seem possible, in the triphenyllead azide none may exist. The decomposition temperatures of both compounds were about the same ($(C_6H_5)_3CN_3$, 180–190°; $(C_6H_5)_3PbN_3$, 190–200°) despite the fact that both reactions proceeded by different mechanisms and to different products.

Acknowledgments.—The elemental analyses were carried out by A. Bernhardt, Mülheim (Ruhr), Germany. Dr. Walter Hübel, of the European Research Laboratories, Brussels, Belgium, was very helpful in attempts to determine the molecular weight of the m.p. 358° compound. Mr. John J. Mahoney has carried out a large part of the experimental work with considerable courage and skill. Dr. F. M. Rugg and Mr. J. J. Smith supported this work with encouragement and interest.

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Triphenylazido Compounds of Group IVA Elements[1]

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Received May 20, 1963

The five compounds $(C_6H_5)_3MN_3$, where M = C, Si, Ge, Sn, and Pb, have been prepared and characterized, and a comparative study of their properties has been carried out. The Si, Ge, and Sn compounds are isomorphous. The C and Si compounds react with triphenylphosphine to give 1:1 complexes, which differ markedly in their properties; the structures of these complexes are discussed. The Si and Ge compounds also form stable phosphineimines, $(C_6H_5)_3MN{=}P(C_6H_5)_3$.

The first organometallic azides, $(C_6H_5)_2BiN_3$, $(C_6H_5)_3Bi(N_3)_2$, and $C_6H_5Tl(N_3)_2$, were reported by Challenger and Richards in 1934.[2] The literature contains no other references to organometallic azides until late 1961, when this field of research suddenly became active. Methods developed recently have made it possible to prepare triphenylmetal azides of all group IVA elements. This paper is concerned with the syntheses and properties of these compounds, with special reference to the influence of the metal atom on the azide group. Azdiotriphenylmethane, $(C_6H_5)_3CN_3$ (I), has been known since 1909.[3] Azidotriphenylsilane, $(C_6H_5)_3SiN_3$ (II), was reported independently by us,[4] by Wiberg, *et al.*,[5] and by Sundermeyer.[6] Azidotriphenylgermane, $(C_6H_5)_3GeN_3$ (III), has not previously been reported, but Luijten and co-workers[7] have prepared azidotriphenylstannane, $(C_6H_5)_3SnN_3$ (IV), while Lieber, *et al.*, have synthesized azidotriphenylplumbane, $(C_6H_5)_3PbN_3$ (V).[8] While our work was in progress a parallel study of triphenylazido compounds of group IV elements, with emphasis on their thermal decomposition, was being carried out by Reichle.[9]

Synthetic Methods.—Two general methods for azide preparation were used. The first was originally used by Wiberg and Michaud[10] to prepare $Si(N_3)_4$, and later modified by Connolly and Urry[11] for the synthesis of $(CH_3)_3SiN_3$. The organometallic halide is refluxed with NaN_3 and $AlCl_3$ (forming $Al(N_3)_3$ *in situ*) in a dried organic solvent such as tetrahydrofuran, under a nitrogen atmosphere. Yields are usually greater than 50% and the method is quite general.

$$(C_6H_5)_3MX + NaN_3 \xrightarrow[\text{THF}]{AlCl_3} (C_6H_5)_3MN_3 + NaX\ (X = Cl, Br) \quad (1)$$

Baldwin and Washburn[12] modified this method somewhat by eliminating $AlCl_3$ and using electron-rich organic solvents, such as acetonitrile, pyridine, or benzene. Lithium azide in pyridine has also been used.[5] We have found that this modified method works well for more reactive silyl halides [*e.g.*, $(CH_3)_3SiCl$, $(C_6H_5)_2SiCl_2$] in any of the proper solvents, and also for $(C_6H_5)_3MX$, provided pyridine is used as solvent. There is little reaction between $(C_6H_5)_3MX$ and NaN_3 in benzene.

