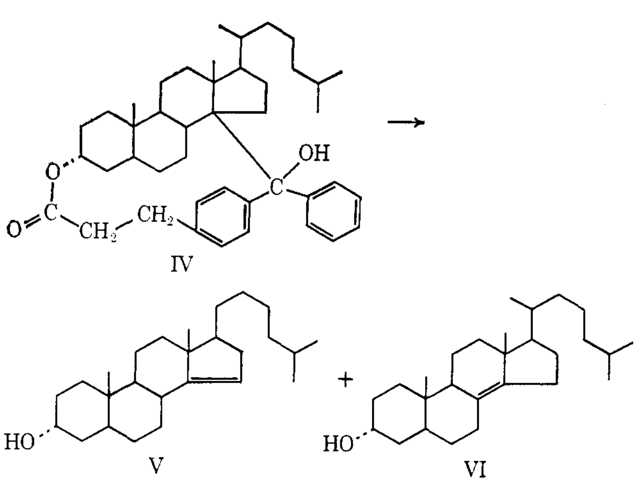

when the photolysis of III is performed in acetone and 35% when benzene is used.

Obviously, it remains to elucidate the solvent effects, and as well to identify the other products of these reactions under various conditions, in particular the chlorinated steroids. However, even the present relatively inefficient conversion of cholestanol to 12-ketocholestanol, and the more efficient conversion to Δ^{14}- and $\Delta^{8(14)}$-cholestenol, are indications of the synthetic potential of "remote oxidation" in performing transformations of a type hitherto restricted to enzymatic reactions.[10]

(10) Support of this work by the National Institutes of Health and a National Institutes of Health Postdoctoral fellowship to S. W. B. is gratefully acknowledged. We also wish to thank Dr. M. Winnik for some of the early work on remote oxidation in steroids. Part of the material in this communication was reported at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-147.

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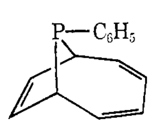
Received October 31, 1969

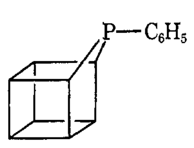
The Photochemical Synthesis of Condensed Bridged Phosphines

Sir:

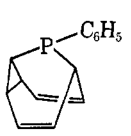
The bridged phosphine I is easily prepared from the cyclooctatetraene dianion and dichlorophenylphosphine.[1] We examined its behavior upon irradiation with ultraviolet light because it seemed likely[2] that highly condensed ring systems, such as II[3] and III,[3c] which would probably be difficult to prepare otherwise, might thereby be synthesized. This route would be considerably shorter than others that have given homocubanes[4] or barbaralanes.[5] In fact both compounds



I



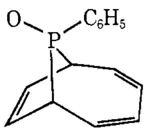
II



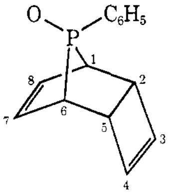
III

II and III can be prepared from I, and in separate experiments, since photolysis through Corex[6a] of the phosphine oxide IV of I in benzene–acetone gives the oxide of II, while photolysis through Pyrex[6b] of the phosphine I itself in benzene gives III.

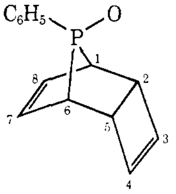
The route from IV to the oxide of II probably[3] proceeds *via* V, and this material can be isolated when IV is photolyzed through Pyrex in benzene solution without



IV



V



VI

added acetone (mp 175–177°, 28% yield), or in acetone solution for a short time (45% yield).[7,8] Simultaneously, cyclooctatetraene is formed, and the nmr spectrum of a photolyzed C_6D_6 solution of IV indicates that the molar amount formed is half that of V. The structure of V was assigned on the basis of the nmr spectrum, which shows that (disregarding the phenyl) the molecule is tricyclic, has a plane of symmetry, and has two isolated double bonds.[9] The *endo* stereochemistry is indicated by the magnitude of $J_{1,2}$.[2,9,10] The *exo* isomer could not be found. The stereochemistry at the phosphorus atom in V is presumably the same as that in IV,[1] and when the phosphorus epimer[1] of IV is photolyzed in benzene through Pyrex it gives in 32% yield VI (mp 107.5–109°),[8] the epimer of V. The features of the nmr spectra of V and VI[11] are similar, indicating that the ring systems are the same. Again the *exo* isomer could not be found.

When benzene solutions containing acetone of IV, V, or VI are photolyzed through Corex, the nmr spectrum shows that the oxide of II is formed. In the case of IV the oxide[8] (mp 122–123°) can be isolated in 25–40% yield and is identified by its nmr spectrum (three

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(1) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Amer. Chem. Soc.*, **88**, 3832 (1966).

(2) However, irradiation of the parent hydrocarbon, bicyclo[4.2.1]-nonatriene, in acetone solution is not reported to give either homocubane or barbaralane—the *exo* and *endo* cyclobutenes form—(*cf.* L. G. Cannell, *Tetrahedron Lett.*, 5967 (1966)), and no other derivative of bicyclo[4.2.1]nonatriene has been photolyzed.

