[lit.[14] bp 75° (0.15 mm)] as a clear, colorless liquid. The infrared absorption (neat) occurred at 690 cm^{-1}; nmr peaks (CDCl$_3$) occurred at τ 2.80 (5 H singlet, phenyl), 2.83–3.32 (3 H multiplet, thiophene), and 5.92 (2 H singlet, CH$_2$).

2-Benzylthiophene-5-carboxylic Acid (XVIII).—Ethereal *n*-butyllithium (4.5 ml, 1.6 *N*, 7.4 mequiv) was added dropwise to a solution of XVII (1.0 g, 5.8 mmoles) in 50 ml of dry ether. The reaction and work-up was carried out according to the procedure described for the preparation of XV. The crude yellow crystalline product weighed 1 g (77%) and had mp 125–127°. An analytical sample was prepared as white plates from benzene and had mp 129–131°.

Anal. Calcd for C$_{12}$H$_{10}$O$_2$S: C, 66.04; H, 4.62; S, 14.69. Found: C, 66.27; H, 4.80; S, 14.80.

Nmr spectra of the crude material and analytical sample were identical. The nmr peaks (CDCl$_3$) occurred at τ −2.00 (1 H singlet, acid), 2.29, 2.35 (1 H doublet, thiophene, $J = 4$ cps), 2.75 (5 H singlet, phenyl), 3.20, 3.27 (1 H doublet, thiophene, $J = 4$ cps), and 5.88 (2 H singlet, methylene); the infrared spectrum showed absorptions (KBr) at 2900 (acid) and 1650 cm^{-1} (C═O).

Registry No.—I, 246-98-0; V, 13132-06-4; VIII, 13132-07-5; IX, 13732-08-6; X, 13132-09-7; XI, 13132-10-0; XII, 13132-11-1; XIII, 13132-12-2; XV, 13132-13-3; XVI, 13132-14-4; XVII, 13132-15-5; XVIII, 13132-16-6; ethyl 2-acetylamino-8H-indeno-[2,1-*b*]thiophene-3-carboxylate, 13127-20-3.

Acknowledgment.—The authors gratefully acknowledge financial aid in the form of a grant by the Senate Research Committee of West Virginia University.

[14] J. T. G. Cadogan, D. H. Hey, and W. A. Sanderson, *J. Chem. Soc.*, 3203 (1960).

Preparation and Some Chemistry of Tricyclopropylphosphine[1]

DONALD B. DENNEY AND FRANK J. GROSS[2]

School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903

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Tricyclopropylphosphine has been prepared in yields as high as 80% by reaction of cyclopropyllithium with triphenyl phosphite. The pK_a of tricyclopropylphosphine is very nearly the same as that of tri-*n*-propylphosphine. The ylide, tricyclopropylphosphinebenzoylmethylene, has been prepared. Its pK_a has been determined and its rate of reaction with benzaldehyde has been compared with that of triphenylphosphinebenzoylmethylene. Several other derivatives of tricyclopropylphosphine have been prepared and characterized. The pK_a measurements and rate data show quite conclusively that tricyclopropylphosphine has properties like those of other trialkylphosphines.

The interaction of a cyclopropane ring with a bonded unsaturated carbon atom has been the subject of a vast amount of study. It is now well recognized that the cyclopropane ring can function as an electron donor and thus one finds extraordinary stabilization of a cyclopropylcarbinyl carbonium ion for example.[3]

It does not appear that any systematic study has been made of the possible modes of interaction of a cyclopropane ring with third-row elements such as silicon, phosphorus, and sulfur. Such studies will certainly be of interest and this report describes a beginning of a broad study in this area. In particular the synthesis and some properties of tricyclopropylphosphine and some of its derivatives are reported.

Results and Discussion

The general method for preparing trisubstituted phosphines involves the reaction of a Grignard or organolithium reagent with phosphorus trichloride.[4] Attempts to prepare tricyclopropylphosphine by treatment of phosphorus trichloride with cyclopropylmagnesium bromide or cyclopropyllithium were not successful, and thus an alternate route for its preparation was sought. Gilman and Vernon[5] and Willans[6] have prepared trisubstituted phosphines by allowing Grignard and organolithium reagents to react with triphenyl phosphite.

