agreement is found for the trans and cis olefin conformations.

For both I and II the initial stage almost certainly involves attack on the double bond rather than the C–Br bond.[14] In view of the extensive evidence for anti-Markovnikov addition to olefins,[15] our reults suggest that I involves a facile 1,2-chlorine migration, probably with a bridged intermediate.[16] The product chloroolefin thus should have Cl on the carbon to which Br was originally bonded. This was verified for Ib and Ic by analysis of fragment ion mass peaks. For II a bond migration mechanism *via* $ClCH_2\dot{C}HCH_2Br \rightarrow ClCH_2CH{=}CH_2 + Br\cdot$ is plausible.[17] The RRKM theory predicts statistical lifetimes of $\gtrsim 2 \times 10^{-12}$ sec for Br emission from the activated chlorobromoalkyl radical in both reactions I and II. The longer lifetime inferred for I thus suggests that the 1,2-chlorine migration is the rate-limiting process which makes the product angular distributions more symmetrical and the energy distributions more statistical for I than for II.

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(15) J. F. Harris, *J. Amer. Chem. Soc.*, **84**, 3148 (1962); F. S. Dainton and B. E. Fleischfressen, *Trans. Faraday Soc.*, **62**, 1838 (1966).

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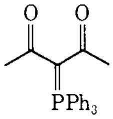
Formation of an Ylide Dianion and Its Application to the Construction of an Eight-Membered Ring

Sir:

The generation of a new anionic center adjacent to a carbonyl group already engaged in the stabilization of an existing electron donating center is a well-established phenomenon[1] and presumably reflects the ability of such a carbonyl unit to stabilize additional electronic charge. The generation of new, more reactive centers is further facilitated by the resistance of the electron-rich carbonyl group to nucleophilic attack by the highly reactive bases necessary for the formation of the new anionic center. It therefore seemed reasonable that carbonyl stabilized carbanions might also be formed in neutral systems containing a carbonyl group already engaged in charge stabilization such as found in acyl ylides, and indeed we[2] and others[3] have found that a highly reactive ylide anion is readily formed from acetylmethylenetriphenylphosphorane upon treatment with *n*-butyllithium or lithium diisopropylamide.[4]

We now wish to report the formation of both the mono- and dianion (**2** and **3**, respectively) from the diacyl ylide diacetylmethylenetriphenylphosphorane (**1**)[5] and the potential utility of dianion **3** in the construction of difficultly obtained ring systems.

Treatment of **1** with 1.2 equiv of either *n*-butyllithium or lithium diisopropylamide in THF at −78° for 5 min gives a highly colored solution containing ylide anion **2** which when treated with methyl iodide results in the formation of the substituted ylide **4**[6] (R_1 = H, R_2 = Me) in 66% yield. Likewise, treatment of **2** with *n*-propyl iodide at room temperature for 0.5 hr gives the corresponding monoalkylated ylide **4** (R_1 = H, R_2 = Pr) in good yield. Ylide anion **2** is stable at 60° for at least 10 min but is not exceptional in its nucleophilicity. Alkylation with *n*-propyl bromide gives **4** (R_1 = H, R_2 = Pr) in only 10% yield after 1 hr at room temperature and a reaction time of 10 hr is required to give a yield comparable to that obtained with *n*-propyl iodide.



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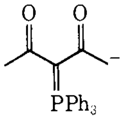

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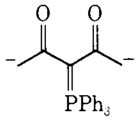

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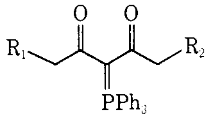


4

Treatment of the initially formed red monoanion **2** with an additional 1.1 equiv of lithium diisopropylamide at −78° for 0.5 hr results in the formation of the black dianion **3**. Addition of excess methyl iodide to the solution containing **3** gives the dialkylated ylide **4** (R_1 = R_2 = Me) in 71% yield along with a 12% yield of monoalkylated ylide **4** (R_1 = H, R_2 = Me).[7] The increased nucleophilicity of ylide dianion **3** is evidenced by the immediate discharge of its characteristic dark color upon addition of methyl iodide at −78° while complete discharge of the lighter color characteristic of the resulting monoanion requires 0.5 hr at room temperature. Treatment of ylide dianion **3** with 1 equiv of *n*-propyl bromide at −78° for 5 min followed by quenching with water gives the substituted ylide **4** (R_1 = H, R_2 = Pr) in good yield which is in sharp contrast to the relatively slow alkylation observed with anion **2** when treated with the same reagent.

