Reactions of Phenylchlorodiazirine with Nucleophiles and Substituted Acetylenes[1,2]

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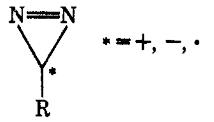
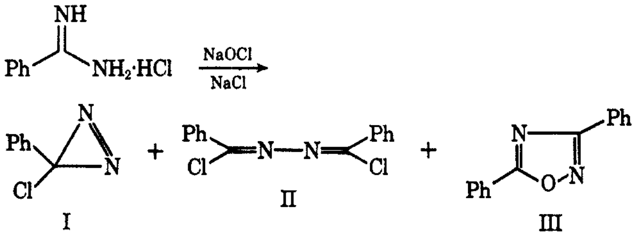
The chemistry of phenylchlorodiazirine (I) has been investigated with emphasis on the nucleophilic attack on the nitrogen-nitrogen double bond and the formation and chemistry of phenylchlorocarbene. Treatment of I with phenyllithium afforded diphenylbenzamidine, whereas reaction with methyllithium gave acetophenone. The reaction of I with sulfonium and phosphonium ylides was also studied. Like other diazirines, phenylchlorodiazirine decomposes thermally to produce phenylchlorocarbene, which may be trapped with triphenylphosphine, tri-*n*-butyltin hydride, and substituted acetylenes.

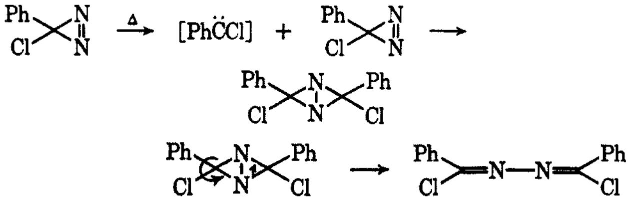
Among the numerous heterocyclic ions which have been prepared, the diazirinium ion is of particular interest. The heterocyclic cation is isoelectronic with the cyclopropenyl cation[4] and consequently would be predicted to be stable according to Hückel's 4n + 2 rule.[5,6] Although this rule strictly applies only to monocyclic hydrocarbons, heterocyclic aromatics possessing this number of π electrons are considered to meet the criteria of aromaticity.[7] Extended Hückel calculations have indicated however, that the diazirinium cation is unstable with respect to a distortion to a diazomethane cation.[8] In an attempt to gain some insight into the chemical and physical properties of the diazirinium ion system, the chemistry of 3-chlorophenyldiazirine has been investigated. The results of some attempts to generate the anion and radical from a 3-halodiazirine are reported in this paper.



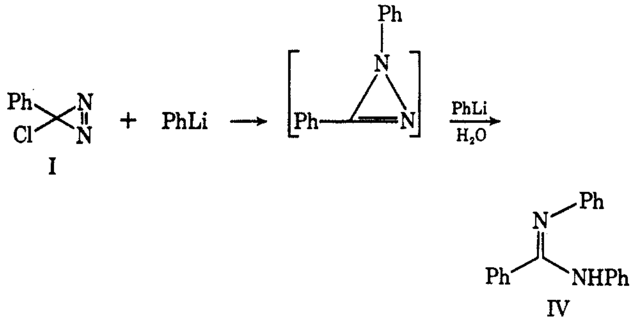
3-Chlorophenyldiazirine (I) was available from the reaction of benzamidine hydrochloride with an aqueous sodium hypochlorite solution.[6] In addition to diazirine I (60%), smaller quantities of 1,4-diphenyl-1,4-dichloro-2,3-diaza-1,3-butadiene (II) (4%) and 3,5-diphenyl-1,2,4-oxadiazole (III) (3%) were formed.



Like other diazirines, phenylchlorodiazirine decomposes thermally to produce phenylchlorocarbene.[9-11] Once formed, the carbene reacts with excess starting diazirine (I) to give a transient diazabicyclo[1.1.0]-butane intermediate.[12] Subsequent bond reorganization readily rationalizes the formation of azine II. In fact, thermolysis of I in benzene gives II in excellent yield. Similarly, irradiation of I in pentane yields II and a mixture believed to be the insertion products of phenylchlorocarbene with *n*-pentane. Evidently II is a secondary product formed from partial decomposition of I under the original reaction conditions.