This has been shown to be the method of choice for the preparation of tricyclopropylphosphine and it has been prepared in yields as high as 80% by reaction of excess cyclopropyllithium with triphenyl phosphite. Tricyclopropylphosphine is a liquid, bp 38–42° (0.6 mm); it has the usual disgusting odor associated with the lower trialkylphosphines. It does not spontaneously ignite in air as do trimethyl- and triethylphosphine. The infrared spectrum shows typical absorptions at 9.85 μ. The nmr spectrum consists of a multiplet centered at 0.4 ppm which is of course in agreement with the assigned structure.

Streuli[7] has determined basicities of a wide variety of trisubstituted phosphines in nonaqueous media by a potentiometric method. The results of these determinations were then correlated with the behavior of the more basic phosphines in mixed aqueous–organic solvents, and finally with analogous basicity studies of amines in water and the same mixed solvent systems. In this manner, it was possible to calculate values for the relative pK_a's of the phosphines in aqueous media.

The pK_a of tricyclopropylphosphine is found to be 7.60 by this method. Freshly distilled tri-*n*-butylphosphine was included in the titration series as a control. The observed pK_a was 8.43 (lit.[6] 8.43). Streuli reports the following pK_a values: tri-*n*-propylphosphine, 8.64; triisobutylphosphine, 7.97; tricyclohexylphosphine, 9.70; and triphenylphosphine, 2.73. In general, triarylphosphines are considerably less basic than trialkylphosphines. This is undoubtedly

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[2] F. J. G. wishes to acknowledge his gratitude to the American Cyanamid Co. for a Junior Educational Award and to the Hatco Chemical Division of W. R. Grace Co. for a fellowship.

[3] N. C. Deno, "Progress in Physical Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1964, pp 148–160.

[4] (a) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950; (b) Houben-Weyl, "Methoden Der Organischen Chemie," Vol. XII, Part 1, E. Müller, Ed., George Thieme Verlag, Stuttgart, 1963, pp 32–43.

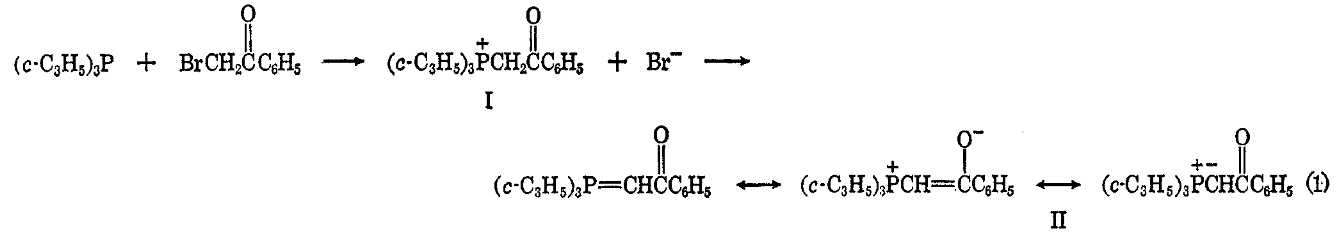
[5] H. Gilman and C. C. Vernon, *J. Am. Chem. Soc.*, **48**, 1063 (1926).

[6] J. L. Willans, *Chem. Ind.* (London), 235 (1957).

[7] C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

due to a combination of inductive and resonance effects which decrease the electron density of the phosphorus atom of the triarylphosphines.[8] The small differences in basicity observed between the trialkylphosphines is probably due in the main to solvation effects. The pK_a of tricyclopropylphosphine is so much like those of the trialkylphosphines that one is led to the conclusion that there is no interaction between the cyclopropane rings in either the phosphine or its conjugate acid which is not present in the tri-*n*-alkylphosphines.

