of diamine I attests to the overwhelming influence of proximity effects in governing the course of reactions wherein 5-membered ring formation is possible. In this connection, Sayigh *et al.* (*3*) have reported that despite the low reactivity of the —NCO group towards a urethane hydrogen, ethylene diisocyanate yielded imidazolidinone-2 derivatives rather than bis-urethanes when treated with large excesses of simple alcohols. Trimethylene diisocyanate under similar conditions yielded almost exclusively the bis-urethanes.



The fact that isocyanate functionality was detected instrumentally during the phosgenation of I suggests that II was formed as an intermediate and that the addition of the —COCl moiety occurred as the final step in the sequence. Consequently, the original objective of synthesizing a stable amino-containing isocyanate probably could be realized by phosgenating a diamine such as I wherein the amino groups are separated by more than 2 carbon atoms.

Compound III and several of its reaction products shown in Figure 1 were submitted for routine biological screening studies and were found to exhibit virtually no activity toward a broad spectrum of viruses, bacteria, fungi, nema, plants, and insects.

EXPERIMENTAL

Melting points were determined with a Mel-Temp (Laboratory Devices, Inc.) capillary tube apparatus and are uncorrected. Microanalyses were performed by European Research Associates, s.a., Brussels, Belgium. Infrared spectra were obtained on a Perkin-Elmer Model 21 Spectrophotometer and NMR spectra on a Varian Associates Model A-60 instrument.

1-Pentachlorophenyl-3-chlorocarbonyl-2-imidazolidinone, III. To a 5-liter, 4-necked glass kettle equipped with a stirrer, gas sparger, thermometer, dropping funnel, and cooling bath was charged 1500 ml. of *o*-dichlorobenzene and 198 grams (2.0 moles) of liquid phosgene. Over a course of one hour at –5° to 0° C., a total of 135 grams (0.435 mole) of *N*-pentachlorophenyl ethylenediamine, I, was added in portions. Following completion of the addition, the cooling bath was removed, and the charge was permitted to rise to room temperature over a period of about three hours. External heating was then applied, and the temperature was raised slowly to 130° C. while phosgene was sparged through the suspension at a rate of 0.75 mole per hour until a clear solution resulted and HCl was no longer evolved. The temperature was then increased to 150° C. and held there for one hour while nitrogen was sparged through the solution to accomplish degassing. As the charge was being stripped of solvent at 10 mm. of Hg, a solid began to precipitate. At 150° C., stripping was discontinued, heptane was added as a slurrying agent, and the solid product was recovered by filtration. The yield of crude material was 173 grams (100%), with incomplete melting at 171–175°. Dissolution of the crude product in 1 liter of hot acetone followed by filtration served to remove a small quantity of insoluble material and to afford, after chilling of the filtrate to −30° C., 148 grams (85.6%) of buff-colored solid, m.p. 173–176°. The material crystallized from hot carbon tetrachloride, in which it is soluble to the extent of 3 to 4 grams per 100 ml., as stout, off-white needles, m.p. 180–181°. The melting point was unchanged by further recrystallization.

Anal. Calcd. for $C_{10}H_4N_2O_2Cl_6$: C, 30.2; H, 1.0; N, 7.0; Cl, 54.3. Found: C, 30.1; H, 1.1; N, 7.0; Cl, 53.6.

The IR spectrum of the product in the form of a KBr pellet was consistent with the structural assignment, indicating the absence of —NCO and —NH functionality and the presence of both an acyl halide and a second type of carbonyl functionality. There were functional group bands at 5.55μ (—COCl), 5.69 and 5.79μ (cyclic urea C=O), 6.75μ (aromatic C=C), and 13.16 and 13.97μ (C—Cl).

1-Pentachlorophenyl-2-imidazolidinone, IV. To a 50-ml. Erlenmeyer flask was charged 0.5 gram of III, 7 ml. of dimethoxyethane, and 1 ml. of water. The mixture was slowly heated almost to a boil, by which time the solid had dissolved to yield a strongly acidic solution. On standing overnight, the solution deposited glistening, pale yellow plate-like crystals (0.33 gram, 78.1%) melting at 204–206°. One recrystallization from benzene afforded white plates of unchanged melting point.

