α,α-Diphenyl-3-pyridinemethanol. An ether solution of *n*-butyllithium was prepared from 11.2 g. (1.62 g.-atoms) of lithium and 111 g. (0.81 mole) of *n*-butyl bromide in 900 ml. of dry ether at −10° under nitrogen. The reaction mixture was stirred 1.5 hr., cooled to −60°, and 128 g. (0.81 mole) of 3-bromopyridine dissolved in 150 ml. of dry ether was added over a 20-min. period at −60 to −40°. The stirred solution was again cooled to −60° and 109 g. (0.60 mole) of benzophenone dissolved in 250 ml. of dry ether was added during a 30-min. period. The mixture was stirred at −40° for 2 hr., the temperature was allowed to increase to 20° and the reaction mixture was decomposed with ammonium chloride solution. The ether layer was evaporated to give the crystalline product; m.p. 115–117° (lit.[8] m.p. 115–116°) after two recrystallizations from methanol; yield 99 g. (64%).

The hydrochloride obtained by Method E melted at 221–231° dec. The salt was recrystallized twice from methanol; m.p. 227–232° dec. (lit.[12] m.p. 150–155° chars).

Anal. Calcd. for $C_{18}H_{16}ClNO$: C, 72.58; H, 5.42; Cl, 11.92. Found: C, 72.70; H, 5.54; Cl, 11.79.

α,α-Diphenyl-3-piperidinemethanol hydrochloride. The hydrogenation of 25 g. (0.08 mole) of α,α-diphenyl-3-pyridinemethanol hydrochloride was carried out in 200 ml. of methanol in the presence of 0.6 g. of platinum oxide, as described in Method F. Yield 20 g. (78%); m.p. 184–186°. Recrystallization of the product from methanol-ether resulted in two crops which apparently are polymorphic crystalline forms: (a) 11 g., m.p. 206–208° after recrystallization from methanol-ether; (b) 8 g., m.p. 184–186° after recrystallization from methanol-ether.

Anal. Calcd. for $C_{18}H_{22}ClNO$: C, 71.15; H, 7.30. (a) Found: C, 71.35; H, 7.57. (b) Found: C, 71.11; H, 7.52.

A solution of 2.5 g. of (a) in methanol was made alkaline with 10% sodium hydroxide. The precipitated product was recrystallized from methanol-water; m.p. 158–160°.

Anal. Calcd. for $C_{18}H_{21}NO$: C, 80.84; H, 7.92. Found: C, 80.78; H, 7.97.

4,4-Diphenyl-3-oxa-1-azabicyclo[3.1.1]nonane. A mixture of 2 g. of α,α-diphenyl-3-piperidinemethanol, 2.3 ml. of formalin and 40 ml. of methanol was refluxed 20 hr. Water was added until the reaction mixture became cloudy. The mixture was cooled and filtered. Yield 1.2 g. (54%); m.p., 118–121° after recrystallization from 50% methanol.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.69; H, 7.58. Found: C, 81.48; H, 7.72.

The acid maleate salt was prepared by dissolving 1 g. of the base in ethanol which contained 0.5 g. of maleic acid. The solution was diluted with ether, cooled, and filtered. The salt was recrystallized from ethanol-ether; m.p. 202–203°.

Anal. Calcd. for $C_{23}H_{25}NO_5$: C, 69.86; H, 6.38. Found: C, 69.79; H, 6.43.

α,α-Di(p-anisyl)-3-pyridinemethanol. To a solution of 3-pyridyllithium, prepared from 6.5 g. (0.94 g.-atom) of lithium, 64.5 g. (0.47 mole) of *n*-butyl bromide, 71 g. (0.45 mole) of 3-bromopyridine, and 700 ml. of dry ether was added a suspension of 83 g. (0.34 mole) of di(*p*-anisyl) ketone in 200 ml. of dry toluene as described above for the preparation of α,α-diphenyl-3-pyridinemethanol. The mixture was stirred 2 hr. at −40° and the temperature was allowed to increase to 25°. After the reaction mixture had been decomposed with ammonium chloride solution, it was filtered to recover 30 g. of di(*p*-anisyl) ketone. The ether-toluene filtrate was concentrated to remove solvent and the residue crystallized from methanol. Yield 30 g. (27%); m.p. 74–80° after two recrystallizations from methanol.