With the hope of documenting the transient existence of the diazirinyl anion, we set out to examine the metal exchange reactions of phenylchlorodiazirine. Treatment of I with phenyllithium in ether afforded diphenylbenzamidine (IV) in excellent yield. Isolation of the amidine suggests that the reaction occurs by attack of phenyllithium on the N-N double bond followed by chloride ion loss and subsequent reaction of the initially formed intermediate with excess phenyllithium. Previous reports by Schmitz[13] have demonstrated the facile addition of related organometallics to diazirines and provide reasonable chemical analogy for the first step. It seems as though the initial intermediate undergoes further reaction with phenyllithium at a faster rate than



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[1] We gratefully acknowledge support of this research by the Public Health Service Grant GM 13990-02.

[2] For a preliminary report of this work, see A. Padwa and D. Eastman, *Tetrahedron Lett.*, 4035 (1967).

[3] Alfred P. Sloan Foundation Fellow, 1968–1970.

[4] R. Breslow, H. Hover, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

[5] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists" John Wiley & Sons, Inc., New York, N. Y., 1961, p 256.

[6] W. H. Graham, *J. Amer. Chem. Soc.*, **87**, 4396 (1965).

[7] R. Breslow, J. Brown, and J. J. Gajewski, *ibid.*, **89**, 4383 (1967).

[8] R. Hoffmann, *Tetrahedron*, **22**, 539 (1966).

[9] H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 1700 (1965).

[10] R. A. Mitsch, *J. Amer. Chem. Soc.*, **87**, 758 (1965).

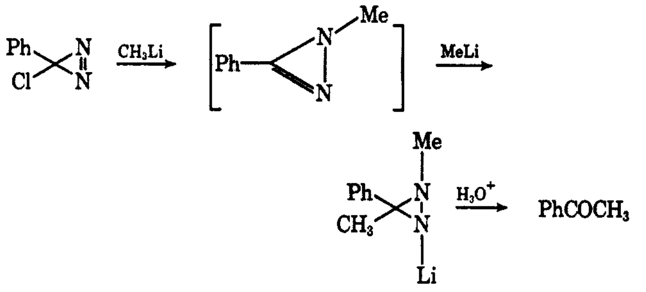
[11] R. A. Moss, *Tetrahedron Lett.*, 4905 (1967).

[12] The formation of oxadiazole III may also originate from the transient diazabicyclo[1.1.0]butane.

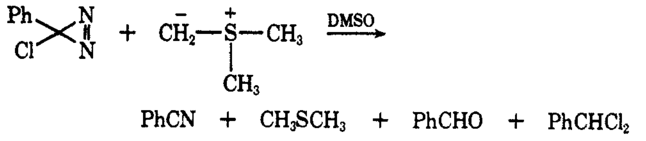
[13] E. Schmitz, "Advances in Heterocyclic Chemistry," Vol. II, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1965, p 129.

does starting material.[14] This explanation accounts for the large amount (50%) of starting material that can be recovered when equivalent quantities of phenyllithium were used. When a 2 mol excess of phenyllithium was employed, a near quantitative yield of IV could be obtained.

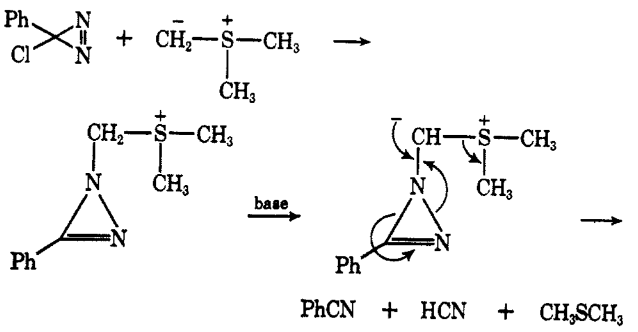
The reaction course followed by treating I with methyllithium in ether proved to be dramatically different. The major product obtained in this case was identified as acetophenone. Careful examination of the residue revealed no detectable amount of dimethylbenzamidine. It appears that the major difference in reaction of I with the two lithium compounds used is related to the direction of addition across the carbon–nitrogen double bond of the initial intermediate. If phenyllithium simply adds across the carbon–nitrogen double bond in the observed direction, then the only phenyl group with which the anion is conjugated is one which is also present in the starting material and which could function just as well in the methyllithium reaction. It therefore appears that attack by phenyllithium is accompanied by ring opening, since the amidine anion which results does indeed have the extra phenyl stabilization in this case. In contrast, methyllithium prefers to undergo stepwise addition at the carbon atom end, since the related amidine anion would be devoid of this overlap. The formation of acetophenone may be readily explained by a hydrolytic fission of the diaziridine upon acid hydrolysis.[14]