Anal. Calcd. for $C_9H_5N_2OCl_5$: C, 32.3; H, 1.5; N, 8.4; Cl, 53.0. Found: C, 32.1; H, 1.5; N, 8.3; Cl, 52.7.

The IR spectrum of the product in a KBr pellet was consistent with the assigned structure, showing —NH absorption and a single carbonyl absorption. There were functional group bands at 3.08μ (N—H), 5.85μ (cyclic urea C=O), 6.7 and 6.79μ (aromatic C=C), and 13.2 and 13.7μ (C—Cl).

1-Pentachlorophenyl-3-(*N*-methyl-*N*-2-hydroxyethylcarboxyamido)-2-imidazolidinone, V. To a 50-ml. Erlenmeyer flask equipped with a magnetic stirrer was charged a mixture of 1.99 grams (0.005 mole) of III, 0.505 gram (0.005 mole) of triethylamine, 20 ml. of diethyl ether, and 20 ml. of benzene. To this stirred solution was added in one portion at ambient temperature 0.38 gram (0.005 mole) of *N*-methylethanolamine. A solid formed immediately; after stirring overnight the suspension was filtered, the white solid slurried in 20 ml. of water to wash out the amine hydrochloride, and the residual solid collected by filtration to give 1.4 grams (64.1%) of crude product, m.p. 142–144°. Recrystallization from benzene afforded stout white plates melting at 146–148°, unchanged by further recrystallization. This product was not affected by prolonged boiling in aqueous acetone, indicating stability of the substituted urea function toward hydrolysis.

Anal. Calcd. for $C_{13}H_{12}N_3O_3Cl_5$: C, 35.8; H, 2.8; N, 9.6; Cl, 40.6. Found: C, 35.7; H, 2.8; N, 10.0; Cl, 40.8.

1-Pentachlorophenyl-3-carbomethoxy-2-imidazolidinone, VI. A mixture of 0.8 gram (0.002 mole) of III and 10 ml. of anhydrous methanol was heated at reflux for 16 hours. Upon cooling, a white crystalline product formed which was collected by filtration and air-dried to give 0.6 gram (75.8%) of crude ester, m.p. 193–196°. The filtrate was strongly acidic. Two recrystallizations from benzene raised the melting point of the product to 200–201°. Admixture of this compound with the aqueous methanol reaction product IV (m.p. 204–206°) caused a 30° to 40° depression in melting point, thus clearly demonstrating that the two products were different species. The IR spectrum (KBr pellet) was also different from that of IV, but resembled III quite closely except for a stronger —CH absorption and a different intensity pattern in the three bands in the carbonyl region. There were functional group bands at 5.6 and 5.83μ (urea C=O), 5.75μ (ester C=O), 6.75μ (aromatic C=C), 7.53μ (ester C—O), 9.15μ (—OCH_3), and 12.95, 13.43 and 14.15μ (C—Cl). The NMR spectrum ($CDCl_3$) clearly indicated the methanol ester structure, however, with only two types of protons present; namely, methyl protons (singlet, 6.17τ) and methylene protons (multiplet, 5.73–6.28τ).

Anal. Calcd. for $C_{11}H_7N_2O_3Cl_5$: C, 33.6; H, 1.8; N, 7.1; Cl, 45.2. Found: C, 33.9; H, 1.8; N, 6.9; Cl, 44.6.

1-Pentachlorophenyl-3-phenylcarboxyamido-2-imidazolidinone, VII. To a solution of 3.97 grams (0.01 mole) of III in 50 ml. of benzene was added in one portion 2 ml. of aniline. The light tan solid which formed almost immediately was filtered off, washed with water, and dried to give 3.55 grams (77.2%) of crude product, m.p. 250–251°. Recrystallization from dimethylformamide afforded stout tan needles, m.p. 251–252°. The thermometric molecular weight in acetone solution was indicated to be 468 ± 3% (theory is 453.5).