Anal. Calcd. for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96. Found: C, 74.77; H, 6.10.

The hydrochloride salt was prepared by Method E. It was recrystallized from isopropyl alcohol–petroleum ether (b.p. 75–90°); m.p. 176–178°.

Anal. Calcd. for $C_{20}H_{20}ClNO_3$: C, 67.13; H, 5.63. Found: C, 67.29; H, 5.79.

α,α-Di(p-anisyl)-3-piperidinemethanol. A mixture of 15 g. (0.047 mole) of α,α-di(*p*-anisyl)-3-pyridinemethanol, 0.4 g. of platinum oxide, and 250 ml. of 80% acetic acid was hydrogenated as described by Method F. The platinum oxide was removed by filtration and the filtrate was made basic with ammonium hydroxide. The precipitated product was recrystallized from methanol. Yield 6 g. (39%); m.p. 169–171°.

Anal. Calcd. for $C_{20}H_{23}NO_3$: C, 73.38; H, 7.70. Found: C, 73.46; H, 7.51.

The hydrochloride salt was obtained by Method E and recrystallized from methanol-ether; m.p. 166–168°.

Anal. Calcd. for $C_{20}H_{26}ClNO_3$: C, 66.03; H, 7.21. Found: C, 66.10; H, 7.09.

Acknowledgment. Evaluation of central depressant activity was carried out in these laboratories under the direction of Dr. H. W. Werner. We are grateful for the special assistance of Drs. Geraldine L. Krueger, Edwin R. Andrews, Mr. Jay K. Seyler, and Mr. Martin Gordon in various phases of this work.

CINCINNATI, OHIO

(12) H. E. French and K. Sears, *J. Am. Chem. Soc.*, 73, 469 (1951).

[CONTRIBUTION FROM THE SOAP RESEARCH AND DEVELOPMENT DEPARTMENT, GROCERY PRODUCTS DIVISION, ARMOUR AND CO.]

Synthesis and Antibacterial Activity of Some New Aminophosphinic Acids[1]

W. M. LINFIELD, ERIC JUNGERMANN, AND A. T. GUTTMANN

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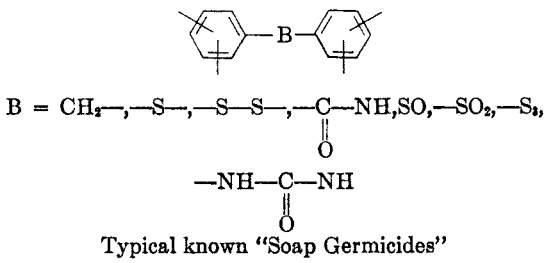
A series of aminophosphinic acids were prepared by the reaction of aryl or long-chain amines with aldehydes and hypophosphorous acid. The antibacterial properties and surface activity of these compounds were studied.

During the past quarter of a century numerous types of antibacterial agents have been synthesized. Among these the surface active quaternary ammonium compounds, various phenolic compounds, and especially bisphenols as well as substituted carbanilides and salicylanilides have received widespread application in the soap and detergent field. The structures of the "soap-germicides"

(1) Presented at the Frederick F. Blicke Symposium of the Division of Medicinal Chemistry at the 138th National Meeting of the American Chemical Society, New York, N. Y., September 1960.

have one common feature: Two substituted benzene rings are linked by a "bridge" which can be a simple divalent atom, or can consist of a larger group:



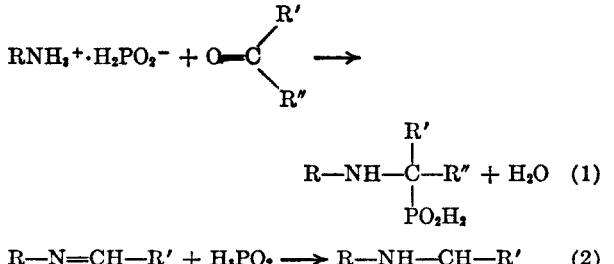
Typical known "Soap Germicides"

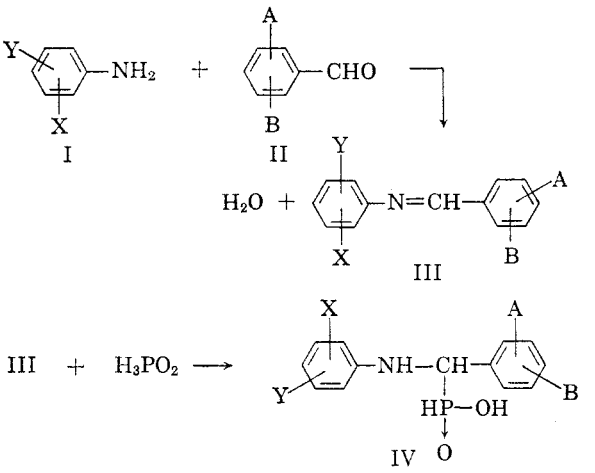
The most important ones in this group are Hexachlorophene(2,2′ - dihydroxy - 3,5,6,3′,5′,6′-hexachlorodiphenylmethane),[2] 3,4,4′-trichlorocarbanilide[3] and halogenated salicylanilides, where B is —CH_2—, NHCONH, or CONH.

The present study was undertaken to investigate the effect of the amphoteric iminomethylene phosphinic acid bridge, —NH—CH(—PO_2H_2)— on the physical and physiological properties of these molecules.

Very little has been reported in the literature on the synthesis of aminophosphinic acids. Raudnitz[4] prepared *p*-*N*,*N*-dimethylaminophenyl phosphinic acid by the reaction of dimethylaniline with phosphorus trichloride followed by hydrolysis. Other aromatic aminophosphinic derivatives were synthesized by Klotz *et al.* by treating *p*-bromophenylphosphinic acid with ammonia in the presence of cuprous oxide.[5]

A method for the synthesis of simple low molecular weight aminophosphinic acids containing the iminomethylene phosphinic acid group was first reported by Schmidt.[6] He obtained these compounds by two routes: (1) condensation of the hypophosphite salt of a primary amine with an aldehyde or ketone, (2) reaction of a Schiff's base with hypophosphorous acid. It was decided to adopt Schmidt's second procedure. The Schiff's base was first prepared in high yield by refluxing equimolar amounts of a substituted aromatic amine and an aromatic aldehyde in an inert solvent with azeotropic removal of the water of reaction, followed by isolation and recrystallization. The resultant Schiff's base was then refluxed in ethanol with 95% hypophosphorous acid and the desired aminophosphinic acid obtained in a low yield (30–50%). The germicidal





IV	A	B	X	Y	% Yield[a]
1	H	H	H	H	36
2	*p*-Cl	H	*p*-Cl	H	30
3	*o*-Cl	H	*p*-Cl	H	31
4	*o*-Cl	H	*o*-Cl	*p*-Cl	30
5	*p*-Cl	H	*m*-Cl	*p*-Cl	30
6	*p*-Cl	*m*-Cl	*m*-Cl	*p*-Cl	35
7	*p*-OH	H	*m*-Cl	*p*-Cl	52
8	*o*-OH	H	*m*-Cl	*p*-Cl	42

[a] Based on the reaction of the Schiff's base with hypophosphorous acid.

activity of these derivatives was determined against a gram positive (*S. aureus*) and a gram negative organism (*E. coli*). The results are summarized in Table I.