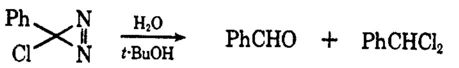


With the above results in hand, we considered it relevant to explore the reactivity of I with other nucleophilic reagents. To this end we undertook the study of the reaction of I with dimethylsulfonium ylide. The reaction was observed to proceed quite readily at room temperature. Removal of the solvent followed by vapor phase chromatography of the residue afforded mostly benzonitrile and dimethyl sulfide, with lesser quantities of benzaldehyde and benzal chloride.

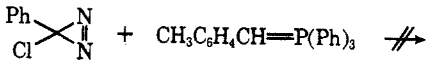


Although no detailed mechanistic study was undertaken, it is possible to formulate a reasonable path for the formation of benzonitrile based on the mechanism previously outlined. As discussed above, initial nucleophilic attack on nitrogen followed by chloride ion loss would lead to a strained sulfonium salt. Removal of a proton from the salt followed by ring cleavage readily accounts for the observed products. The formation of the remaining products obtained from the above reaction may be attributed to the decomposition of unreacted starting material upon aqueous work-up. When phenylchlorodiazirine (I) was treated with aqueous *t*-butanol, benzaldehyde and benzal chloride were the only two products isolated. It seems reasonable to assume that phenylchlorocarbene inserts into the O–H bond of solvent, and the reactive chloro ether so produced undergoes solvolysis under the reaction conditions.





In the expectation that a study of the reaction of I with other ylides might illuminate the mechanism for nitrile formation, phenylchlorodiazirine was treated with a phosphonium ylide. Treatment of I with *p*-toluylmethylene triphenylphosphorane for 2 hr at room temperature produced small amounts of benzal chloride and benzonitrile (4%). The remaining organic products were brown to black tars with ill-defined spectra, unresolved by careful chromatography. In view of the difficulty of isolating characterizable products from this reaction, we abandoned further study of the reaction of I with phosphonium ylides.



In an attempt to further demonstrate the generality of nucleophilic attack on the nitrogen double bond, phenylchlorodiazirine was treated with triphenylphosphine under two different sets of conditions. In the first case, which utilized benzene as the solvent, a 28% yield of α-chlorobenzyltriphenylphosphonium chloride

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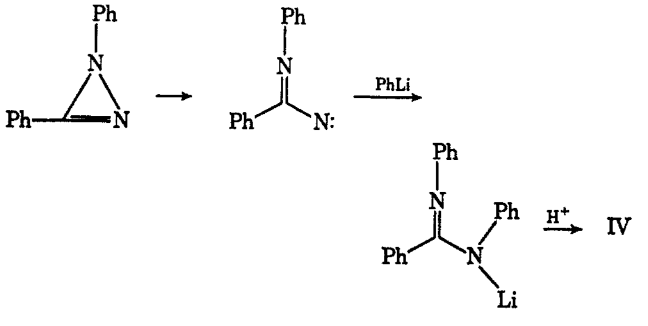
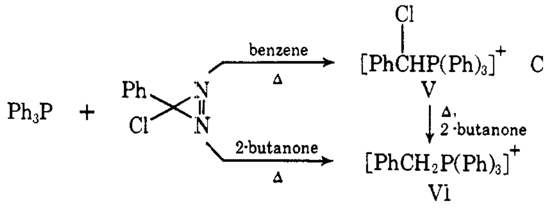
[14] A referee has suggested that since the initial intermediate is antiaromatic it may rearrange to a nitrene which in turn may rapidly react with phenyllithium to give the observed product. This could explain the unexpected direction of addition of phenyllithium to the C=N double bond and also its faster rate of addition relative to I.