The second general method was that employed by Luijten.[7] This reaction is more convenient than the first, but also more limited in scope. Sodium azide, dissolved in water, is shaken with an ethereal solution of the organometallic halide. Hydrolysis provides hydrazoic acid, the actual azidizing agent, which passes into the ether layer and reacts with the organometallic hydroxide.

$$(C_6H_5)_3MOH + HN_3 \xrightarrow{\text{ether}} (C_6H_5)_3MN_3 + HOH \quad (2)$$

$$(C_6H_5)_3MX + 2H_2O \longrightarrow (C_6H_5)_3MOH + H_3O^+ + X^- \quad (2a)$$

$$N_3^- + H_3O^+ \longrightarrow HN_3 + H_2O \quad (2b)$$

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[1] This research was supported by the Air Force Office of Scientific Research of the Air Research and Development Command, under Grant No. AF-AFOSR-62-244.

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Rapid reactions and high yields of azide are obtained when ethereal solutions of HN_3 and of organometallic hydroxides are mixed. However, only III, IV, and V may be prepared by method 2; I and II do not form even in trace quantities.[13] The $(C_6H_5)_3MOH$ compounds that react with HN_3 are the ones shown by previous studies to be the most basic hydroxides of the series.[14]

Physical Properties.—All five azides are white crystalline solids, indefinitely stable at room temperature. They are insoluble in water but are generally soluble in organic solvents, particularly those of high polarity. Hexane serves as an excellent recrystallizing solvent. The melting point rises and the solubility in organic liquids falls monotonically with increasing atomic weight of the central atom.

II is thermally the most stable of the group, being only partly decomposed after 60 hr. of heating at 220°. V is least stable, undergoing rapid decomposition above 160°.[8b] As suggested previously,[4] dative π-bonding from nitrogen to silicon may stabilize II toward thermal decomposition, and, to a decreasing extent, stabilize III, IV, and V as well. None of the compounds shows any tendency to detonate when struck. All are stable in ordinary light but decompose when subjected to strong ultraviolet irradiation.

Compounds II, III, and IV crystallize as transparent rhombohedral plates, while V forms monoclinic needles. X-Ray powder diffraction patterns show that II, III, and IV are isomorphous, while the reported X-ray pattern of V indicates a different structure.[8b]

Infrared Spectra.—Each compound was studied over the region from 625 to 4000 cm.$^{-1}$, both as a Nujol mull and in CCl_4 solution. The spectra are quite similar (Table I) and may be correlated with the spectra of monosubstituted organobenzenes given by Katritzky and Lagowski[15] and of phenyltin compounds reported by Poller.[16]

The azide group gives rise to an asymmetric stretching band near 2100 cm.$^{-1}$ and a symmetric stretching band near 1300 cm.$^{-1}$. Going from I to III to IV, the former band decreases slightly in frequency; since this parallels a similar trend in the various phenyl ring vibrations of these compounds, the decrease is probably due to mass effects. However, the asymmetric azide frequency for II is some 50 cm.$^{-1}$ higher than predicted. Dative π-bonding between nitrogen and silicon would be expected to increase the contribution of form B to the azide resonance hybrid.

$$(C_6H_5)_3Si{-}\underset{..}{N}{=}\overset{+}{N}{=}\underset{..}{\overset{-}{N}}{:} \qquad (C_6H_5)_3Si{-}\underset{..}{\overset{-}{\ddot{N}}}{-}\overset{+}{N}{\equiv}N$$

A B

Increased contribution from B should lead to an enhancement of the asymmetric frequency. Similar effects are noticed in $(CH_3)_3SiN_3$[11] and H_3SiN_3,[17] both of which absorb at higher frequency than organic azides.[18]

The high frequency for the asymmetric azide band could also result from a wider M–N–N bond angle in II than in the other azides. Dative π-bonding from N to Si might be expected to increase the bond angle, but marked differences in stereochemistry for II, III, and IV are unlikely in view of the isomorphism found for these compounds. Trends in the symmetric stretching frequencies are not clear because this absorption is masked by other bands in III and IV. However, the symmetric band also appears to fall at higher than normal frequency in II and in other silyl azides.[11,17]

The asymmetric band for V appears at a lower frequency than predicted and is near that found for ionic azides (~2050 cm.$^{-1}$).[19] This result suggests a high degree of ionicity in the bonding between lead and azide in V.