Anal. Calcd. for $C_{16}H_{10}N_3O_2Cl_5$: C, 42.3; H, 2.2; N, 9.3. Found: C, 43.1; H, 2.6; N, 9.2.

Carbonylbis(1-pentachlorophenyl)-2-imidazolidinone, VIII. A mixture of 0.9 gram (0.0023 mole) of III and 0.76 gram (0.0023 mole) of IV in 20 ml. of carbon tetrachloride was heated under reflux for 20 hours. During this time, HCl was evolved and a solid was deposited. The suspension was filtered hot to afford 0.9 gram (57.5%) of the fluffy white solid, m.p. 309–311°. Inasmuch as no suitable recrystallization solvent could be found, the crude material was washed with acetone and dried for analysis. The infrared spectrum (KBr pellet) was consistent with the assigned structure, displaying two carbonyl bands presumably due to the open chain (5.89μ) and cyclic (5.73μ) urea groups. There were also functional group bands at 6.79μ (aromatic C=C) and at 13.38, 13.50, and 14.15μ (C=Cl).

Anal. Calcd. for $C_{19}H_8N_4O_3Cl_{10}$: C, 32.8; H, 1.2; N, 8.1; Cl, 51.0. Found: C, 32.7; H, 1.3; N, 8.4; Cl, 51.3.

1-Pentachlorophenyl-3-carboxyamido-2-imidazolidinone, IX. To a mixture of 1.99 grams (0.005 mole) of III, 30 ml. of benzene, and 10 ml. of water stirred magnetically at room temperature was added in several portions 10 ml. of concentrated ammonium hydroxide. A solid formed almost immediately. After an additional 15 minutes of stirring, the mixture was filtered, the solid was washed with water, collected by filtration, and air-dried to afford 1.17 grams (61.5%) of crude buff-colored product, m.p. 271.5–273.5°. Although insoluble in most common organic solvents and in water, the product crystallized from acetone as clusters of small white needles, m.p. 279–280°. The infrared spectrum (KBr pellet) was consistent with the assigned structure, having strong —NH_2 bands at 2.96, 3.07, and 6.29μ, a doublet in the carbonyl region at 5.85μ (cyclic urea C=O) and 5.97μ (amide C=O), an aromatic C=C band at 6.74μ, a C—N band at 7.23μ and C—Cl bands at 12.97, 13.16, and 13.96μ.

Anal. Calcd. for $C_9H_6N_3O_2Cl_5$: C, 31.8; H, 1.6; N, 11.1. Found: C, 32.0; H, 1.7; N, 11.2.

The compound could be hydrolyzed to IV by refluxing in aqueous dimethoxyethane containing an excess of potassium hydroxide. Under these conditions, ammonia was evolved and IV was formed in good yield. The dimethoxyethane is required for solvent purposes; in aqueous base alone, hydrolysis did not occur.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Bremmer, B.J., *Ind. Eng. Chem. Prod. Res. Develop.* **5** (4), 340-46 (1966).
(2) Rocklin, A. L., *J. Org. Chem.* **21**, 1478 (1956).
(3) Sayigh, A.A.R., Tilley, J.N., Ulrich, H.J., *J. Org. Chem.* **29** (11), 3344-7 (1964).
(4) Siefken, W., *Ann.* **562**, 75 (1949).

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Synthesis of Some Bis(Halomethyl) Phosphorylmethyltriphenylphosphonium Halides and a Stable Phosphine Methylene

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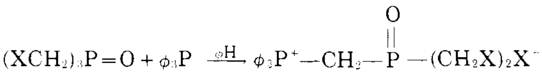
The 1 to 1 triphenylphosphine adducts of tris(chloromethyl)phosphine oxide, tris(bromomethyl)phosphine oxide, and tris(iodomethyl)phosphine oxide were prepared in 80% yield. The chloro derivative was converted to triphenylphosphinebis(chloromethyl)phosphorylmethylene by reaction with aqueous ammonium hydroxide. The phosphine methylene was stable and capable of regenerating the predecessor by reaction with hydrogen chloride. It also reacted with bromine to form bis(chloromethyl)phosphorylmethyltriphenylphosphonium bromide. Infrared and NMR spectra of the subject compounds were recorded.

