small amount of n-octadecyl bromide, 2.74 g. (67%) of unreacted triphenyl-2-phenylethylgermane and 0.63 g. of product boiling over the range 180–185° at 0.005 mm. Recrystallization of this latter fraction from methanol gave 0.5 g. (28.6%) based on unrecovered starting material) of n-octadecyldiphenyl-2-phenylethylgermane, m.p. and mixture m.p. 34.5–35.5°.

Cleavage of tri-n-hexylphenylgermane. (*Attempted*). A mixture of 2.03 g. (0.005 mole) of tri-n-hexylphenylgermane, 0.3 g. (0.043 g.-atom) of lithium and 7 ml. of ethylene glycol dimethyl ether was stirred for 24 hr. to yield a deep red solution giving a positive Color Test I. The solution was pipetted into a dropping funnel and added to 1.7 g. (0.01 mole) of n-hexyl bromide dissolved in 20 ml. of GDME. After stirring 5 min., Color Test I was negative. Water was added and the mixture extracted with ether. The ether portions were dried and the solvents distilled to leave a residue which was distilled under reduced pressure to give 1.3 g. (65%) of starting material, b.p. 186–188° (0.7 mm.), n_D^{19} 1.4959.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Acid-Catalyzed Addition of Phosphine to Olefins

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Phosphine adds to olefins in the presence of non-oxidizing acid catalysts to give good yields of monoalkylphosphines and small amounts of dialkylphosphines. Reaction takes place readily at 30 to 60° under 20 to 40 atmospheres of phosphine. Because tertiary olefins react most easily, a carbonium ion mechanism seems likely. Nearly stoichiometric amounts of catalyst are needed because monoalkylphosphines react with the catalyst to form monoalkylphosphonium salts.

Phosphine adds to olefins in the presence of acid catalysts.[1] This addition is particularly interesting because phosphine is intermediate in basicity between two other hydrides: hydrogen sulfide and ammonia. Hydrogen sulfide reacts stepwise with olefins in the presence of acid catalysts to yield mercaptans and thioethers.[2] Because olefins are more basic than hydrogen sulfide or mercaptan, a carbonium ion intermediate can form easily and only a small amount of catalyst is needed. By contrast, no carbonium ion can form in the presence of ammonia. However, weakly basic derivatives of ammonia, such as urea, permit carbonium ions to form and can add to olefins with acid catalysts.[3]

The addition of phosphine to olefins has therefore been studied to determine qualitatively the relation of phosphine to hydrogen sulfide and ammonia in the presence of acid catalysts. Olefin reactivity was studied with primary, tertiary,[4] cyclic, and substituted olefins with methanesulfonic acid as catalyst. As catalysts, mineral acids, carboxylic acids, sulfonic acids, hydrogen halides, and Lewis acids were tested with a polypropene as the olefin. The effects of temperature and catalyst concentration were measured with methanesulfonic acid and a polypropene. Product distribution between mono- and dialkylphosphine was determined with typical olefins.

EXPERIMENTAL

Phosphine was prepared by adding water to a mixture of phosphorus and phosphorus tetraiodide[5] at 80° and scrubbing the evolved gases with aqueous sodium hydroxide. The scrubbed gases were dried in a coil cooled in Dry Ice and condensed in a pressure vessel cooled in liquid nitrogen. The mass spectrum showed the product to be pure phosphine.

Ten olefins were studied. Propene, dodecene-1, isobutene, and 2-ethylhexene-1 were commercial materials. C_{12}-polypropene was fractionated from a mixture of polypropenes obtained by polymerization with phosphoric acid. This fraction contained about 85% tertiary olefins. Polybutenes were obtained by polymerizing mixed butenes and butanes with aluminum chloride. Fractions containing an average of 26 and 65 carbon atoms were used. Two cyclic olefins, 1-methylcyclopentene-1 and 4-methylcyclohexene-1 were synthesized. A mixture of the two di-isobutene isomers was chlorinated and the product was fractionated to isolate the unsaturated monochloride.