Hydrolysis.—All five azides are stable to water and atmospheric moisture, undergoing hydrolysis only slowly. Reaction is much more rapid in mixed organic–aqueous media, such as acetone–water. The rate may be estimated qualitatively by adding small amounts of $Fe(NO_3)_3$ and observing the formation of the deep red complex ion $Fe(H_2O)_5N_3^{+2}$. Hydrolysis rates decrease in the order II > III > IV, V, I—the same order as is found for the corresponding halogen compounds. Hydrolysis of II is markedly catalyzed by small amounts of acid, but there is little corresponding effect on other compounds of the series.

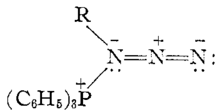
Reactions with Triphenylphosphine.—Most organic azides react with triphenylphosphine to give nitrogen and phosphineimines.

$$RN_3 + (C_6H_5)_3P \longrightarrow RN{=}P(C_6H_5)_3 + N_2 \qquad (3)$$

Compound I is one of the very few organic azides that gives a stable complex $(C_6H_5)_3CN_3 \cdot P(C_6H_5)_3$ (VI), which cannot be converted to the phosphineimine.[20] For this reason and also because VI shows no asymmetric azide band as a solid, Leffler assigns it structure C. Formation of phosphineimines from organic azides is also thought to proceed through the formation of unstable complexes, probably having structure D.

$$(C_6H_5)_3C{-}\ddot{N}{=}\ddot{N}{-}\ddot{N}{=}P(C_6H_5)_3$$

C



D

Compound II, like I, reacts with triphenylphosphine to form a complex $(C_6H_5)_3SiN_3 \cdot P(C_6H_5)_3$ (VII). However, the properties of VII differ greatly from those of VI. Whereas VI is thermally quite stable, ultimately decomposing to the same products as I alone, VII liberates nitrogen readily above 30° to give P,P,P-

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[13] On the other hand, it has been reported that I can be produced from $(C_6H_5)_3COH$ and concentrated HN_3 in chloroform. See W. H. Saunders and J. C. Ware, *J. Am. Chem. Soc.*, **80**, 3328 (1958).

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TABLE I

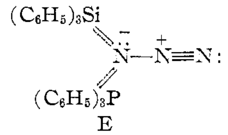
INFRARED FREQUENCY FOR AZIDES[a]

Assign.	K and L[15]	Poller[16]	$(C_6H_5)_3CN_3$	$(C_6H_5)_3SiN_3$	$(C_6H_5)_3GeN_3$	$(C_6H_5)_3SnN_3$	$(C_6H_5)_3PbN_3$
C–H str.			3110 s	3100 s	3092 s	3090 s	3075 s
C–H str.			3080 h	3070 h	3076 h	3080 h	*
C–H str.			3000 s	3000 s	3037 s	3045 s	3058 s
C–H str.			*	*	2955 w	2954 w	2960 w
?			2350 w	2300 w	2274 w	2300 w	2350 w–m
NNN as. str.			2110 v	2149 v	2100 v	2093 v	2046 v
Phenyl ring			1975 h	1983 h	1980 h	1970 h	1970 h
Phenyl ring			1965 w	1967 w	1961 w	1950 w	1950 w
Phenyl ring			*	1909 h	1901 h	1892 h	1888 h
Phenyl ring			1885 w	1898 w	1890 w	1875 w	1870 w
Phenyl ring			1815 w	1829 w	1827 w	1822 w	1815 w
Phenyl ring			1807 w	1782 w	1768 w	1765 w	1755 w
Phenyl ring			1670 w	1664 w	1655 w	1645 w	1635 w
C–C str.	1581–1579		1581 m	1587 m	1581 m–w	1573 m–w	1567 w
C–C str.	1511–1475	1477	1491 s	1485 s	1483 s	1479 s	1476 s
C–H str.	1447–1446	1429	1446 m–s	1429 v	1431 v	1429 v	1430 v
?		1330–1320	1325 w	1339 w	1336 w	1333 w	1325 w–m
?		1302–1290	*	*	1305 w	1291 w	1294 w
NNN sym. str.			1261 m	1308 m	*	*	1261 m
?		1258–1250	*	1259 w	1261 w	1254 w	*
β-C–H str.	1181–1170	1188–1278	1184 w	1184 w	1185 w	1184 w	*
β-C–H str.	1160–1150	1160–1145	1160 w	1162 w	1154 w	1157 w	*
C–H str.	*ca.* 1070	1076–1062	1080 w	1117 v	1093 v	1073 v	1059 v
C–H str.	*ca.* 1030	1025–1014	1030 s	1027 m–s	1024 m–s	1019 m–s	1016 m–s
Phenyl ring	1000	999–996	1008 s	1000 m	997 m	995 m	994 m
γ-C–H str.	*ca.* 900	925–901	900 m	917 w	917 w	908 w	*
?			*	862 w	850 w	850 w	859 w
?			*	810 w	805 w	800 w	800 m
C–H vib.			*	750 h	740 h	735 h	727 h
C–H vib.		*ca.* 730	720 s	735 s	732 s	729 s	721 s
C–H vib.		*ca.* 700	700 s	700 s	696 s	694 s	685 s
C–H vib.			*	695 h	675 h	*	680 h
NNN bending			666 w	660 w	660 w	658 w	655 w