IN THE SIMPLEST PROCESS for the preparation of phosphonium compounds an alkyl halide and a tertiary phosphine are mixed and heated (*1*). The authors have prepared the 1-to-1 adducts of triphenylphosphine and some halomethylphosphine oxides. The ionic halogens were replaced by a picrate moiety for proof of structure.



$$(XCH_2)_3P{=}O + \phi_3P \xrightarrow{\phi H} \phi_3P^+{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}(CH_2X)_2X^- \quad (1)$$

Schlosser reported that acyl- or benzoylmethylidetriphenylphosphonium halides undergo deuterium exchange without the use of a catalyst (*3*). The authors observed that the phosphoryl group affects the lability of the methylene hydrogens in a like manner, when deuterium oxide was added to a chloroform solution of bis(chloromethyl)phosphorylmethyltriphenylphosphonium chloride (I) during an NMR analysis.

Ramirez synthesized hexaphenylcarbodiphosphorane, which reacted with water to form triphenylphosphinediphenylphosphorylmethylene (*2*). The stability of the latter compound was explained by the effect of the adjacent phosphoryl group on the negative charge. By reaction of I with an aqueous 2% solution of ammonium hydroxide, the authors prepared triphenylphosphinebis(chloromethyl)phosphorylmethylene (IV).

$$\phi_3P{-}CH_2{-}P{-}(CH_2Cl)_2Cl \xrightarrow{NH_4OH} \phi_3P{=}CH{-}P{-}(CH_2Cl)_2 \text{ (IV)} \quad (2)$$

The stability of IV was affected by its slight hygroscopic properties. NMR studies showed that water reacts slowly with IV to produce a phosphonium compound, undoubtedly the phosphonium hydroxide. The reaction of a benzene solution of IV with hydrogen chloride regenerated I. Methylene chloride solutions containing bromine were decolorized by IV. However, the only product obtained was bis (chloromethyl) phosphorylmethyltriphenylphosphonium bromide (V) and not the expected product, a bromomethyltriphenylphosphonium bromide.

The reaction of ammonium hydroxide with dibromomethylphosphorylmethyltriphenylphosphonium bromide (II) produced only a quantitative yield of triphenylphosphine oxide.

EXPERIMENTAL

Bis (chloromethyl) phosphorylmethyltriphenylphosphonium Chloride (I). Tris(chloromethyl)phosphine oxide (3.0 grams, 0.0153 mole) was refluxed with triphenylphosphine (4.19 grams, 0.016 mole) in benzene for 18 hours. The resulting solution was filtered and yielded 5.8 grams (83%) of crude I [m.p. 230-1.5° C. (methanol-benzene)]. The infrared spectrum (KBr) (Perkin-Elmer Model 137B Infracord) exhibited peaks at 3.25(w), 3.35(w), 3.42(w), 3.55(m), 3.70(w), 6.3(w), 6.75(w), 6.95(w), 7.15(w), 7.32(w), 7.48(w), 7.60(w), 8.08(m), and 8.20(m) with a shoulder at 8.30(m), 8.42(m), 8.60(w), 9.0(s), 10.05(w), 11.86(m), 12.14(s), 12.9(s), 13.25(s), 13.62(s), and 14.45 microns(s). The NMR spectrum (Varian A-60A spectrometer) of a deuteriochloroform solution showed a phenyl complex centered at δ7.8 p.p.m., two doublets centered at δ5.6 p.p.m., $JP{-}CH$ = 13 c.p.s., and a complex centered at δ3.95 p.p.m. in a ratio of 15:2:4, respectively. The addition of deuterium oxide eliminated the two doublets centered at δ5.6 p.p.m.