TABLE I

ANTIBACTERIAL PROPERTIES OF AROMATIC AMINOPHOSPHINIC ACIDS

	RNH—CHR′—PO_2H_2		Minimum Concentration (p.p.m.) Required to Inhibit Growth	
	R	R′	*S. aureus*	*E. coli*
1	C_6H_5—	C_6H_5—	500	1000
2	*p*-ClC_6H_4—	*p*-ClC_6H_4—	20	500
3	*p*-ClC_6H_4—	*o*-ClC_6H_4—	31	1000
4	2,4-$Cl_2C_6H_3$—	*o*-ClC_6H_4—	20	1000
5	3,4,-$Cl_2C_6H_3$—	*p*-ClC_6H_4—	20	500
6	3,4-$Cl_2C_6H_3$—	3,4-$Cl_2C_6H_3$—	7.8	250
7	3,4-$Cl_2C_6H_3$—	*p*-HOC_6H_4—	7.8	1000
8	3,4-$Cl_2C_6H_3$—	*o*-HOC_6H_4—	62	1000

(2) W. S. Gump and G. R. Walter, *J. Soc. Cosmetic Chemists*, 11, 307 (1960).
(3) D. J. Beaver, D. P. Roman, and P. J. Stoffel, *J. Am. Chem. Soc.*, 79, 1236 (1957).
(4) H. Raudnitz, *Ber.*, 60, 743 (1927).
(5) I. M. Klotz and R. T. Morrison, *J. Am. Chem. Soc.*, 69, 473 (1947).
(6) H. Schmidt, *Ber.*, 81, 477 (1948).

A second series of aminophosphinic acids was synthesized in which one of the aromatic rings was replaced by a fatty alkyl group of twelve to eighteen carbon atoms. This was done by utilizing a fatty amine in the general synthetic procedure. The intermediate Schiff's bases were not isolated as in the case of the diaryl derivatives, but were reacted *in situ* with the hypophosphorous acid (Method A). Yields in the order of 70–90% were obtained which is very much higher than in the completely aromatic series. It was found that when the hypophosphite salt of the amine was formed first, followed by reaction with the aldehyde (Method B), lower yields and less pure products were obtained than by the first procedure (Method A).

Both the aliphatic-aromatic and the aromatic aminophosphinic acids are weak acids titratable potentiometrically in nonaqueous solvents. The free acids were water-insoluble, and they presumably exist as zwitterions $R-\overset{+}{N}H_2-\underset{\underset{PO_2H^-}{|}}{CH}-R'$. Their alkali salts are readily soluble in water. The long-chain derivatives synthesized and their bacteriological activity are summarized in Table II.

TABLE II

ANTIBACTERIAL PROPERTIES OF THE LONG-CHAIN ALKYL-ARYL AMINOPHOSPHINIC ACIDS

RNH—CHR′—PO_2H_2			Minimum Concentration Required to Inhibit Growth	
R	R′	Yield, %	*S. aureus*	*E. coli*
n-$C_{12}H_{25}$	C_6H_5	96	1000	1000
n-$C_{18}H_{37}$	C_6H_5	82	250	500
n-$C_{12}H_{25}$	*p*-ClC_6H_4	69	1000	1000
n-$C_{12}H_{25}$	3,4-$Cl_2C_6H_3$	70	1000	1000
n-$C_{18}H_{35}$ (Oleyl)	3,4-$Cl_2C_6H_3$	26	500	500

The antibacterial properties of the long-chain derivatives reported in Table II are very much lower than those of the purely aromatic compounds in Table I. The relationship between structure and activity in the aromatic series (Table I) is quite complex. Chlorination again enhances the activity of the compounds. However, the position of the halogen in the ring is an important factor. While the scope of this study was much smaller than that of Beaver *et al.* on carbanilides[3] or that of Gump and Walter on the bisphenols[2] it appears that the general findings of these two groups of researchers with respect to the spatial relationships of the constituents are borne out in this study as well. As in the case of the carbanilides it was found that chlorine substitution in the *meta* or *para* positions enhanced the activity more than that in the *ortho* position. This is shown in a comparison between compounds 2, 3, and 4.