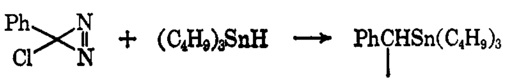
(V) was obtained. The second set of conditions used 2-butanone as solvent and resulted in the formation of benzyltriphenylphosphonium chloride (VI). It was noted



that refluxing V in 2-butanone for 2 hr resulted in the formation of VI. The above reactions apparently proceed by thermal decomposition of I to phenylchlorocarbene, which is subsequently trapped by triphenylphosphine.[15,16] It is interesting to note that the behavior of I with triphenylphosphine is substantially different from the diazirine ring-opening defluorination reaction observed with difluorodiazirine.[17] The reaction seems to be more closely related to the behavior of bis(trifluoromethyl)diazirine with trivalent organophosphorous derivatives.[18]

As a result of the above experiments, it is possible at this time to draw some conclusions concerning the reactivity of I with nucleophilic reagents. It is obvious from the results on hand that the reaction of phenylchlorodiazirine occurs readily with carbanions and less readily with nucleophilic reagents. As discussed in some detail by Mitsch,[17] a major factor responsible for nucleophilic attack on a diazirine is the electron availability of the nucleophilic reagent. In no case was there any evidence for diaziridinyl anion formation. It appears that the heterocyclic 4-π-electron system, like the cyclopropenyl anion,[19] is quite unstable and resists formation.

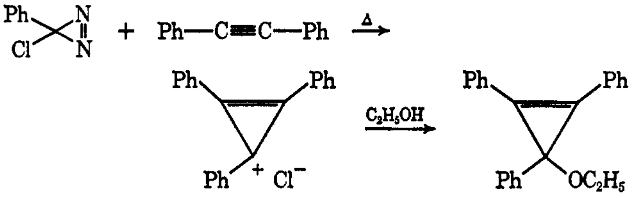
In connection with our attempts to generate the diaziridinyl anion, we felt it desirable to obtain data on the stability of the related 3-π-electron system. Accordingly, we set out to examine the reaction of tri-n-butyltin hydride with I in the hope of documenting the transient existence of the radical. It is generally accepted that the reaction of alkyl halides with organotin hydrides proceeds by a free-radical chain mechanism.[20] Furthermore, it is known that the reduction of alkyl chlorides with tin hydrides occurs more readily than addition to multiple double bonds.[21] The reaction between I and tri-n-butyltin hydride in refluxing ether gave α-chlorobenzyl tri-n-butyltin hydride (VII). The



VII

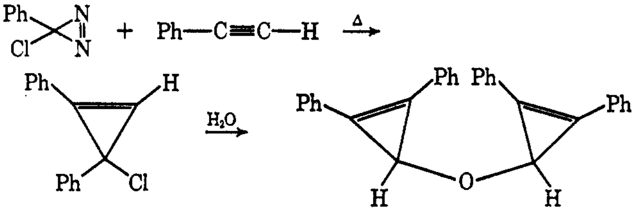
structure of the product was confirmed by nmr and mass spectroscopy. The nmr spectrum ($CDCl_3$) showed a broad multiplet between τ 8.70 and 9.10, a singlet at τ 5.31 for the benzylic proton, with the expected tin satellites ($J_{SnH} = 23$ cps), and a singlet at τ 2.80 ppm for the aromatic hydrogens. The mass spectroscopically determined molecular weight was 416, and there were peaks at m/e 379 and 381 corresponding to the loss of chlorine. The formation of this product is readily accounted for by the insertion of phenylchlorocarbene into the tin–hydrogen bond. The insertion of dichlorocarbene into a tin-hydrogen bond has already been reported on by Seyferth and Burlitch and provides reasonable chemical analogy for the above reaction.[22] It appears that the decomposition of I to phenylchlorocarbene precludes diaziridinyl-radical formation.

Inasmuch as both heat and light caused phenylchlorodiazirine (I) to lose nitrogen, it became of further interest to investigate the reaction of phenylchlorocarbene with reagents possessing π bonds. Graham has already reported on the reaction of I with cyclohexene.[6] Treatment of I with diphenylacetylene in refluxing benzene produced a single component in high yield which was subsequently identified as *sym*-triphenylcyclopropenyl chloride (VIII). The structure of this material was fully established by conversion to 1,2,3-triphenylcyclopropenyl ethyl ether (IX) by refluxing in ethanol. Compound IX was converted to the known triphenylcyclopropenyl bromide[23] by saturating an ethereal solution of IX with hydrogen bromide.



VIII IX

Similarly, the reaction of I with phenylacetylene gave 1-chloro-1,2-diphenylcyclopropene, which could be converted to the known bis-Δ′-1,2-diphenylcyclopropenyl ether[24] by recrystallizing the chloride from aqueous ethanol. The formation of the cyclopropenyl chlorides



in high yields suggests that this method can be effectively utilized for the preparation of these small-ring carbocyclic systems.

