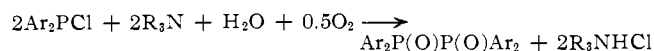


phosphinous chlorides for the formation of the phosphorus-phosphorus bond. The method to be described uses quite mild conditions; in its present form, it has provided a synthesis of tetraaryldiphosphine dioxides in one step. Organic compounds containing the phosphorus-phosphorus bond are rare, and new synthetic approaches are needed.⁵ The method may prove to be adaptable to the preparation of other derivatives of diphosphine.

Exposure to the atmosphere of an ether solution of molar equivalents of a diarylphosphinous chloride and a tertiary amine results in the precipitation of the amine hydrochloride and the tetraaryldiphosphine dioxide. More of the latter can be recovered from the solution. The process is facilitated if a small amount (about 0.5 molar equiv.) of water is present initially, but excessive amounts cause hydrolysis of the chloride to the *sec*-phosphine oxide. Three different diphosphine dioxides have been obtained in 50–80% yield by this new reaction.

To account for the formation of diphosphine dioxides, it is necessary to assume that both hydrolysis and oxidation reactions are involved. No attempt has been



made yet to isolate intermediates of this complex process. The amine plays a vital role, as no coupling occurs in its absence. When either diphenylphosphine oxide or diphenylphosphinic chloride are included in the reaction mixtures, no improvement of the yield of diphosphine dioxide occurs, and when a mixture of the oxide and the phosphinic chloride is exposed to an amine in ether, a different reaction takes place.⁶ These observations suggest a process in which phosphorus-phosphorus bond formation precedes the hydrolysis and oxidation steps, with the amine involved in the coupling reaction. The amine cannot, however, act in a manner similar to metals in their coupling reaction, since it does not function as a reducing agent. Possibly an amine-phosphinous chloride complex, similar to that between amines and phosphorus trihalides,⁷ forms first and is susceptible to attack by a second molecule of phosphinous chloride, with displacement of the amine.⁸ These events would lead to an intermediate $[\text{Ar}_2\ddot{\text{P}}-\text{P}^+\text{Ar}_2\text{Cl}]\text{Cl}^-$, which is then stabilized by hydrolysis and oxidation. The over-all process is mechanistically unusual, involving first electrophilic and then nucleophilic behavior in the same kind of atom; substantiation is required and is now being sought.

The reaction has been conducted in ether, benzene, or tetrahydrofuran; the amine has been diethylaniline or triethylamine. The following procedure for tetraphenyldiphosphine dioxide is typical. A solution of 11.9 g. (0.0539 mole) of diphenylphosphinous chloride in 50 ml. of ether was added in 1 hr. to a chilled solution of 8.04 g. (0.0539 mole) of diethylaniline and 0.60 g. (0.0333 mole) of water in 60 ml. of ether. The mixture was stirred overnight unprotected from the atmosphere. A precipitate (10.4 g.) was washed with

200 ml. of water, leaving 4.64 g. of crude product. The ether filtrate left a solid on evaporation, which on washing with 100 ml. of water left 3.96 g. of crude diphosphine dioxide. The combined crude products (0.0214 mole, 79.4%) were thoroughly dried and recrystallized from dry acetone-ether (if water is present in this step, some hydrolysis occurs, and a precipitate of diphenylphosphinic acid results). The product had m.p. 167–169° (lit.⁹ m.p. 167°), the correct C, H, and P values, and an infrared spectrum in agreement with that reported.⁹ Heating in water caused cleavage to diphenylphosphinic acid and diphenylphosphine oxide in good yield. The dioxide is stable to air, but is readily oxidized by potassium permanganate or iodine solutions.

In similar fashion two new compounds were prepared: tetra(*p*-tolyl)diphosphine dioxide, 54%, m.p. 184–186° (*Anal.* Calcd. for $\text{C}_{28}\text{H}_{28}\text{O}_2\text{P}_2$: C, 73.35; H, 6.16; P, 13.51. Found: C, 73.58; H, 6.09; P, 13.61); 1,2-diphenyl-1,2-di(*p*-chlorophenyl)diphosphine dioxide, 63%, m.p. 155–156° (*Anal.* Calcd. for $\text{C}_{24}\text{H}_{18}\text{Cl}_2\text{O}_2\text{P}_2$: C, 61.16; H, 3.85; P, 13.15. Found: C, 61.45; H, 3.93; P, 12.99).

(9) W. Kuchen and H. Buchwald, *Ber.*, **91**, 2871 (1958).

(10) Philip Morris Research Assistant, 1962–1964.