As a rule the activity increases with increasing chlorine substitution and thus compound 6 is more effective than 5 or 4. This finding again parallels those in the carbanilide or bisphenol series. Thus we found the 3,3′,4,4′-tetrachloro derivative to be the most active of the series.

It was interesting to note the effect of substitution by a hydroxyl-group into the benzene ring. This brought about a drastic reduction of the effectiveness against *E. coli* as compared with an analogous chlorine derivative. The effectiveness against *S. aureus* on the other hand was found to be fairly good. Here again the position in the ring played an important part, only this time substitution in the *ortho* position results in a higher activity than that in the *para* position. Thus we find an analogy between the aminophosphinic acids and the bisphenols.

Surface active properties. The surface active properties of the long-chain aminophosphinic acids (Table II) were checked. Wetting speeds were determined according to the method of Draves and Clarkson[7] and the surface tension measurements were carried out with a Du Nouy tensiometer. The C_{12} members of the series produced a marked reduction of the surface tension of water. Correlation between wetting data and surface tension reduction could not be achieved. It was noted that the surface tension picture for the C_{12} compounds remains practically unchanged regardless of the nature of the R′ group. Concerning the wetting characteristics optimum wetting was obtained when the molecular structure was properly balanced, *i.e.* when the hydrophilic group PO_2H_2 was located as centrally as possible and the hydrophobic R and R′ groups were of such sizes that the sum of their effective chain lengths amounted to C_{16}. The effective chain length for the benzene ring as far as surface activity is concerned amounts to about C_4. The *n*-dodecyl derivative where R′ was a phenyl group is the only one of this series of compounds to meet the above structural requirement. Thus there is an analogy between this series of compounds and the series of alkyl aroylsulfopropionates reported by Hedrick, Linfield, and Eaton.[8] These results are summarized in Table III.

EXPERIMENTAL[9]

Hypophosphorous acid. Concentrated hypophosphorous acid (95%) was obtained by evaporation of the commercial 50% aqueous solution at 40–50° and 3–5 mm. The concentrated hypophosphorous acid will slowly evolve phosphine on standing. *To minimize the explosion hazard the acid was stored*

(7) C. Z. Draves and R. G. Clarkson, *Am. Dyestuff Reptr.*, **20**, 201 (1931).

(8) G. W. Hedrick, W. M. Linfield, and J. T. Eaton, *Ind. Eng. Chem.*, **44**, 314 (1952).

(9) Microanalysis by Alfred Bernhardt, Mikroanalytisches Laboratorium im Max Planck Institut fuer Kohlenforschung, Muelheim, Germany. All melting points are uncorrected.

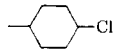
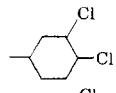
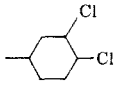
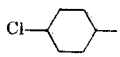
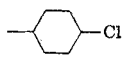
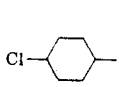
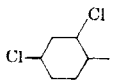
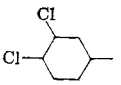
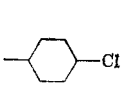
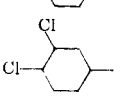
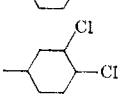
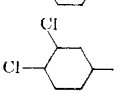
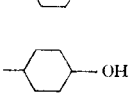
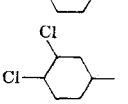
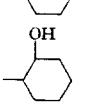
TABLE III

