

A DIBENZOCYCLONONATETRAENE PHOSPHONIUM YLIDE¹

Mordecai Rabinovitz and Aviv Gazit,

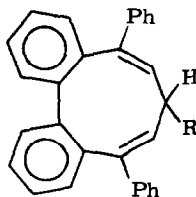
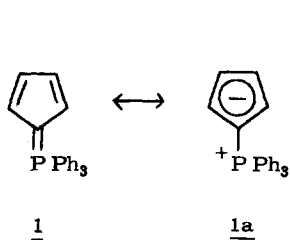
Department of Organic Chemistry,

The Hebrew University of Jerusalem, Jerusalem, Israel

(Received in UK 23 June 1972; accepted for publication 6 July 1972)

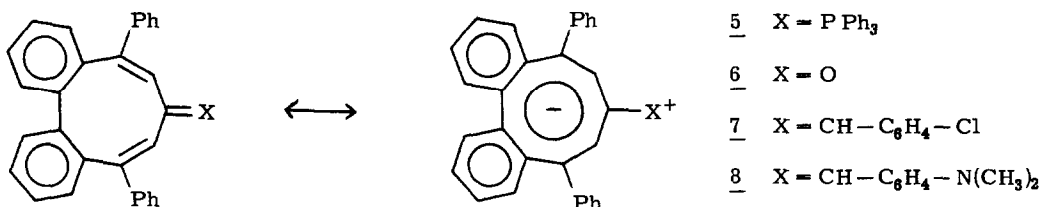
Cyclopentadiene phosphonium ylide 1 is highly stable and relatively unreactive, e.g., in the Wittig reaction. This behavior has been attributed to its "aromaticity", i. e., a large contribution of the dipolar ylide structure 1a in the ground state.^{2,3} It seemed of interest to study the higher "homologous" ylides of 1, and we wish to report the synthesis and properties of an annelated derivative of cyclononatetraenylidene phosphorane 5.⁴

Reaction of 2,7-diphenyl-3,4:5,6-dibenzocyclononatetraene 2,⁵ with N-bromosuccinimide (3 hrs., reflux, carbon tetrachloride) yielded the unstable bromo derivative 3. Nmr (CDCl₃) δ = 7.00, multiplet; 5.5 ppm triplet, 1 H, J = 5 Hz.⁶ Reaction of 3 with triphenylphosphine (carbon tetrachloride, reflux) yielded 60% of the triphenylphosphonium bromide 4, white crystals, m.p. 211° (anal. calc. for C₄₇H₃₈BrP: C, 79.3; H, 5.1; Br, 11.3; P, 4.4. Found C, 78.8; H, 5.4; Br, 12.0; P, 4.2). Treatment of 4 in ethanol with 25% aqueous ammonium hydroxide precipitated deep red-violet crystals of the phosphorane 5, m.p. 180° (80% yield). $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 259 (ϵ 29,300), 266 (30,000), 272 (29,100), 300 (31,600), 435 nm (2,330). Nmr (CDCl₃) δ = 7.2-8.0 ppm, multiplet.⁸ The phosphorane 5 appears to be stable at room temperature under argon, but it reacts rapidly with oxygen to give the ketone 6⁵ and triphenyl phosphine oxide. Hydrolysis of 5 gave the hydrocarbon 2 and triphenylphosphine oxide. Reaction of 5 with aldehydes (reflux in



- 2 R = H
3 R = Br
4 R = P⁺Ph₃Br⁻

benzene, 5 hrs., argon atmosphere) gave the nonafulvenes 7 and 8 (9% and 5% yields, respectively),⁹ whilst reaction with fluorenone and tropone failed to give the corresponding mixed fulvalenes. Heating the bromine 3 with Ph_3As and dibenzyl sulphide did not yield the expected salts. Due to the reactivity of the phosphorane 5 towards oxygen its dipole moment could not be measured. In the nmr spectrum the vinylic protons merge with the aromatic multiplet, the former being shifted to lower field relative to the respective absorption in the nonafulvenes.¹⁰ The long wave band in the uv is shifted to shorter wave lengths in more polar solvents,¹¹ suggesting that this band is due to an intramolecular charge transfer, related to a contribution of a dipolar ylide to the ground state. This shift is considerably smaller than in the cyclopentadiene ylide 1. All these properties show that compound 5 is structurally intermediate between the stabilized 1 and the normal reactive unstabilized phosphoranes.



References

1. Fulvenes and Thermochromic Ethylenes, Part 74.
2. For recent literature see: D. Lloyd and M. I. C. Singer, *Tetrahedron*, **28**, 353 (1972); B. H. Freeman, D. Lloyd and M. I. C. Singer, *Tetrahedron*, **28**, 343 (1972). For earlier literature see: A. W. Johnson, "Ylide Chemistry," Academic Press, New York, 1967.
3. Z. I. Yoshida et al., *Tetrahedron Letters*, 1519, 1523, 1527 (1971).
4. A recent attempt to prepare cyclononatetraene sulphonium ylide has failed. E. W. R. Casper, Ph. D. Thesis, Columbia University, N. Y., 1969.
5. M. Rabinovitz, E. D. Bergmann and A. Gazit, *Tetrahedron Letters*, 2671 (1971).
6. The diallylic proton of 5-iodocyclopentadiene appears at 5.54 ppm.⁷
7. R. Breslow and J. M. Hoffman, Jr., *J. Am. Chem. Soc.*, **94**, 2110 (1972).
8. Due to the high reactivity of 5, a correct analysis was secure only for phosphorus.
9. The products were identified by TLC, nmr, ir and mixed m.p. with authentic samples.
10. M. Rabinovitz and A. Gazit, *Tetrahedron Letters*, 721 (1972).
11. $\lambda_{\text{max}}^{\text{C}_6\text{H}_{12}}$ 260, 266, 273, 295, 442 nm; $\lambda_{\text{max}}^{\text{C}_6\text{H}_8}$ 300, 444 nm; $\lambda_{\text{max}}^{\text{EtOH}}$ 260, 266, 273, 300, 435 nm.