[a] Abbreviations: v, very strong; s, strong; m, medium; w, weak; h, shoulder; *, masked or missing.

triphenyl-N-(triphenylsilyl)phosphineimine, $(C_6H_5)_3SiN{=}P(C_6H_5)_3$ (VIII). Also, unlike VI, VII shows an asymmetric azide absorption band, both as a solid and in chloroform solution, at a very low frequency of 2018 cm.$^{-1}$. It seems probable, therefore, that VII has the structure D. Examination of models suggests that this structure is possible for the silicon compound but unlikely for the more sterically hindered carbon compound VI.

The stability of VII, the first isolated complex with probable D structure, requires comment. Triphenylphosphine can act as an "amphoteric" Lewis complexing agent. In azide complexes, it can accept an electron pair into a σ-type bonding orbital and donate back electronic charge from its unshared electron pair into the π-system. (Opposite processes apparently occur when phosphines complex with transition metals.) In silyl azide–phosphine complexes of type D, extensive π-electron delocalization is possible from phosphorus through nitrogen to silicon.



E

This delocalization may stabilize the structure enough so that VII can be isolated, but not sufficiently to prevent loss of nitrogen above 30° to give the very stable phosphineimine. In the complex, a net weakening of the azide N–N bonds must take place, lowering the azide stretching frequencies.

Compound VIII has previously been reported by Wiberg, *et al.*[5,21] It may be prepared from VII, or directly from II and triphenylphosphine, either as solids or in solution, by heating. VIII is remarkably resistant toward hydrolysis and thermal decomposition.

Attempts were made to carry out similar reactions between triphenylphosphine and other members of this group of azides. III appears to react with triphenylphosphine upon heating to give the germanium analog of VIII; there was no evidence for an azide–triphenylphosphine complex analogous to VII. IV and V gave no reaction, even when fused with triphenylphosphine at 180°. None of the azides gave any reaction with excess triphenylarsine or triphenylstibine under mild conditions.

Experimental

Preliminary.—Mallinckrodt anhydrous ether was taken directly from unopened cans. Eastman Kodak tetrahydrofuran was distilled from lithium aluminum hydride and used immediately. Benzene was dried by fractional distillation. Triphenylchloromethane (Eastman Kodak) was recrystallized from dry benzene and triphenylchlorosilane was recrystallized from hexane

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[21] Wiberg also stated that II and triphenylphosphine react at room temperature without nitrogen evolution to form a compound which was thought to be an isomer of VIII.[5] This compound was probably the complex VII.

before use. Other organometallic halides, sodium azide, and triphenylphosphine were reagent grade samples used without further purification.

Azidotriphenylmethane.—A 1-l., three-necked flask was fitted with a stirrer and a reflux condenser. Triphenylchloromethane (6.0 g., 0.022 mole) and sodium azide (2.2 g., 0.034 mole) were refluxed in 250 ml. of dry benzene for 23 hr. The benzene solution was decanted and evaporated under vacuum. The solid residue was recrystallized three times from hexane to give 1.2 g. (19%) of I, m.p. 64° (lit.[11] 64–65°). *Anal.* Calcd. for $C_{19}H_{15}N_3$: C, 79.97; H, 5.30; N, 14.73. Found: C, 80.16; H, 5.47; N, 14.70.