Nmr studies of acetylmethylenetriphenylphosphoranes[8] have indicated the existence of a conformational

(1) For a recent review of the chemistry of dianions of β-dicarboxyl compounds see T. M. Harris and C. M. Harris, *Org. React.*, **17**, 155 (1969).

(2) M. P. Cooke, Jr., *J. Org. Chem.*, in press.

(3) J. D. Taylor and J. F. Wolf, *J. Chem. Soc., Chem. Commun.*, 876 (1972).

(4) A related dianion of a β-keto phosphonate has also been reported: P. A. Grieco and C. S. Pogonowski, *J. Amer. Chem. Soc.*, **95**, 3072 (1973).

(5) P. A. Chopard, R. J. G. Searle, and F. H. Devitt, *J. Org. Chem.*, **30**, 1015 (1965).

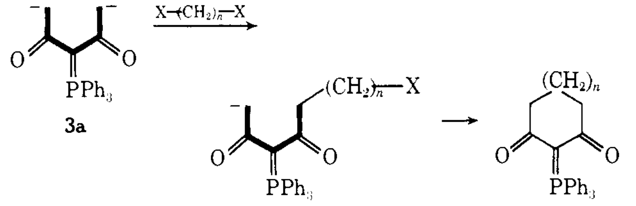
(6) Elemental analyses and spectral properties of all new compounds were in accord with assigned structures.

(7) While the formation of alkylated ylide might be explained by sequential formation of monoanions which are subsequently alkylated, we have found that treatment of **1** with 2.2 equiv of lithium diisopropylamide followed by immediate addition of excess methyl iodide gives predominantly monoalkylated ylide **4** (R_1 = H, R_2 = Me) while the dialkylated ylide **4** (R_1 = R_2 = Me) is found to be the major product when the addition of methyl iodide is delayed for 0.5 hr. The absence of 1,1-dimethylated ylide, whose formation might be expected in a scheme involving sequential anion formation, lends further support to the argument that dianion **3** is the reactive intermediate.

(8) (a) H. I. Zeliger, J. P. Snyder, and H. J. Bestman, *Tetrahedron Lett.*, 3313 (1970); (b) I. F. Wilson and J. C. Tebby, *ibid.*, 3769 (1970).

preference in these compounds in which the carbonyl oxygen adopts a cis orientation with respect to the phosphonium group. Variable temperature studies also indicate the presence of a high barrier to the carbon–carbon bond rotation required for the adoption of the trans conformation. In light of these results the presence of a single methyl resonance in the nmr spectrum of **1** suggests that this ylide exists in a "U" conformation[9] in which both oxygen atoms are cis to the phosphonium group in that the methyl groups present in the "sickle" conformation[9] would likely be nonequivalent.[10] In the absence of an appreciable alteration of the barrier to the bond rotations required for conformer–conformer interconversion, dianion **3**, derived from conformationally rigid **1**, would likewise possess the "U" conformation depicted in **3**, forcing a cis, proximal relationship between the nucleophilic centers. In this event dialkylation of **3a** with difunctional alkylating agents could result in ring formation owing to a favored intramolecular alkylation within the intermediate ylide anion **5**.

Attempts to effect such a ring closure by the alkylation of **3** with either methylene iodide or 1,2-dibromoethane failed to give identifiable products.[11] However, treatment of **3** (prepared from **1** and *n*-butyllithium) with 1,3-diiodopropane results in the formation of the desired cyclic ylide **6** ($n = 3$), mp 139–140°, isolated in 25% yield.[12,13] *Anal.* Calcd for $C_{26}H_{25}O_2P$: C, 77.98; H, 6.29. Found: C, 78.00; H, 6.12.