Detailed studies were carried out with C_{12}-polypropene because of its stability toward acids. This stability was demonstrated by stirring a sample with an equimolar amount of methanesulfonic acid for 16 hr. at 85° and distilling the recovered olefins. A plot of the refractive index and boiling point at 5% increment of the distillation showed no significant variation from a similar distillation of untreated C_{12}-polypropylene. Also, no measurable polymeri-

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(1) H. C. Brown, U. S. Patent 2,584,112 (1952).

(2) W. A. Proell and W. F. Wolff, U. S. Patent 2,615,786 (1952).

(3) H. C. Brown, U. S. Patent 2,548,585 (1951).

(4) Olefins in which one of the carbon atoms of the double bond is also bonded to two other carbon atoms; isobutene is the simplest example.

(5) W. C. Fernelius, "Inorganic Synthesis, Vol. II", McGraw-Hill Book Co., Inc., New York, New York, 1946, p. 41.

zation occurred. By contrast, 1-methylcyclopentene polymerizes rapidly at room temperature even with smaller amounts of acid.

Thirteen acids were studied as catalysts. Methanesulfonic acid was distilled twice to remove water and sulfuric acid, 85% phosphoric acid was reacted with sufficient phosphorus pentoxide to form 100% phosphoric acid, and dodecylphosphonous acid and phosphonium iodide were synthesized. The other catalysts were used as obtained commercially.

Phosphine was added to olefins in a 100-ml. stainless steel Magne-Dash reactor. The reactor was thoroughly flushed with nitrogen before each run. Usually, about 0.2 moles of olefin was charged, the phosphine was pressured in, the reactor was heated to the desired temperature, and then the catalyst was added. Solid catalysts had to be charged first; to minimize polymerization, the reactor was then cooled in Dry Ice before olefin was added. For the experiments with propene, isobutene, and C_{65}-polybutene, *n*-heptane was used as a solvent.

After a run was completed, the reactor was cooled, the excess phosphine was vented, and the product was diluted with heptane and washed with water to remove the catalyst. All product handling was done under nitrogen. The heptane solution was analyzed both by measuring total phosphorus content and by potentiometrically titrating the acids in an aliquot oxidized with hydrogen peroxide.[6] Good agreement was obtained between the values for total phosphorus and total acid. Total yield of alkyl phosphine was calculated from these values.

The dialkylphosphine was measured directly by potentiometric titration with hydrogen chloride in acetic acid; this titration showed no trialkylphosphines to be present. A Beckman Model 2-H *p*H meter with a calomel-glass electrode pair was used. Solvent was C.P. glacial acetic acid, titrant was *N*/10 anhydrous HCl in C.P. glacial acetic acid. In this system, dialkylphosphines titrated at about 560 millivolts and trialkylphosphines at 500 millivolts.

To substantiate that alkylphosphines were the product of the addition reaction, three derivatives were prepared from the adduct of phosphine to C_{12}-polypropene: the phosphonous acid, the phosphonic acid, and the dipotassium phosphonate.

t-Dodecylphosphonous acid was obtained by oxidizing a heptane solution of the C_{12}-polypropene product with 30% hydrogen peroxide at 50°. Titration of the oil phase from the oxidation indicated a 79% yield of *t*-dodecylphosphonous acid and a 6% yield of *t*-dodecylphosphonic acid. Most of the remaining 15% was recovered as phosphoric acid in the aqueous phase. The isolated product was a pale yellow syrup. Potentiometric titration gave a curve with two breaks that corresponds to a mixture of 93 mole % phosphonous acid and 7 mole % phosphonic acid. Neutral equivalent: Calcd., 235; Found, 238.

t-Dodecylphosphonic acid was obtained by oxidizing a heptane solution of the phosphonous acid with concentrated nitric acid at 90°. Titration of the oxidized solution indicated a 92% yield of mixed acids. The isolated product—again a pale yellow syrup—comprised 91 mole % of phosphonic acid and 9 mole % of phosphonous acid. Neutral equivalent: Calcd., 249; Found, 256. Phosphorus: Calcd., 12.4%; Found, 12.3%.