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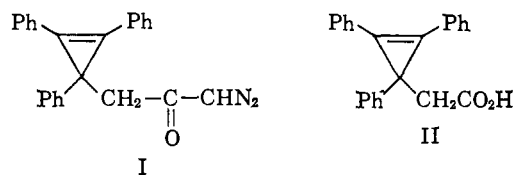
LOUIS D. QUIN
HARVEY G. ANDERSON¹⁰

RECEIVED MARCH 26, 1964

Rearrangements of 1-(1,2,3-Triphenylcyclopropenyl)-3-diazopropan-2-one

Sir:

The recent communication on the photolysis of 1,2-diphenyl-3-diazomethylketocyclopropene to give 4,5-diphenyltricyclo[1.1.1.0^{4,5}]pentan-2-one¹ has prompted us to report in preliminary form our studies on 1-(1,2,3-triphenylcyclopropenyl)-3-diazopropan-2-one (I). Compound II, (1,2,3-triphenylcyclopropenyl)acetic acid, precursor to I and prepared by hydrolysis of the crude reaction product from treatment of triphenyl-



cyclopropenyl bromide with ethyl bromoacetate in the presence of zinc in refluxing benzene-ether, had m.p. 181–183° dec. *Anal.* Calcd. for $\text{C}_{23}\text{H}_{18}\text{O}_2$: C, 84.63; H, 5.56. Found: C, 84.65; H, 5.55. Compound I, prepared from the acid chloride of II in the usual manner, had m.p. 119–122° dec. *Anal.* Calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}$: C, 82.26; H, 5.18; N, 8.00. Found: C, 82.05; H, 5.21; N, 7.91. The n.m.r., ultraviolet, and infrared spectra were consistent with the structure.

When I was treated with copper powder in refluxing benzene for 1 hr. and the crude reaction product chromatographed on basic alumina, there was obtained after recrystallization a 57% yield of ketone III, 4,5,6-triphenyltricyclo[2.1.1.0^{5,6}]hexan-2-one,² m.p.

(1) S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964).

(2) The first example of such an intramolecular cyclization was reported by G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961).

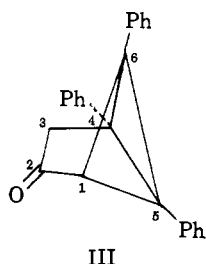
(5) The subject has recently been reviewed: J. E. Huheey, *J. Chem. Educ.*, **40**, 153 (1963).

(6) L. D. Quin and H. G. Anderson, in preparation.

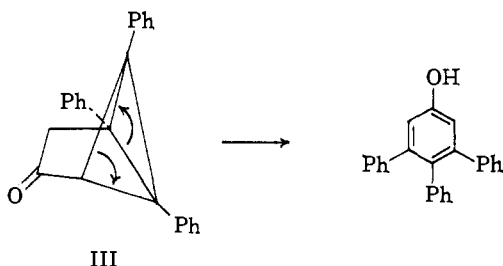
(7) R. R. Holmes, *J. Phys. Chem.*, **64**, 1295 (1960); *J. Am. Chem. Soc.*, **82**, 5285 (1960).

(8) Some analogy may be found in the synthesis of a diphosphine by displacement of an amine from an aminophosphine with a secondary phosphine: A. Burg, *ibid.*, **83**, 2226 (1961).

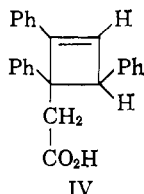
155.5–156°. *Anal.* Calcd. for $C_{24}H_{18}O$: C, 89.42; H, 5.63; mol. wt., 322. Found: C, 89.24; H, 5.68; mol. wt., 318 (thermoelectric osmometer). Its in-



frared spectrum showed a five-membered ketone band at 1750 cm^{-1} ; the n.m.r. spectrum had a fifteen-proton multiplet centered at τ 2.8 (phenyl hydrogens), a one-proton singlet at τ 6.8 (bridgehead hydrogen), and a two-proton singlet at τ 7.4 (methylene hydrogens). The ultraviolet spectrum (dioxane) showed a shoulder at $243\text{ m}\mu$ ($\log \epsilon$ 4.23) and was thus similar to that reported by Masamune¹ for his diphenylbicyclobutane which has λ_{\max} $242\text{ m}\mu$ ($\log \epsilon$ 4.17). Quantitative conversion of III to 3,4,5-triphenylphenol (identified by comparison with an authentic sample)³ at 180° provided additional evidence for the proposed structure.