Tricyclopropylphosphine reacted exothermically with phenacyl bromide in benzene to yield the phosphonium salt (I) (eq 1). Treatment of I with sodium ethoxide in ethanol afforded the phosphorane (II). The pK_a of this material was determined by the method of Speziale and Ratts[9] and was found to be 8.04. The pK_a's of triphenylphosphinebenzoylmethylene and triphenylphosphinecarbethoxymethylene were determined at the same time. These values were found to be 6.08 and 8.8, respectively. The literature value for the latter is 9.2.[9]

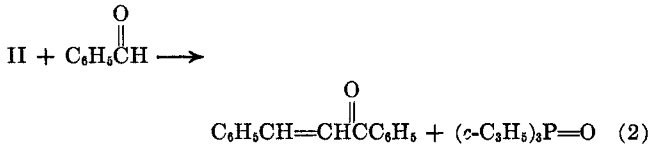


$$(c\text{-}C_3H_5)_3P + BrCH_2\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow \underset{I}{(c\text{-}C_3H_5)_3\overset{+}{P}CH_2\overset{O}{\overset{\|}{C}}C_6H_5} + Br^- \longrightarrow$$

$$(c\text{-}C_3H_5)_3P{=}CH\overset{O}{\overset{\|}{C}}C_6H_5 \longleftrightarrow \underset{II}{(c\text{-}C_3H_5)_3\overset{+}{P}CH{=}\overset{O^-}{\overset{|}{C}}C_6H_5} \longleftrightarrow (c\text{-}C_3H_5)_3\overset{+}{P}\overset{-}{C}H\overset{O}{\overset{\|}{C}}C_6H_5 \quad (1)$$

Comparison of the values for II and triphenylphosphinebenzoylmethylene show a difference of 2 pK_a units between the substances with II being the stronger base. This is in agreement with the results obtained from the pK_a measurement of the phosphine. Electron donation by induction in II will destabilize the negative charge in II and stabilize the positive charge in I, the net effect being a weaker acid than one in which electron-withdrawing groups, *e.g.*, phenyl, are bonded to phosphorus. It is unfortunate that no pK_a data are available on the trialkylphosphinebenzoylmethylenes; thus it is not possible to compare II with them. Special electron release to the positively charged phosphorus would make II a stronger base than trialkylphosphinebenzoylmethylenes; however, they would also be expected to be stronger bases than triphenylphosphinebenzoylmethylene. Since the difference in basicity between II and triphenylphosphinebenzoylmethylene is only 2 units, it seems safe to conclude that, if there is any special electron release to phosphorus in II by the cyclopropane rings, it must not contribute very much to the electron density on the phosphorus.

Speziale and Ratts[9] have shown that, within a given structural class of phosphoranes, the basicity parallels the nucleophilicity. Hence, it was of interest to compare the rate of reaction of II with that of triphenylphosphinebenzoylmethylene. Benzaldehyde was chosen as the coreactant. It was shown that II does react with benzaldehyde to give *trans*-chalcone and tricyclopropylphosphine oxide (eq 2).



$$II + C_6H_5\overset{O}{\overset{\|}{C}}H \longrightarrow C_6H_5CH{=}CH\overset{O}{\overset{\|}{C}}C_6H_5 + (c\text{-}C_3H_5)_3P{=}O \quad (2)$$

The relative rate of reaction of II compared with that of triphenylphosphinebenzoylmethylene was found to be 20:1. Again, this is in agreement with the pK_a data.

Tricyclopropylphosphine oxide was obtained as a product of the above reaction and a sample was also prepared by treatment of tricyclopropylphosphine with *t*-butyl hydroperoxide. The material has not yet shown any unusual properties.

The results of these studies indicate that there is no special electron release to phosphorus by cyclopropane rings attached to tri- and tetrasubstituted phosphorus atoms. This is perhaps not unreasonable since such release would require interaction with d orbitals or hybrid orbitals with partial d character. The usual mode of electron release by a cyclopropane ring involves interaction with a p orbital, cyclopropylcarbinyl carbonium ion being a case in point. Future studies will be aimed at preparing substances like $(C_3H_5)_3P^{\cdot +}$ and $(C_2H_5)P^+$; in these materials electron release from the cyclopropane ring can occur by interaction of a p orbital on phosphorus.