The dipotassium salt was prepared by treating a *n*-heptane solution of the phosphonic acid with the theoretical amount of potassium hydroxide in an aqueous solution, distilling off the water, filtering the remaining heptane solution, and removing the heptane. The salt was an amorphous brittle solid. Phosphorus: Calcd., 9.7%; Found, 9.5%. Potassium: Calcd., 22.3%; Found, 21.4%.

DISCUSSION OF RESULTS

The yields of monoalkylphosphines obtained from the different olefins with methanesulfonic acid as catalyst are summarized in Table I. Best yields were obtained with tertiary olefins. A simple carbonium ion mechanism therefore seems likely. A normal Markownikoff addition presumably takes place to yield a product with the phosphorus atom bonded to the tertiary carbon atom:

$$R_2C{=}CH_2 + H^+ \rightleftarrows R_2\overset{+}{C}{-}CH_3 \qquad (1)$$

$$R_2\overset{+}{C}{-}CH_3 + PH_3 \rightleftarrows [H_3P{-}C(R_2)CH_3]^+ \qquad (2)$$

$$[H_3P{-}C(R_2)CH_3]^+ \rightleftarrows H_2P{-}C(R_2)CH_3 + H^+ \qquad (3)$$

Among the tertiary olefins, the lower yields for isobutene, 2-ethylhexene-1, and 1-methylcyclopentene-1 are probably due to the relative ease of polymerization of these compounds, compared to the C_{12}-polypropene. The high yields obtained from the polybutenes reflect a surprising degree of reactivity.

Mineral acids, sulfonic acids, carboxylic acids, hydrogen fluoride, and Lewis acids all catalyze phosphine addition. Table II compares the activity of these catalysts using C_{12}-polypropene as the olefin. The catalysts all show the same magnitude of activity with the exception of the phosphoric acid-phosphorus pentoxide. This mxiture was extremely viscous; hence the low yield may reflect inadequate stirring rather than low activity. Dodecylphosphonous acid, hydrogen iodide (as phosphonium iodide), aluminum bromide, phosphoric acid on Kieselguhr, oxalic acid, and Filtrol clay were also tested; none gave yields above 5 per cent. Sulfuric acid was reduced to an unidentified solid.

Nearly stoichiometric amounts of catalyst are required for complete reaction. In Fig. 1 are com-

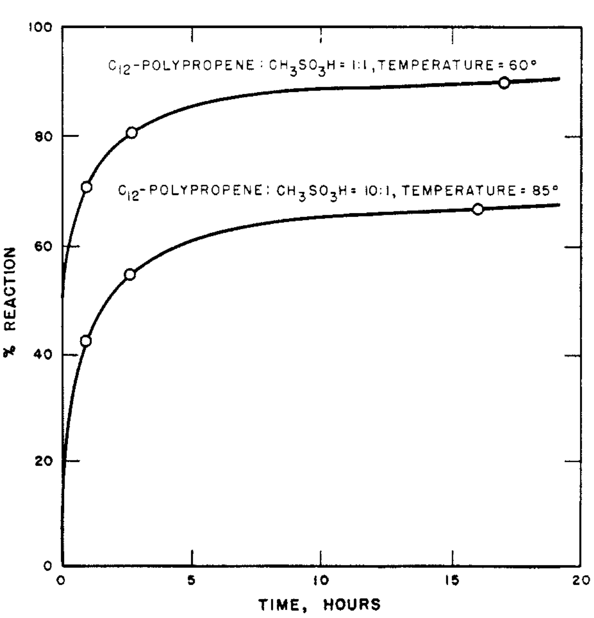

Fig. 1. Effect of catalyst concentration

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(6) Addition of 1 ml. of a non-ionic detergent greatly facilitated the titration in the two-phase system.

pared reaction rate curves in which the C_{12}-polypropene: CH_3SO_3H mole ratio was 1:1 and 10:1. PH_3 pressure was 38–43 atmospheres. In both cases the reaction is nearly complete in 3 to 4 hours. With the 1:1 ratio the amount of reaction at this time corresponds closely to the tertiary olefin content of the feed. Subsequent slow reaction probably results from reaction of non-tertiary olefins. With the 10:1 ratio, reaction is slower and stops at 60 to 70% even though a higher temperature is used. The reaction is not limited by polymerization because the C_{12}-polypropene used as olefin was shown not to polymerize at 85°C even with greater amounts of catalyst. Hence, reactive tertiary olefin is undoubtedly present at the end of the reaction.