Azidotriphenylsilane.—In the same apparatus as described above, 12.5 g. (0.094 mole) of anhydrous aluminum chloride and 25.3 g. (0.389 mole) of sodium azide were refluxed together in 500 ml. of dry tetrahydrofuran for 4 hr., after which time 41.8 g. (0.142 mole) of triphenylchlorosilane was added and the entire mixture was refluxed for 5 days. The tetrahydrofuran layer was decanted and evaporated under vacuum, leaving a white residue. This was recrystallized twice from hexane to give 33.8 g. (79%) of II, m.p. 81°. *Anal.* Calcd. for $C_{18}H_{15}N_3Si$: C, 71.72; H, 5.02; N, 13.94. Found: C, 71.50; H, 5.02; N, 13.89.

Azidotriphenylgermane.—A solution of 1.50 g. (3.9 mmoles) of triphenylbromogermane in 120 ml. of anhydrous ether was shaken for 10 min. in a 1-l. separatory funnel with a solution of 0.50 g. (7.7 mmoles) of sodium azide in 100 ml. of distilled water. Separation and evaporation of the ethereal layer gave a white residue, showing a strong azide band and weak OH band in the infrared. Careful recrystallization from hexane yielded 0.81 g. (59%) of III, m.p. 102–103°. *Anal.* Calcd. for $C_{18}H_{15}N_3Ge$: C, 62.50; H, 4.37. Found: C, 62.53; H, 4.45.

Azidotriphenylstannane.—A solution of 2.50 g. (6.5 mmoles) of triphenyltin chloride in 60 ml. of anhydrous ether and a solution of 0.50 g. (7.7 mmoles) of sodium azide in 100 ml. of distilled water were shaken together for 10 min. in a 1-l. separatory funnel. Removal and evaporation of the ethereal layer gave a solid white residue, which was recrystallized twice from hexane to give 2.17 g. (85%) of the desired product IV, m.p. 115° (lit.[7] 115–116°). *Anal.* Calcd. for $C_{18}H_{15}N_3Sn$: C, 55.15; H, 3.86; N, 10.72. Found: C, 55.02; H, 3.91; N, 10.59.

Azidotriphenylplumbane.—A mixture of 2.80 g. (5.9 mmoles) of triphenyllead chloride in 400 ml. of anhydrous ether with 0.50 g. (7.7 mmoles) of sodium azide in 25 ml. of distilled water were shaken in a 1-l. separatory funnel. Large amounts of a white solid, identified as a mixture of triphenyllead chloride and triphenyllead hydroxide, were formed at the liquid–liquid interface. The solid was removed by filtration, and the ethereal layer was evaporated. The solid residue was recrystallized from hexane, giving 0.30 g. (11%) of V, decomposing at *ca.* 185°.[8] *Anal.* Calcd. for $C_{18}H_{15}N_3Pb$: C, 44.99; H, 3.15; N, 8.74. Found: C, 44.39; H, 3.33; N, 8.26.

In another preparation, 1.86 g. (3.9 mmoles) of $(C_6H_5)_3PbOH$ was prepared in the manner of West, *et al.*,[14] and put in 150 ml. of anhydrous ether. HN_3 (7.5 ml., 0.855 *N*) was extracted with two 25-ml. volumes of ether. These were combined and added to the ethereal $(C_6H_5)_3PbOH$. After shaking, the ether was allowed to evaporate, and the residue was recrystallized from hexane. Compound V (1.51 g., 77%), identified by its infrared spectrum, was recovered.

Reaction of Triphenylmetal Hydroxides with HN_3.—Portions of triphenylmethanol, triphenylsilanol, triphenylbromogermane, triphenyltin hydroxide, and triphenyllead hydroxide, 0.01 g. each, were dissolved in 25-ml. volumes of ether. Each portion was shaken with about 3 ml. of 0.163 *N* aqueous HN_3. The crystals were recovered by evaporation and examined by infrared spectrophotometry. $(C_6H_5)_3COH$ and $(C_6H_5)_3SiOH$ showed no signs of azide formation, while there were strong azide bands for the other three. $(C_6H_5)_3GeBr$ showed an appreciable hydroxide band, while the tin and lead compounds had hardly any. In a similar experiment, $(C_6H_5)_3COH$ and $(C_6H_5)_3SiCl$ were treated with 0.855 *N* HN_3. Again, no azide was formed in either case.