Experimental Section[10]

Tricyclopropylphosphine.—Triphenyl phosphite (27.2 g, 0.088 mole) was slowly added to 500 ml of a 0.7 *N* solution of cyclopropyllithium in ether at 10–15°. After the addition the homogeneous reaction mixture was heated under reflux for 18 hr. At the end of this time, the reaction mixture was cooled to 5° and treated with stirring with 100 ml of 2.5 *N* sodium hydroxide solution. A copious white precipitate formed. Addition of 700 ml of water to the slurry completely dissolved the precipitate. The ether layer was separated and the aqueous layer was washed with two 150-ml portions of peroxide-free ether. The combined ether extracts were dried over magnesium sulfate. The ether was removed *in vacuo*, and the residue was distilled. The major fraction (10.6 g, 80%) had bp 38–42° (0.6 mm). The infrared spectrum (neat) showed absorption due to cyclopropyl ring deformation at 9.85 μ. The nmr spectrum (neat) exhibited a multiplet centered at 0.4 ppm. This material was not analyzed for C, H, and P because of the difficulty in handling it. Further structure proof is presented below, where the preparation of derivatives is recorded.

Determination of the pK_a of Tricyclopropylphosphine.—The basicity of tricyclopropylphosphine was determined by Streuli's method.[7] Standard solutions of 1,3-diphenylguanidine and tricyclopropylphosphine were prepared in spectral grade nitromethane. Aliquots (10 ml) of these solutions were then titrated with 0.0503 *N* perchloric acid in nitromethane. The potential of the solution being titrated was measured with a Beckman

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[8] R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 2.

[9] A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **85**, 2790 (1963).

[10] All nmr spectra were obtained on a Varian Model A-60. Chemical shifts are recorded in parts per million (ppm) relative to tetramethylsilane as an internal standard. Melting points were determined on a Mel-Temp block and they are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Model 21 spectrophotometer. All gas-liquid partition chromatographic analyses were performed with an F & M Model 700.

Model 76 expanded-scale pH meter fitted with a glass electrode and a "sleeve-type" calomel electrode. The pK_a of tricyclopropylphosphine was found to be 7.72 and 7.48 in duplicate determinations.[11]

Tricyclopropylphenacylphosphonium Bromide (I).—Tricyclopropylphosphine (9.2 g, 0.06 mole) in 250 ml of benzene was treated with a solution of 12.0 g (0.06 mole) of phenacyl bromide in 50 ml of benzene. The solution became warm during the addition, and a fine white crystalline precipitate was formed. The mixture was stirred for 2 hr at room temperature and then heated under reflux with stirring for 1 hr. The cooled reaction mixture was filtered to give 16.75 g (79%) of product. This material was recrystallized from 150 ml of ethylene dichloride, mp 175–176.5°. The infrared spectrum (Nujol mull) showed a sharp carbonyl absorption at 5.92 μ. The nmr spectrum ($CDCl_3$) showed a multiplet centered at 1.35 (cyclopropyl protons), a doublet at 5.1 (J = 13.5 cps, methylene protons), a multiplet centered at 7.56, and a smaller multiplet centered at 8.30 ppm (phenyl protons). The areas were in the ratio 15.7:2:5.2 (calcd, 15:2:5).

Anal. Calcd for $C_{17}H_{22}BrOP$: C, 57.79; H, 6.21. Found: C, 58.01; H, 6.33.

Tricyclopropylphosphinebenzoylmethylene (II).—Tricyclopropylphenacylphosphonium bromide (12.12 g 0.034 mole) was dissolved in *ca.* 250 ml of ethanol containing 0.034 mole of freshly prepared sodium ethoxide. The solution was stirred for 24 hr at room temperature, and then the solvent was removed *in vacuo* at 50°. The residue was dissolved in 50 ml of benzene and filtered. After removal of benzene at 50° *in vacuo*, a quantitative yield of light tan crystals, mp 79.5–81°, was obtained. The equivalent weight was determined by titration with perchloric acid in acetic acid (found, 273; calcd, 272). The infrared spectrum showed a sharp carbonyl absorption at 6.26 μ.

Determination of the Rates of Reaction of Benzaldehyde with Tricyclopropylphosphinebenzoylmethylene and Triphenylphosphinebenzoylmethylene.—The rates of the reactions of the two phosphoranes with benzaldehyde were measured at 45.2° by infrared spectroscopy. The second-order rate constants were found to be $5.06 \times 10^2 \pm 0.23$ l./mole/min for II and $2.5 \times 10^3 \pm 0.4$ l./mole/min for triphenylphosphinebenzoylmethylene.