Several other factors could limit the conversion when the lesser amount of catalyst is used. The higher temperature also used would decrease the phosphine concentration and make the equilibrium shown in Equation 2 less favorable. However, a run carried out at 90° with an olefin catalyst ratio of 1:1 showed a conversion of 86% at 4 hours, somewhat higher than that obtained at 60°, and indicated that temperature does not significantly affect phosphine concentration. Another explanation for the limited conversion with the small amount of catalyst is that the monoalkylphosphine formed is a much stronger base than phosphine or the olefin and ties up the catalyst as a phosphonium ion. If so, higher temperatures should favor an increased conversion because, similarly to ammonium and phosphonium halide, the dissociation of alkylphosphonium ions (Equation 3) would also be favored by increased temperature. The released protons would then catalyze further reaction. This theory is supported by the results summarized in Fig. 2. These are yields from runs carried out at 30, 60, and 85° and a PH_3:C_{12}-polypropene:CH_3SO_3H mole ratio of 2.8:1:0.1.

All runs lasted 16 hours and the yields are believed to reflect equilibrium yields and not reaction rate. The difference in total conversion is interpreted as representing the change in equilibrium,

$$RPH_2 + H^+ \rightleftarrows [RPH_3]^+,$$

as a function of temperature. Thus at 30° about 2 equivalents of RPH_2 are sufficient to deactivate the catalyst; at 60° nearly 6 equivalents are required.

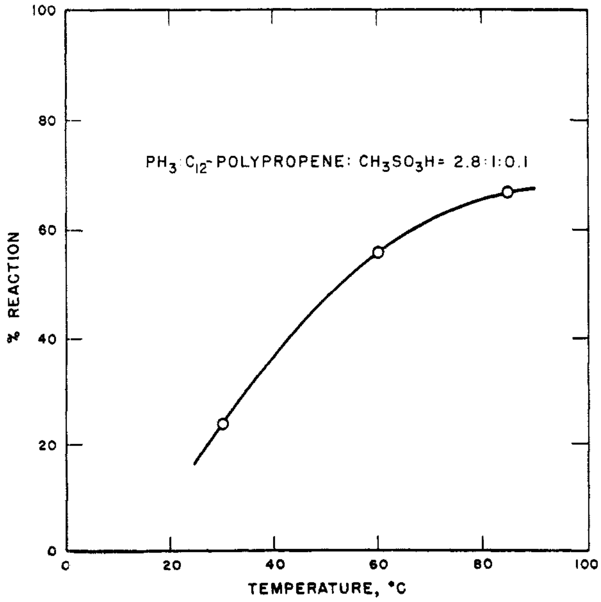

Fig. 2. Effect of temperature

TABLE I

REACTIVITY OF OLEFINS

	Moles per Mole Olefin					
	PH_3	CH_3-SO_3H	Time, Hrs.	Temp., °C.	Pressure, Atm.	Mole % RPH_2 + R_2PH
Propene	3.3	1.0	16	80	38	20
Dodecene-1	2.8	1.0	16	60	43	14
Isobutene	2.9	1.0	3	60	33	61
2-Ethylhexene-1	4.2	1.0	16	60	43	76
C_{12}-Polypropene	4.3	1.0	16	60	47	90
C_{26}-Polybutene	3.8	1.0	17	90	39	72
C_{65}-Polybutene	20.0	10.0	16	95	..	81
1-Methylcyclopentene-1	1.8	0.5	16	60	30	41
4-Methylcyclohexene-1	1.8	0.5	16	60	32	33
Monochlorodiisobutene	2.4	1.0	16	60	35	21