Experimental Section[25]

Preparation of Phenylchlorodiazirine (I).—3-Chlorophenyldiazirine was prepared by a slight modification of the procedure

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(15) A. J. Speziale, G. J. Marco and K. W. Ratts, *J. Amer. Chem. Soc.*, **82**, 1260 (1960).

(16) D. Seyferth, S. O. Grim and T. O. Read, *ibid.*, **82**, 1510 (1960).

(17) R. A. Mitsch, *ibid.*, **89**, 6297 (1967).

(18) D. M. Gale, W. J. Middleton, and C. G. Krespan, *ibid.*, **88**, 3617 (1966).

(19) R. Breslow and P. Dowd, *ibid.*, **85**, 2729 (1963).

(20) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *ibid.*, **84**, 3584 (1962).

(21) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

(22) D. Seyferth and J. B. Burlitch, *J. Amer. Chem. Soc.*, **85**, 2667 (1968).

(23) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961).

(24) D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960).

(25) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. All infrared spectra were determined in carbon tetrachloride as solvent unless otherwise stated. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. Ethyl alcohol (95%) was used as the solvent unless otherwise stated. The nuclear magnetic resonance spectra were determined at 60 Mc with the Varian Associates high resolution spectrometer. Tetramethylsilane was used as an internal standard.

of Graham.[6] To a solution of 53 g of lithium chloride and 37 g of benzamidine hydrochloride in 800 ml of dimethylsulfoxide and 600 ml of hexane was added rapidly and with stirring 310 g of sodium chloride in 1800 ml of a 7% sodium hypochlorite solution. The reaction mixture was cooled in an ice bath and vigorous mechanical stirring was employed throughout the addition. After stirring for an additional 15 min, the hexane layer was removed and the aqueous layer was washed with several portions (100 ml) of ether. The combined washings were dried over sodium sulfate and the solvent was removed under reduced pressure. Distillation of the residue gave 12 g (60%) of phenylchlorodiazirine, bp 33–35° (0.5 mm). Spectral ir peaks appeared at 6.38, 11.01, 13.22, and 14.51 μ; uv λ_{max} 388 mμ.

The residue from the distillation was chromatographed on a 3 × 98 cm silica gel column. The column was eluted with benzene, and the eluent, in 50 ml of fractions, was concentrated and dried *in vacuo*. Fractions 2 and 3 contained 0.3 g of 1,4-diphenyl-1,4-dichloro-2,3-diaza-1,3-butadiene (II): mp 121–122° (lit.[26] mp 122–123°); ir 6.25, 8.25, and 10.91 μ. The identity of this product was further confirmed by heating 0.1 g of the dichloroazine in 50 ml of aqueous ethanol for 16 hr to give 2,5-diphenyl-1,3,4-oxadiazole, mp 135–136° (lit.[27] mp 135–136°). Fractions 4 and 5 contained 0.4 g of 3,5-diphenyl-1,2,4-oxidiazole, mp 105–106 (lit.[28] mp 108°). Verification of this product was obtained by comparison with an authentic sample prepared by a procedure described by Clarke.[29]

Photolysis of I in Pentane.—A solution of 600 mg of I in 200 ml of pentane was irradiated with an internal, water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter for 1 hr. At the end of this time, the solution was evaporated to dryness to give a red oil which partially solidified on standing. The solid was separated from the crude oil by filtration and was subsequently identified as 1,4-diphenyl-1,4-dichloro-2,3-diaza-1,3-butadiene (0.15 g, 28%). The red oil was taken up in methylene chloride and filtered through a column of carbon black. The solvent was removed *in vacuo*, leaving a yellow oil (0.55 g, 71%). The oil was tentatively identified as a mixture of isomeric phenyl hexylchlorides as evidenced by infrared and nmr spectroscopy.

Thermal Decomposition of Phenylchlorodiazirine.—A solution of 1.0 g of I in 70 ml of benzene was refluxed for 3 hr. Removal of the solvent left a white solid that was identified as 1,4-diphenyl-1,4-dichloro-2,3-diaza-1,3-butadiene (0.95 g). The above procedure was repeated using 60 ml of *t*-butyl alcohol. Evaporation of the solvent and analysis of the residue by glpc using a 6 ft × 0.25 in. 10% DEGS on Chromsorb W (60–80 mesh) at 110° revealed the presence of benzaldehyde (65%) and benzal chloride (35%). These materials were identified by comparison with authentic samples.