Evidence for the indicated structure of **6** ($n = 3$) is provided by its pmr spectrum ($CDCl_3$) which contains three broad resonance peaks at τ 2.39, 7.05, and 8.22 with an integral ratio of 15:4:6 representing phenyl, methylene adjacent to carbonyl, and remaining ring methylene protons, respectively. The infrared spectrum (KBr) of **6** ($n = 3$) contains carbonyl bands at 1590 and 1540 cm^{-1} comparable to the bands (1590, 1535 cm^{-1}) present in ylide **4** ($R_1 = R_2 = Me$). The presence of a molecular ion at *m/e* 400 in its mass spectrum further supports the proposed structure.

The unusual formation of an eight-membered ring by this type of intramolecular process, normally unfavorable in the formation of medium-sized rings, suggests great potential utility for the construction of difficultly obtained ring systems by the use of such conformationally restricted reagents. We are presently exploring the utility of this concept.

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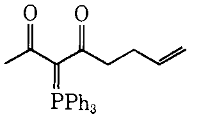
[10] The "W" conformation[9] would also allow methyl group equivalence but does not permit the cis oxygen–phosphonium group relationship suggested by chemical shift data.[8]

[11] The color of **3** is immediately discharged upon the addition of 1,2-dibromoethane suggesting that this reagent may be susceptible to a facile 1,2 debromination.

[12] No attempt has been made to optimize the yield or this reaction.

[13] When dianion **3** is prepared from **1** and lithium diisopropylamine and treated with 1,3-diiodopropane only a trace of cyclic ylide **5** is formed and **i** is observed to be the major product. This product is apparently the result of a base promoted dehydroiodination of either the alkylating agent or of the intermediate iodide **5** ($n = 3$, $X = I$). The intervention of such a process may be the result of the enhanced basicity of one of the anionic species in the presence of the diisopropylamine generated in the anion forming step. Such an effect has been observed with alkyllithium reagents in the presence of amines.[14]



i

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Fluorescence Characteristics of Phytochrome and Biliverdins

Sir:

Fluorescence of phytochrome (P_r) in solution has been reported by Hendricks, *et al.*,[1] and Correll, *et al.*[2] The latter workers obtained the fluorescence maximum of purified rye phytochrome in solution at 672 nm. More recently, however, highly purified and proteolytically undegraded phytochrome from rye showed no fluorescence in solution at room temperature.[3] The lack of fluorescence at room temperature has been confirmed in the present work. This communication describes low-temperature fluorescence characteristics of purified phytochrome and its model bilinoid pigments, biliverdin and biliverdin dimethyl ester.

Phytochrome was isolated from rye seedlings grown in the dark and was purified (absorbance at 280 nm/absorbance at 665 nm = 1.46) according to Tobin and Briggs.[3] Biliverdin (Sigma Chemical Co.) and biliverdin dimethyl ester (synthesized according to the literature[4]) were purified on various thin-layer chromatographic adsorbents. The best purification of the former was achieved by chromatography on polyamide layer with methanol–water (3:1), as described by Petryka and Watson.[5] Fluorescence spectra (uncorrected for detector response) were recorded on a high-resolution spectrometer with a single photon counting detector as described recently.[6]

Figure 1 shows the fluorescence spectrum of phytochrome at 14°K. In addition to the "normal" fluorescence maximum at 674.6 nm, there appears an unexpected fluorescence at 440 nm when the molecule is excited in the region of its second absorption band with

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[2] D. L. Correll, E. Steers, Jr., K. M. Towe, and W. Shropshire, Jr., *Biochim. Biophys. Acta*, **168**, 46 (1968).

[3] E. Tobin and W. Briggs, *Photochem. Photobiol.*, submitted for publication.

[4] D. A. Lightner and D. C. Crandall, *FEBS* (*Fed. Eur. Biochem. Soc.*) *Lett.*, **20**, 53 (1972).

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