(3) (a) W. L. Dilling, *Chem. Rev.*, **66**, 384 (1966); (b) G. J. Fonken, *Org. Photochem.*, **1**, 197 (1967); (c) R. Steinmetz, *Fortschr. Chem. Forsch.*, **7**, 445 (1967).

(4) (a) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 3157 (1964); (b) W. G. Dauben and D. L. Whalen, *Tetrahedron Lett.*, 3743 (1966); (c) K. V. Scherer, Jr., R. S. Lunt, III, and G. A. Ungefug, *ibid.*, 1199 (1965); (d) G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *ibid.*, 3737 (1966); (e) C. G. Chin, H. W. Cuts, and S. Masamune, *Chem. Commun.*, 880 (1966); (f) P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 698 (1967); (g) J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967).

(5) (a) V. Biethan, H. Klusacek, and H. Musso, *Angew. Chem. Intern. Ed. Engl.*, **6**, 176 (1967); (b) W. von E. Doering, *et al.*, *Tetrahedron*, **23**, 3943 (1967); (c) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967); (d) H. Tsuruta, K. Kurabayashi, and T. Mukai, *Tetrahedron Lett.*, 3775 (1967); (e) J. Daub and P. von R. Schleyer, *Angew. Chem. Intern. Ed. Engl.*, **7**, 468 (1968).

(6) (a) $\lambda \geq 280$ mμ; (b) $\lambda \geq 300$ mμ.

(7) First prepared in this laboratory by C. N. Lazaridis.

(8) Satisfactorily analyzed for C, H, P. Exhibits the required parent peak in the mass spectrum.

(9) Aromatics, τ 2.65 (5.14 H); H_7, 3.73 (1.97 H, doublet $|J_{PH}| = 11$ Hz, triplet $|J_{6,7}| = 3.2$ Hz); H_3, 4.50 (1.90 H, singlet); H_1, 6.77 (2.04 H); H_2, 7.10 (1.95 H, doublet $|J_{1,2}| = 3.2$ Hz); simultaneous irradiation at the resonance frequency of phosphorus and H_1 collapses the olefinic resonances to two singlets.

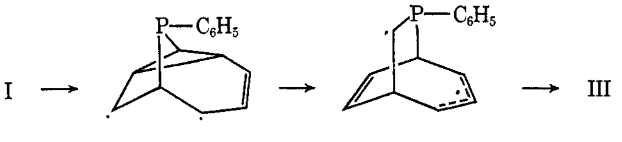
(10) (a) T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, **32**, 1301 (1967), footnote 20; (b) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 623 (1966).

(11) Aromatics, τ 2.6 (5.16 H); H_7, 4.0 (doublet, $|J_{PH}| = 12.5$ Hz, triplet, $|J_{6,7}| = 3.5$ Hz), H_3, 4.21 (singlet), total of H_7 and H_3 = 3.92 H; H_1, 6.2 (1.97 H, doublet $|J_{1,2}| = 2.9$ Hz), 6.95 (1.95 H); simultaneous irradiation at the resonance frequency of phosphorus and H_2 collapses the olefinic resonances to two singlets.

multiplets at τ 2.57, 6.12, and 6.61 in intensity ratios 4.90:1.96:6.14). Reduction with trichlorosilane in triethylamine-benzene[12] gives II (mp 58–59°) in 76% yield.[8]

In contrast, when benzene solutions of I are photolyzed through Pyrex, the major product[13] isolated (25% yield) after chromatography on silica gel is III (mp 43–45°).[8] The corresponding phosphine oxide (mp 101–102.5°),[8] formed by H_2O_2 oxidation of the crude product, was easier to isolate (30% yield), and could be reduced (Si_2Cl_6, C_6H_6)[16] back to the phosphine (III, 76% yield). The oxide shows at room temperature an nmr spectrum similar to that of the parent hydrocarbon:[5b] with the phosphorus spin decoupled, besides phenyl protons, two triplets ($|J| = 8.0$ Hz) at τ 3.90 and 4.32, a multiplet at 5.70, and a triplet ($|J| = 7.2$ Hz) at 7.42 in the intensity ratio 2.09:3.90:1.77. Upon cooling to −96° the pattern changes to multiplets at τ 3.89, 4.31, 7.22, and 7.84 in the intensity ratio 2:2:3:1. The kinetic parameters, estimated as $E_a = 7$ kcal, $\log A = 9$, are similar to those measured for the hydrocarbon.[5b] The nmr features of the phosphine III are similar: at ambient temperature in C_6D_6 multiplets at τ 2.89, 4.47, 6.25, and 7.54 of intensities 5.12:1.95:3.88:2.05; at −92° in $CFCl_3$–CD_2Cl_2, aromatics and multiplets at τ 4.16, 4.62, 6.76, and 7.42 of intensities 3:1:1:3.