Reaction of I with Organometallics.—To a solution of 4.6 g of I in 200 ml of ether was added slowly and with stirring 0.06 mol of phenyllithium in ether. The reaction mixture was stirred for an additional 30 min and was then quenched by the addition of water. The ether layer was separated and the aqueous layer was extracted with three 50-ml portions of ether. The ethereal extracts were combined and dried over sodium sulfate. Removal of the solvent left a white solid, which was recrystallized from ethanol to give 8.0 g of N,N-diphenylbenzamidine, mp 145–146°. Proof of structure was obtained by hydrolysis to aniline and benzanilide and also comparison with an authentic sample.[30] When equivalent quantities of phenyllithium and I were used, the yield of N,N-diphenylbenzamidine diminished (45%) and starting material (50%) could be recovered. The procedure outlined above was repeated using phenylmagnesium bromide. Again N,N-diphenylbenzamidine was the only detectable product. Repetition of the above procedure using methyllithium afforded acetophenone without any detectable formation of dimethylbenzamidine.

Reaction of I with Dimethylsulfonium Methylide.—Dried dimethyl sulfoxide (10 ml) and sodium hydride (0.32 g) were reacted in a nitrogen atmosphere at 60° until the hydrogen evolution ceased. The solution was cooled to −10° and enough anhydrous tetrahydrofuran was added to keep the solution from solidifying.[31] To the above solution was added 2.7 g of trimethylsulfonium iodide in 10 ml of dimethyl sulfoxide. The reaction mixture was stirred for 5 min, and then 1.0 g of phenylchlorodiazirine was added dropwise with vigorous stirring. The mixture was allowed to stir at room temperature for 2 hr and was then poured onto 500 g of crushed ice. The aqueous solution was extracted three times with 100-ml portions of ether. The ethereal extracts were combined, dried over sodium sulfate, and concentrated *in vacuo*. Analysis of the residue by glpc using a 6 ft × 0.25 in. DEGS on Chromosorb W at 120° revealed the presence of three components. These products were assigned as benzaldehyde (5%), benzonitrile (25%), and benzal chloride (5%). These materials were identified by retention time and infrared comparisons with authentic samples. The formation of dimethyl sulfide was evident from its characteristic odor.

Reaction of I with *p*-Toluylmethylenetriphenylphosphorane.—A mixture of 9.2 g of *p*-methyl-α-bromotoluene and 13.1 g of triphenylphosphine in 300 ml of benzene was heated to reflux for 2 hr. The resultant white precipitate was removed by filtration, washed with cold benzene, and dried. To a suspension of 2.84 g of triphenyl-*p*-methylbenzylphosphonium bromide in 30 ml of ether was added an equivalent amount of butyllithium in hexane. To the above solution was added 1.0 g of phenylchlorodiazirine in 10 ml of ether. The mixture was allowed to stir at room temperature for 2 hr. At the end of this time the mixture was poured onto ice and the aqueous layer was extracted with several portions of ether. The ethereal extracts were dried over sodium sulfate and the solvent was removed under reduced pressure. Analysis of the resulting residue by glpc on a 6 ft × 0.25 in. 10% DEGS column (Chromosorb W) at 110° revealed the presence of benzal chloride and benzonitrile (4%). No detectable quantities of *p*-tolylnitrile were evident. The bulk of the reaction product appeared to be a tarry phosphorus-containing mixture.

Reaction of I with Triphenylphosphine. A. In Benzene.—A solution of 1.0 g of I and 1.7 g of triphenylphosphine in 60 ml of benzene was refluxed for 3 hr. The solvent was removed under reduced pressure and the crude oil was shaken for several hours with 80 ml of acetone. The resultant white precipitate (0.4 g) was purified by trituration with refluxing acetone. This material was identified as α-chlorobenzyltriphenylphosphonium chloride: mp 258–259°; ir 6.95 and 9.01 μ.

Anal. Calcd for $C_{25}H_{21}Cl_2P$: C, 70.93; H, 5.00. Found: C, 70.64; H, 5.01.

Evaporation of the combined acetone washings left 1.2 g of a hygroscopic yellow solid whose infrared spectrum indicated a mixture of the phosphonium salt and triphenylphosphine oxide.