Treatment of I with silver oxide under conditions for a Wolff rearrangement⁴ led to a 38% yield of crude, once-recrystallized acid, tentatively assigned structure IV, (1,2,4-triphenylcyclobut-2-enyl)acetic acid. The analytical sample had m.p. $178.5\text{--}180^\circ$. *Anal.* Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.42; H, 5.78. The infrared spectrum showed a carbonyl band at 1710 cm^{-1} . The ultraviolet spectrum (ethanol) had λ_{\max} $257\text{ m}\mu$ ($\log \epsilon$ 4.12). In comparison, 1-phenylcyclobutene has λ_{\max} $255\text{ m}\mu$ ($\log \epsilon$ 4.14).⁵



The n.m.r. spectrum showed a one-proton singlet at τ -0.1 (acid hydrogen), a fifteen-proton complex multiplet centered at τ 2.8 (phenyl hydrogens), a somewhat broad one-proton singlet at τ 3.7 (vinyl hydrogen), a somewhat broad one-proton singlet at τ 5.4 (tertiary hydrogen), and two one-proton doublets ($J = 14\text{ c.p.s.}$) centered at τ 6.5 and 7.4 (methylene hydrogens).

(3) Prepared by the method of A. Smith, *Chem. Ber.*, **26**, 65 (1893), as modified by J. B. Garner, *Am. Chem. J.*, **31**, 143 (1904); B. Prager, *et al.*, "Beilsteins Handbuch der Organischer Chemie," 4th Ed., Julius Springer, Berlin, Germany, 1923, Vol. VI, p. 721, Vol. VIII, p. 220.

(4) The reaction was run at 80° in dioxane-water in the presence of silver oxide, sodium thiosulfate, and sodium carbonate.

(5) J. W. Wilt and J. D. Roberts, *J. Org. Chem.*, **27**, 3430 (1962).

Typical of the spectra of other cyclobutenes,⁶ the splitting of the vinyl hydrogen is very small, if not nonexistent, and was not resolved in our spectrum. The methylene hydrogens are nonequivalent because of their proximity to asymmetric carbon atoms^{7a} and their splitting is typical of a *geminal* AB system.^{7b} Thus the analysis and spectra are consistent with the proposed structure IV.

A reasonable mechanism for the formation of IV could involve prior formation of III which cleaves in the presence of base. However, reaction of III with mild base or under the Wolff rearrangement conditions led to *little or no acidic product*.⁸ Similarly, I, in the absence of silver oxide, gave a low yield of acidic material. Therefore, IV is most likely formed *via* a route which involves intimate association with silver.⁹

Although a tricyclo[2.1.1.0^{5,6}]hexyl system has been prepared previously,¹⁰ the unique position of the keto group in III allows an unusual opportunity for the investigation of several properties of this strained system. Such studies of III and its derivatives are in progress.

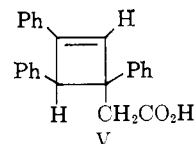
Acknowledgment.—The author wishes to thank Professor Ernest Wenkert for the n.m.r. spectra and the National Science Foundation for a postdoctoral fellowship.

(6) See, for example, E. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, **86**, 453 (1964).

(7) (a) See L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 99 ff for a detailed explanation of this phenomenon; (b) *ibid.*, p. 85.

(8) In fact under these conditions, a new ketone is formed whose structure is now being investigated.

(9) A referee has suggested an alternative structure to IV: (1,3,4-triphenylcyclobut-2-enyl)acetic acid (V). With the data now available it is



not possible to distinguish between structures IV and V. However, we prefer IV at this time for the following reason. A mechanism involving base cleavage of a silver complex of III (or a similar species) leads directly to IV whereas mechanisms leading to V involve several intermediates which we feel would collapse just as readily to 3,4,5-triphenylphenol. But in fact no phenol can be detected by infrared analysis of the crude product from the attempted Wolff rearrangement of I.

(10) J. Meinwald, C. Swithenbank, and A. Lewis, *J. Am. Chem. Soc.*, **85**, 1880 (1963).

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RECEIVED MARCH 13, 1964

The Acetaldehyde-2-Deoxy-D-ribose 5-Phosphate Aldolase Complex: Comparison of the Product Obtained on Borohydride Reduction and Hydrolysis with Synthetic N⁶-Ethyllysine

Sir:

Previous investigations have demonstrated that interaction of rabbit skeletal muscle aldolase and yeast transaldolase with their respective substrates, dihydroxyacetone phosphate and fructose 6-phosphate, involves Schiff base intermediates.¹⁻⁴ Moreover, it

(1) B. L. Horecker, S. Pontremoli, C. Ricci, and T. Cheng, *Proc. Natl. Acad. Sci. U. S.*, **47**, 1942 (1961).

(2) E. Grazi, T. Cheng, and B. L. Horecker, *Biochem. Biophys. Res. Commun.*, **7**, 250 (1962).

(3) E. Grazi, P. T. Rowley, T. Cheng, O. Tchola, and B. L. Horecker, *ibid.*, **9**, 38 (1962).

(4) J. C. Speck, Jr., P. T. Rowley, and B. L. Horecker, *J. Am. Chem. Soc.*, **85**, 1012 (1963).