SURFACE ACTIVE PROPERTIES OF SODIUM SALTS OF AMINOPHOSPHINIC ACIDS

Compound R—NH—CH(R′)—PO_2H_2		Wetting Speed in 0.1% Soln. at 25° in sec.[7]	Surface Tension in Dynes/cm. at 25°				
			0.1%	0.05%	0.01%	0.005%	0.001%
R	R′						
n-$C_{12}H_{25}$	H	160	36.9	38.6	36.5	35.4	42.0
n-$C_{18}H_{37}$	H	300	47.1	52.9	56.8	61.8	60.0
n-$C_{12}H_{25}$	C_6H_5—	9	34.9	33.9	34.2	58.9	47.6
n-$C_{18}H_{37}$	C_6H_5—	300	33.7	34.8	35.8	55.5	60.7
n-$C_{12}H_{25}$	p-ClC_6H_4—	300	30.8	32.9	32.9	33.5	45.5
n-$C_{12}H_{25}$	3,4-$Cl_2C_6H_3$—	300	32.8	32.7	33.5	33.5	39.5
n-$C_{18}H_{35}$	3,4-$Cl_2C_6H_3$—	300	30.2	32.1	35.2	38.4	67.6

TABLE IV

ANALYTICAL DATA OF AMINOPHOSPHINIC ACIDS

Chemical Structure of R—NH—CHR′—PO_2H_2			Equiv. Weight		% C		% H		% P		% Cl	
R	R′	M.P.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_{12}H_{25}$		198	339.4	339	67.22	66.37	10.11	9.89	9.13	8.88		
$C_{18}H_{37}$		186–188	423.6	417	70.88	71.16	10.94	10.77	7.31	7.40		
$C_{12}H_{25}$		205–206	373.9	368	61.03	61.60	8.90	8.88	8.29	7.88		
$C_{12}H_{25}$		197–199	408.4	415	55.88		7.90		7.59	7.55		
$C_{18}H_{35}$[a]		194–195	490.5	486	61.22	62.05	8.63	8.57	6.32	5.73		
		149–150[b]	247.2	286	63.15	63.43	5.71	5.66	12.53	11.39[b]		
		82–87[c] g.	316.1	328	49.39	49.27	3.51	3.97	9.80	8.84	22.43	22.20
		87–90 g.	316.1	331	49.39	49.18	3.51	3.81	9.80	9.70	22.43	22.90
		84–87 g.	350.6	366	44.53	44.05	3.16	3.13	8.84	8.55	30.34	29.40
		76–80 g.	350.6	372	44.53	44.22	3.16	3.12	8.84	8.43	30.34	30.64
		75–80 g.	385.0	388	40.55	39.76	2.62	2.48	8.05	7.85	36.84	36.44
		147–149	332.1	329	47.01	47.07	3.64	3.74	9.33	8.63	21.35	20.89
		105–108	332.1	344	47.01	47.58	3.64	3.86	9.33	8.79	21.35	20.67

[a] From commercially available oleylamine (Armeen OD). [b] Reported 150°.[6] In view of close m.p. agreement and reasonable C and H analyses, the low P determination was not rechecked. [c] These compounds, marked with g., go through a glassy or softening stage which makes it difficult to determine an exact m.p.

under nitrogen, and the container was purged with nitrogen every 2 days.

Diaryl aminophosphinic acids. The preparation of (3,4-*dichloro-phenylamino*)-4'-*hydroxybenzylphosphinic* is given as typical example for the synthesis of this class of compounds. Physical properties and analyses of all aminophosphinic acids prepared are shown in Table IV.

The Schiff's base from 3,4-dichloroaniline and *p*-hydroxybenzaldehyde was prepared by boiling equimolar amounts of the reactants in benzene, with azeotropic removal of water, followed by filtration and recrystallization from benzene. To 80 g. (0.3 mole) of this Schiff's base in 200 ml. ethanol heated to 65° was added 21 g. 95% hypophosphorous acid (0.3 mole). The reaction mixture was refluxed for 2.5 hr. The solution was then cooled, 48 g. of 50% sodium hydroxide (0.6 mole) was added dropwise, and the reaction mixture evaporated to dryness on the water bath under vacuum. The residue was agitated with 300 ml. of warm water, cooled, and extracted with ether until the ether layer appeared completely colorless. From eight to nine extractions were required. The aqueous portion was freed from residual ether by heating and bubbling nitrogen through it. After cooling, the aqueous solution was added dropwise, with rapid stirring, to 300 ml. of 3*N* hydrochloric acid. The precipitated phosphinic acid was filtered and redissolved in aqueous sodium hydroxide, the solution again extracted with ether, and the phosphinic acid reprecipitated by adding to aqueous hydrochloric acid as shown above. After filtration, washing with water, and drying *in vacuo* over phosphorus pentoxide 52 g. (52% yield) of a light yellow powder was obtained, m.p. 147–149°.