B. In 2-Butanone.—A solution of 1.0 g of I and 1.7 g of triphenylphosphine in 70 ml of 2-butanone was refluxed for 2 hr. The resultant white precipitate was crystallized from chloroform–acetone to give benzyltriphenylphosphonium chloride. When a 0.1 g sample of α-chlorobenzyltriphenylphosphonium chloride and 0.1 g of triphenylphosphine was heated to reflux in 70 ml of 2-butanone, a quantitative yield of benzyltriphenylphosphonium chloride was obtained.

Reaction of I with Tributyltin Hydride.—Tri-*n*-butyltin hydride was synthesized by the method of Kuivila and Beumel[32] and purified by distillation before use. A mixture of 1.0 g of I and 2.0 g of tri-*n*-butyltin hydride in 100 ml of ether was refluxed for 3 days. The reaction mixture was poured into a 10% sulfuric acid solution and the aqueous layer was extracted with ether. The ether was washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The crude residue was chromatographed on a 3 × 50 cm Florisil column. The column was eluted with 400 ml of benzene and the eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. Fraction 4 contained 1.6 g of a yellow oil. The oil was subjected to a molecular distillation at 120° (0.5 mm). The clear oil obtained was assigned as α-chloro-benzyltri-*n*-butyltin hydride, as evidenced by its nmr and mass spectral data: ir 3.45, 6.23, 6.71, 6.82, 7.25, 9.30, 11.40, 13.05, and 14.40 μ. The nmr spectrum ($CDCl_3$) has a broad multiplet between τ 8.70 and 9.10 (27 H), a singlet at τ 5.31 (with satellite peaks due to tin–hydrogen coupling, J = 23 cps), and a singlet at τ 2.80 (5 H). The mass spectrum (60 eV) has parent peaks at m/e 414 and 416, as well as peaks at m/e 379 and 381 corresponding to the loss of chlorine.

Reaction of I with Diphenylacetylene.—A mixture of 1.0 g of I and 1.17 g of diphenylacetylene in 70 ml of benzene was heated to reflux for 4 hr. The solvent was removed *in vacuo* and the colorless oil obtained was solidified upon standing. The crude

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[26] E. Gunther, *Chem. Ber.*, **21**, 517 (1888).

[27] R. Stolle, *J. Prakt. Chem.*, **73**, 278 (1906).

[28] E. Beckman, *Chem. Ber.*, **22**, 1589 (1889).

[29] K. Clarke, *J. Chem. Soc.*, 4251 (1954).

[30] A. J. Hill and M. V. Cos, *J. Amer. Chem. Soc.*, **48**, 3214 (1926).

[31] E. J. Corey and M. Chaykovky, *ibid.*, **87**, 1353 (1965).

[32] H. G. Kuivila and O. F. Beumel, *ibid.*, **83**, 1246 (1961).

solid was placed on a porous plate to remove the residual oils. The colorless solid obtained rapidly decomposed upon standing to a dark oil. The structure of this material was concluded to be *sym*-triphenylcyclopropenyl chloride from the following data. Crystallization of the solid from ethanol-water gave 1,2,3-triphenylcyclopropenyl ethyl ether as white prisms: mp 121–122°; ir (KBr) 5.50 μ; uv (95% ethanol) 317 (ϵ 21,800), 302 (ϵ 22,100) 228 (ϵ 26,500), and 223 mμ (ϵ 27,600). The nmr spectrum ($CDCl_3$) has a triplet at τ 8.77 (3 H), a quartet at τ 6.32 (2 H), and a multiplet at τ 2.60–2.25 ppm (15 H).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.29; H, 6.54.

A 0.5-g sample of 1,2,3-triphenylcyclopropenyl ethyl ether in 50 ml of ether was saturated with hydrogen bromide gas at 0° and was allowed to stand overnight at room temperature. The resulting solid that precipitated was crystallized from acetonitrile to give 0.33 g of triphenylcyclopropenyl bromide. The bromide was identified by comparison of infrared and mixture melting point with those of an authentic sample.[23] The ir spectrum of the bromide was almost identical with that of the original solid.

Reaction of I with Phenylacetylene.—A mixture of 1.0 g of I and 0.7 g of phenylacetylene in 70 ml of benzene was refluxed for 4 hr. The solvent was removed under reduced pressure to give a yellow oil which solidified upon standing. The oily solid was placed on a porous plate to give 0.9 g of a yellow solid. If the crude material is not purified immediately, violent decomposition occurs and a dark oil is produced. The yellow solid was crystallized from cold pentane to give 1-chloro-1,2-diphenylcyclopropene: mp 82–85°; ir 5.50 μ; uv (acetonitrile) λ_{max} 316 (ϵ 23,400), 301 (ϵ 29,600), and 288 mμ (ϵ 23,400). The nmr spectrum ($CDCl_3$) has a singlet at τ 5.05 (1 H) and a multiplet between τ 2.27 and 2.61 (10 H).