Considering what is known about related photochemical reactions, the difference between the photolyses leading to V and VI (and then to the oxide of II) and the photolysis leading to III appears to be the difference between a singlet[17] and triplet reaction.[18] The mechanism for the formation of III may[18a–c] be that indicated below.



Acknowledgments. We are grateful to N. J. Turro for advice, Badische Anilin und Sodafabrik, A.G., for gifts of cyclooctatetraene, and the National Institutes of Health (MH-08912) for its support.

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[12] (a) H. Fritsche, V. Hasserodt, and F. Korte, *Chem. Ber.*, **98**, 171 (1965); (b) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967).

[13] Other chromatography fractions showed peaks attributable to 9-phenyl-9-phosphabicyclo[6.1.0]nonatriene,[1,14] and to the phosphorus epimer of I.[1,15]

[14] *Cf.* A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 762 (1967).

[15] *Cf.* K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 4958 (1965).

[16] K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 2788 (1969).

[17] J. Saltiel, R. M. Coates, and W. G. Dauben, *ibid.*, **88**, 2745 (1966).

[18] (a) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969); (c) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968); (d) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *ibid.*, **90**, 4465 (1968); (e) L. A. Paquette and G. R. Krow, *ibid.*, **90**, 7149 (1968); (f) J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967).

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Received November 6, 1969

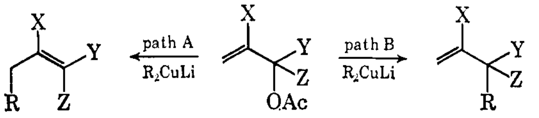
Stereoselective Synthesis of Olefins.[1] Reaction of Dialkylcopper–Lithium Reagents with Allylic Acetates

Sir:

The recently reported reaction[2] of organocopper–lithium complexes[3] with a steroidal allylic acetate to give alkylated *trans*-trisubstituted olefins in 33–40% yield suggested that such reactions might be stereospecific. We wish to report a preliminary investigation of the scope, stereoselectivity, and synthetic utility of this unusual reaction and to describe a novel application to synthesis of stereoisomers of juvenile hormone.

In reactions of dialkylcopper–lithium "ate"[4] complexes[5] with acyclic allylic acetates of type **1**, we have found that *two* alkylation paths are generally available: displacement of acetate with allylic rearrangement (path A) and direct displacement (path B). Both the olefin isomer ratio from path A and the extent of path B are highly predictable.

Scheme I



1, X, Y, Z = H or alkyl
Y > Z

Alkylations summarized in Table I indicate that *trans*-trisubstituted olefins are formed stereoselectively in high yield from **1** when (i) X is equal to or smaller than the entering alkyl of reagent and (ii) Z is hydrogen. When the substituent Y in **1** contains potential coordinating ligands for copper(I), a slight decrease in stereoselectivity is seen (**3**[6,7] and **4**[7,8] *vs.* **2**), but when Y is ethoxycarbonyl in **6**,[7,9] alkylation is completely inhibited.

Direct displacement of acetate in **2**, **3**, and **4** is a very minor reaction (**1**, Z = H) when ether is the solvent, but modification of the coordinated reagent by using tetra-

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[1] Contribution No. 2 from the Research Laboratory of Zoecon Corp.

[2] P. Rona, L. Tökes, J. Tremble, and P. Crabbé, *Chem. Commun.*, 43 (1969).

[3] (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966); (b) H. O. House and W. F. Fischer, Jr., *ibid.*, **33**, 949 (1968); (c) H. Gilman, R. G. Jones, and L. A. Woods, *ibid.*, **17**, 1630 (1952); (d) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969).

[4] W. Tochtermann, *Angew. Chem. Int. Ed. Engl.*, **5**, 351 (1966); G. Wittig, *Quart. Rev.* (London), **20**, 191 (1966).

[5] Prepared by titration of cuprous iodide (1.2 equiv) with alkyllithium (2.3 equiv) in ether, avoiding excess alkyllithium by use of the Gilman I test: H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, **47**, 2002 (1925). Though represented as R_2CuLi, these reagents are probably solvated tetrahedral metal clusters.

[6] Prepared from 2-methylhept-2-en-6-one by ketalization, hematoporphyrin-photosensitized oxygenation (methanol), sodium borohydride reduction, acetylation, and chromatography; *cf.* C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

[7] Satisfactory elemental analyses and infrared and nmr spectra were obtained (Varian T-60 or HA-100 spectrometers using deuteriochloroform solutions with tetramethylsilane as internal reference) for this compound.

[8] Prepared from methyl *trans*-3,7-dimethylocta-2,6-dienoate by "one-flask" photosensitized oxygenation in pyridine, *in situ* reduction of hydroperoxides with trimethyl phosphite (2 equiv, 5°), and selective acetylation of the secondary allylic alcohol with acetic anhydride, followed by silica chromatography.

[9] Prepared in 40% yield from ethyl 3-methyl-2,3-epoxybutanoate and 15% acetic anhydride in refluxing acetic acid.