Long-chain alkylaryl aminophosphinic acids. The preparation of *N-dodecylaminobenzylphosphinic acid* is a typical example, and is given as below: *Method A.* A mixture of 55.5 g. (0.3 mole) dodecylamine and 32 g. benzaldehyde (0.3 mole) in 150 ml. benzene was heated under reflux until the calculated amount of water had separated in the Stark and Dean trap. The solution of the Schiff's base was then cooled to 50°, and 21 g. of 95% hypophosphorous acid (0.3 mole) was added dropwise. The temperature rose to 63° and the color became slightly darker. After 2.5 hr. heating under reflux, the solution became turbid. It was cooled, diluted with three volumes of ether, and allowed to stand overnight at −10°. The precipitate was filtered, redissolved in hot benzene, filtered to remove turbidity, and reprecipitated by dilution with ether and cooling to −10°. After filtration washing with ether, and drying over phosphorus pentoxide, 98 g. (96% yield) of a white crystalline powder was obtained, m.p. (recrystallized from ethanol) 198°.

Method B. Using the same amounts and proportions of reactants as in Method A, the hypophosphorous acid was added to the benzene solution of dodecylamine, followed by addition of benzaldehyde. The mixture was heated under reflux until the calculated amount of water had separated. After cooling, the viscous and turbid reaction mixture was diluted with 3 volumes of ether and worked up as described in Method A. Only 76 g. (75% yield) of phosphinic acid was obtained, m.p. (from ethanol) 197–198°.

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[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

The Dimerization of Vinyl- and Allylsilanes with Trialkylaluminums[1]

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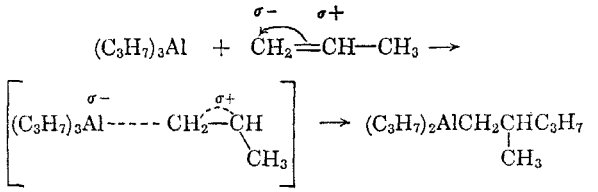
Vinyl- and allyltriorganosilanes dimerize when heated at 200° with small amounts of triisobutylaluminum. The structures of the dimers from allyltriphenylsilane and vinyltriphenylsilane were established by conversion to saturated products which were compared with material prepared by alternate syntheses.

The dimerization of monoalkyl substituted ethylenes with trialkylaluminums was discovered by Ziegler and associates.[2] A variety of α-olefins can be dimerized to compounds of predictable structure—*i.e.*, propylene to 2-methylpent-1-ene, but-1-ene to 2-ethylhex-1-ene, etc. The probable mechanism for this dimerization[3] involves the approach of the π electrons of the olefinic double bond to the vacant *p* orbital of aluminum of the trialkylaluminum. A concerted shift of one of the alkyl groups attached to aluminum with its pair of electrons to satisfy the developing positive center on carbon and relief of the partial negative center about aluminum results in the formation of a new branched chain substituent on aluminum. The reaction can be represented with tri-*n*-propylaluminum and propylene as below:



The displacement of the so formed branched 2-methylpentyl group from aluminum takes place by a similar type approach of propylene toward aluminum but, rather than alkyl migration, transfer of a hydride ion from the tertiary β-carbon center is favored and tri-*n*-propylaluminum and 2-methylpent-1-ene are generated.

(1) Presented at the Frederick F. Blicke Symposium of the Division of Medicinal Chemistry at the 138th National Meeting of the American Chemical Society, New York N. Y., September 1960.

(2) K. Ziegler, *Angew. Chem.*, 64, 323 (1952).

(3) R. Robinson, *Chem. Age (London)*, 74, 997 (1956).