The structure of this material was further confirmed by briefly heating the solid in an aqueous ethanol solution. Removal of the solvent and crystallization of the white solid from benzene–hexane gave 0.15 g of bis-Δ'-1,2-diphenylcyclopropenyl ether, mp 164–166° (lit.[24] 163–165). The spectroscopic data obtained were in complete agreement with that reported by Breslow.[33]

Registry No.—I, 4460-46-2; V, 20420-97-7; VII, 20420-98-8; IX, 13668-03-6; 1-Chloro-1,2-diphenylcyclopropene, 20421-00-5.

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Olefin–Tetracyanoethylene Oxide Adducts and Some of Their Derivatives[1a]

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The reaction of tetracyanoethylene oxide with methyl erucate (methyl *cis*-13-docosenoate) and methyl brassidate (methyl *trans*-13-docosenoate) gave 2,2,5,5-tetracyano-3-(11-carbomethoxyundecyl)-4-octyltetrahydrofurans (2 and 3) in good yields. In methanol containing 5% hydrogen chloride, both 2 and 3 undergo partial and selective methanolysis to give 2,5-dicyano-2,5-dicarbomethoxytetrahydrofuran derivatives (4 and 5). The newly formed carbomethoxy groups are *trans* to their adjacent alkyl groups. Both 2 and 3 also are partially and selectively hydrolyzed on the surface of silica gel to give 2,5-dicyano-2,5-dicarbamoyltetrahydrofuran derivatives (10 and 11) in good yields. The newly formed carbamoyl groups have a *cis* relationship to each other.

Adducts of tetracyanoethylene oxide (TCNEO, **1**) *via* the unusual *cis* cycloaddition to olefins, acetylenes, and aromatics[2–4] are products having potential for further modifications to provide compounds of diverse functionality. We have prepared TCNEO adducts **2** and **3** of methyl erucate and methyl brassidate, the respective *cis* and *trans* isomers of methyl 13-docosenoate. Homogeneity of each adduct was determined by tlc on silica gel, on which the two can be readily resolved. The adducts were isomeric 2,2,5,5-tetracyano-3-(11-carbomethoxyundecyl)-4-octyltetrahydrofurans, as judged by ir, nmr, and elemental analyses.

Esters.—In contrast with the complete methanolysis of TCNEO adducts obtained by somewhat different conditions,[2] we found that both adducts may undergo partial and selective methanolysis. Reaction at room temperature with methanol containing 5% hydrogen chloride converts **2** and **3** to **4** and **5**, respectively, in 90% yield. Their ir and nmr spectra are consistent for dicyanodicarbomethoxytetrahydrofuran derivatives.

The methanolysis products of the two TCNEO adducts could have their respective ring substituents in several different geometric configurations. However, most of these can be excluded as likely possibilities. Since the cycloaddition of TCNEO to olefins is *cis*,[2,3] we may reasonably assume that the ring alkyl substituents have a *cis* relationship in compounds **2** and **4** and a *trans* relationship in compounds **3** and **5**. Chemical shift values for the ring protons, when compared with literature values,[2] are consistent with this interpretation. Nmr analyses of both methanolysis products **4** and **5** show that the six protons associated with the carbomethoxy groups on the rings occur as a sharp singlet[5] (τ 6.09 and 6.08, respectively). Thus, in both **4** and **5**, the two carbomethoxy groups on the ring appear to be in magnetically equivalent environments. The two ring protons in **4** and **5** are also magnetically equivalent (multiplets at τ 7.20 and 7.37, respectively). These observations imply that, in compounds **4** and **5**, one carbomethoxy is attached at position 2 and the other at position 5. If *gem* functions were present, the ring protons could be expected to have greatly different chemical shift values due to the marked difference in diamagnetic anisotropy of the cyano and carbomethoxy groups. Also, each carbomethoxy group should have identical geometric relationships with its adjacent ring alkyl substituent. Apparently the methanolysis reaction has considerable stereoselectivity.

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[3] W. J. Linn, *ibid.*, **87**, 3665 (1965).

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[5] The band width at half peak height is approximately 1 Hz.