Azidotriphenylsilane–Triphenylphosphine Complex.—A solution of 0.486 g. (1.6 mmoles) of II and 0.423 g. (1.6 mmoles) of triphenylphosphine in 100 ml. of anhydrous ether was allowed to stand in the dark at 0° for 4 days. Evaporation of the ethereal layer gave a white solid, which was repeatedly extracted with a cold ether–hexane mixture. Evaporation of the solvents gave 0.352 g. (39%) of VII. It had no melting point but readily converted to the phosphineimine above room temperature. *Anal.* Calcd. for $C_{36}H_{30}N_3SiP$: C, 76.70; H, 5.37. Found: C, 76.71; H, 5.44.

The complex has an infrared spectrum similar to the parent compounds, with the following exceptions; the asymmetric azide band appears at 2018 cm.$^{-1}$; there is a strong band at 1260 cm.$^{-1}$, probably due to both the symmetric stretching frequency and the P=N stretching band[22]; there are new bands at 1437 and 1097 cm.$^{-1}$, typical of phenyl–phosphorus absorptions; and there is a general intensification of the phenyl ring vibrations already present. The complex decomposes slowly at room temperature and rapidly at 60°. It is insoluble in petroleum ether, ethyl ether, carbon tetrachloride, benzene, and pyridine, but is slightly soluble in chloroform.

Attempts to make this complex in other solvents have uniformly given the phosphineimine. Infrared studies of mixtures of the azide and phosphine dissolved in carbon tetrachloride, benzene, and acetonitrile showed a slow, steady decline in the intensity of the azide peak, with no appreciable shift or new azide band appearing.

P,P,P-Triphenyl-N-(triphenylsilyl)phosphineimine.—A mixture of 0.1981 g. (0.6 mmole) of $(C_6H_5)_3SiN_3$ and 0.1724 g. (0.6 mmole) of triphenylphosphine were allowed to react in ether to form the complex, which was then put into about 50 ml. of benzene and refluxed for 0.5 hr. A whitish yellow residue remained; this was repeatedly washed with hexane–ether mixtures and dried under vacuum to give 0.1088 g. (31%) of VIII, m.p. 214° (lit.[5] 215–216°). This compound is insoluble in most common organic solvents, dissolving slightly in tetrahydrofuran. It is stable to hydrolysis, being split only slowly by strong acid. The infrared spectrum is very similar to that of the complex, the only major differences being the disappearance of the azide band and great intensification of bands at 1260 and 810 cm.$^{-1}$ due to P=N and P—N stretching modes. *Anal.* Calcd. for $C_{36}H_{30}NPSi$: C, 80.70; H, 5.64; N, 2.62. Found: C, 80.16; H, 5.64; N, 2.61.

Attempts to Make P,P,P-Triphenyl-N-(triphenylgermyl)-phosphineimine.—A 1:1 mixture of $(C_6H_5)_3GeN_3$ and triphenylphosphine in benzene was allowed to stand for 6 weeks, samples being removed daily for determination of infrared spectra. The azide asymmetric stretching band slowly disappeared. Evaporation of the benzene yielded small amounts of a yellowish solid, whose spectrum showed a strong band at 1274 cm.$^{-1}$ and was otherwise very similar to the silyl phosphineimine. Attempts to make the imine by fusion of the two solids at 180° gave a compound containing no nitrogen (apparently hexaphenyldigermoxane).

Infrared Spectra.—All spectra were run on a Perkin-Elmer Model 237 double beam recording spectrophotometer linear in wave number. Sodium chloride plates were used for solid mulls, while a 0.50-mm. sodium chloride cell was used for solution studies. Polystyrene peaks were used for calibration: the 2850 and 1603 cm.$^{-1}$ for the 400–1250 cm.$^{-1}$ range, and the 1603 and 906 peaks for the 2000–625 cm.$^{-1}$ range. All frequencies are accurate to ±5 cm.$^{-1}$.

Acknowledgments.—The authors are grateful to the American Oil Foundation of The American Oil Co. for a grant to purchase the infrared spectrophotometer used in these studies and to Miss R. Ma for assistance in determining the X-ray powder patterns. J. S. T. thanks the Monsanto Chemical Corp. for a Summer Research Fellowship.

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