Reaction of II with Benzaldehyde.—A solution of 4.9 g (0.013 mole) of II and 1.4 g (0.013 mole) of benzaldehyde in 85 ml of benzene was heated under reflux for 72 hr. The solvent was removed *in vacuo* on a steam bath. The residue was triturated with 50 ml of water. An oily reddish orange residue remained. This material was dissolved in 25 ml of boiling petroleum ether (bp 30–60°). Upon cooling yellow needles separated, mp 57–58.5° (lit.[12] mp 58°). The infrared and nmr spectra were identical with the spectra of an authentic sample of *trans*-chalcone.

Tricyclopropylphosphine Oxide.—Tricyclopropylphosphine (3.0 g, 0.02 mole) was dissolved in 25.0 ml of pentane. The resulting solution was cooled to −10°. *t*-Butyl hydroperoxide (75%) (2.66 g, 0.02 mole) was added dropwise at −10°. The mixture was allowed to warm to room temperature. The solvent was removed *in vacuo* to yield 4.55 g (100%) of an oily residue. The material was evaporatively distilled. A small fraction distilled at a block temperature of 95° (0.8 mm). As the temperature of the block was raised to 125°, white crystalline material sublimed onto the cold finger. The oxide was obtained as a low melting, less than 40°, hygroscopic solid. The infrared spectrum was very complex; however, P=O absorption was present at 8.6 and cyclopropyl absorption at 9.7 μ. The nmr spectrum had absorptions at 0.68 and 0.88 ppm.

The same material was obtained by extracting the aqueous solution from the reaction of II with benzaldehyde.

Methyltricyclopropylphosphonium Bromide.—Tricyclopropylphosphine (1.54 g, 0.01 mole) in 25 ml of ether was allowed to react with 2.5 g (0.03 mole) of methyl bromide. The reaction mixture was stirred overnight at room temperature in a stoppered flask. After 18 hr, a slurry had formed. The slurry was filtered to give 2.0 g (80%) of material of mp 257–263°. Recrystallization from chloroform yielded material of mp 271–272.5°. The equivalent weight was determined by titration with perchloric acid in acetic acid in the presence of mercuric acetate (calcd, 249; found, 246). The infrared spectrum (1% KBr pellet) had absorptions at 3.25, 3.35, 6.95, 7.05, 9.60, 10.85, and 11.15 μ. The nmr spectrum (CD_3OD) showed a complex multiplet centered at 1.14 and a doublet at 1.75 ppm (J = cps).

Anal. Calcd for $C_{10}H_{18}BrP$: C, 48.25; H, 7.30. Found: C, 48.26; H, 7.50.

Tricyclopropyltriphenylmethylphosphonium Bromide.—Tricyclopropylphosphine (10.0 g, 0.065 mole) in 50 ml of anhydrous tetrahydrofuran was allowed to react with 21.1 g (0.065 mole) of triphenylmethyl bromide in 100 ml of tetrahydrofuran. After stirring 24 hr, the mixture was filtered to give 25.0 g (81%) of product of mp 201–202.5°. This material was recrystallized from water. It appeared that a hydrate was formed during the purification. A cream-colored solid was isolated which turned light yellow on drying *in vacuo* at 70°. This material had mp 202–203°, and the equivalent weight was found to be 485 (calcd, 477). The infrared spectrum (1% KBr pellet) had absorptions at 3.35, 6.25, 6.92, 7.1, 9.7, 13.20, 13.60, and 14.35 μ. The nmr spectrum ($CDCl_3$) showed a multiplet at 1.15 and 7.3 ppm of equal area.

Anal. Calcd for $C_{28}H_{30}BrP$: C, 70.50; H, 6.42; P, 6.48. Found: C, 70.51; H, 6.38; P, 6.27.

Registry No.—I, 13118-23-5; II, 13143-76-5; tricyclopropylphosphine, 13118-24-6; tricyclopropylphosphine oxide, 13118-25-7; methyltricyclopropylphosphonium bromide, 13118-26-8; tricyclopropyltriphenylmethylphosphonium bromide, 13118-27-9.

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[11] Full details can be found in the thesis of F. J. Gross, Rutgers, The State University, 1967.

[12] "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965, p 583.