TABLE II

EFFECTIVENESS OF CATALYSTS

	C_{12}-Polyprolene Moles per Mole					
	PH_3	Catalyst	Time, Hrs.	Temp., °C.	Pressure, Atm.	Mole % RPH_2 + R_2PH
Methanesulfonic acid	4.2	1.0	3	60	38	81
Benzenesulfonic acid	2.4	0.5	3	60	36	72
Trifluoroacetic acid	3.7	1.0	3	60	37	60
85% H_3PO_4 + P_2O_5	3.8	1.0	3	60	44	17
Methanesulfonic acid	2.8	1.0	1.5	30	24	40
Boron trifluoride etherate	3.6	0.8	3	30	26	30
Hydrogen fluoride	3.7	1.0	3	30	29	53

Small amounts of dialkylphosphines are formed. Data summarizing the product distribution from phosphine addition to a primary, a tertiary, and two cyclic olefins are shown in Table III. The amounts of dialkylphosphine formed are small and reflect the tendency of the more basic monoalkylphosphine to exist as RPH_3^+. Because monoalkylphosphines are more basic than phosphine and capture most of the protons present, the concentration of both olefin cation and free monoalkylphosphine is low. Hence, formation of dialkylphosphine is slow. Olefin type appears to have little effect on the product distribution.

The increased basicity of monoalkylphosphines over that of phosphine decreases carbonium ion formation in acid-catalyzed systems so that addition of RPH_2 to olefins is a slow reaction. Therefore, high yields of monoalkylphosphines can be obtained. Acid-catalyzed addition of phosphine to tertiary olefins provides a synthesis of alkylphosphines having phosphorus bonded to a tertiary carbon atom.

TABLE III

COMPOSITION OF PRODUCTS

Time = 16 hours Catalyst = CH_3SO_3H

	Olefin Reacted, Mole %	°C.	PH_3, Atm.	Product Composition, Mole %	
				RPH_2	R_2PH
Dodecene-1	28	90	41	98	2
4-Methylcyclohexene-1[a]	34	60	32	97	3
1-Methylcyclopentene-1	41	60	30	90	10
C_{12}-Polypropene	91	90	50	96	4

[a] Rapid isomerization to 1-methylcyclohexene-1 is caused by the acid catalyst.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

Unsymmetrical Tetraalkylmethanes. III.[1] Syntheses from 3-Ethyl-3-methylglutaric Acid

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Two unsymmetrical tetraalkylmethanes, 11-ethyl-11-methyltricosane (X) and 11-ethyl-11-methylpentacosane (XIV), have been synthesized from 3-ethyl-3-methylglutaric acid by the reactions summarized in Chart I.

In the course of an investigation of methods for the synthesis of unsymmetrical tetraalkylmethanes, a number of procedures have been considered for building up the desired quaternary carbon atom structure. The possibility of an approach of some generality appeared to be through β,β-disubstituted glutaric acids. These compounds may be obtained from the condensation of simple or cyclic ketones with alkyl cyanoacetates according to the method of Guareschi,[4] which has been extended by Vogel.[5]

The present report describes the methods by which two relatively high molecular weight unsymmetrical tetraalkylmethanes were synthesized from 3-ethyl-3-methylglutaric acid. The reactions employed are summarized by the equations shown in Chart I.

The direct conversion of 3-ethyl-3-methylglutaric anhydride to a 3-ethyl-3-methyl-5-keto acid, such as compound XII, was suggested by the work of Newman and Smith[6] who have studied the addition of Grignard reagents to anhydrides at low temperatures. However, negative results were obtained when an ether-pyridine solution of 3-ethyl-3-methylglutaric anhydride was treated with ethylmagnesium bromide.

It was decided then to synthesize the keto acid, XII, through the ester–acid chloride, II. This compound was obtained readily from 3-ethyl-3-methylglutaric anhydride via the intermediate ester acid, I.

Percival, Wagner, and Cook[7] have prepared highly-branched ketones in quite satisfactory yields by the reaction of acid chlorides with Grignard reagents at −65° in the presence of ferric chloride. It was felt, however, that this method would have no special advantages, for the present purposes,

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[1] Paper II. N. Rabjohn and H. H. Farmer, *J. Org. Chem.*, **23**, 522 (1958).

[2] Abstracted in part from the Ph.D. thesis of H. H. Farmer, 1955.

[3] Supported in part by the Petroleum Research Fund of the American Chemical Society.

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[6] M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948).

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