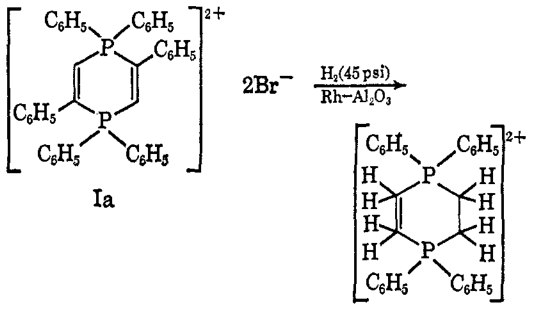
Hydrogenation of Ia employing 5% rhodium on alumina at 45 psi in methanol gave colorless 1,1,2,4,4,5-hexaphenyl-1,4-diphosphoniacyclohexane dibromide (IIIa), mp 269–272° (from acetonitrile–methanol). *Anal.* Calcd for $C_{40}H_{36}Br_2P_2{\cdot}H_2O$: C, 63.49; H, 5.03; Br, 21.16; P, 8.70. Found: C, 63.33; H, 4.89; Br, 20.40; P, 8.77.



Ia

IIIa

(2)

Compound IIIa was also produced by the reaction of *cis*- or *trans*-β-styryldiphenylphosphines[7] (V) with hydrogen bromide in glacial acetic acid (eq 3). As in the case of Ia, the structure of IIIa was established through elemental analysis, solubility, infrared spectrum, formation and analysis of a picrate (IIIb), and proton nmr spectra (Table I).

$$\underset{\text{V}}{2C_6H_5CH{=}CHP(C_6H_5)_2} \xrightarrow[\text{HAc}]{\text{HBr}} \text{IIIa} \qquad (3)$$

Compound IIIb had mp 230–233° (from acetonitrile). *Anal.* Calcd for $C_{52}H_{40}N_6O_{14}P_2$: N, 8.12; Br, 0.00. Found: N, 8.00; Br, 0.00. Absorption in the visible region by Ia is not understandable in terms of the delocalization present in a β-styryldiphenylphosphonium salt since the benzyl bromide salts of *cis*- and *trans*-β-styryldiphenylphosphine (VI) are colorless.

Table III lists the ultraviolet absorbances of Ia and IIIa, along with those of *cis*- and *trans*-VI for comparison. Only a shoulder from the ultraviolet region was found in the visible spectrum of Ia.

Table III. Ultraviolet Absorptions of Methanol Solutions

Compd	λ, mμ	ε
Ia	267 (peak emerging from large shoulder)	18,600
IIIa	269 (shoulder covering the 218 region)	4,600
cis-VI	270	1,100
	218	2,400
trans-VI	278	2,500
	217	3,000

Support for extensive delocalization of the π cloud is obtained from the ^{31}P nmr data listed in Table IV.

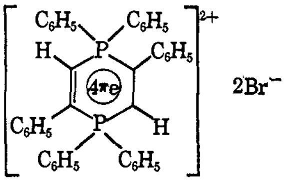
Table IV[a]

Compd	Shift
Ia	+3.5
IIIa	−20.4
IV	−2.8
cis-VI	−13.0

[a] At 40.5 Mc/sec; ^{31}P nmr shifts in parts per million of methanol solutions relative to an external standard of 85% H_3PO_4.

It is seen that the shielding of the phosphorus nucleus is substantially greater in Ia than in any other model compounds. In fact, Ia represents the first report of a phosphonium salt with a positive ^{31}P nmr shift. Most simple phosphonium salts display ^{31}P shifts in the −20- to −30-cps region.[8,9]

The above data are most easily accommodated by assuming delocalization of the π-electronic charge over the phosphorus atoms.



Acknowledgment. This work was supoorted by National Science Foundation Grant No. GP-3823.

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[7] A. M. Aguiar and T. G. Archibald, *Tetrahedron Letters*, **45**, 5541 (1966).

[8] M. M. Crutchfield, Monsanto Co., St. Louis, Mo., private communication.

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Heavy-Atom Solvent Effect on the Photodimerization of Acenaphthylene

Sir:

Owing to their ability to enhance spin–orbit coupling, heavy-atom solvents have been used extensively in the study of singlet–triplet absorption and emission spectra.[1] In addition to an effect on the radiative processes, it is known that these solvents often promote nonradiative singlet-to-triplet intersystem crossing.[2] Two recent studies have attempted to make use of this external heavy-atom effect to affect increased intersystem crossing in photochemical reactions. However, no change was observed when heavy-atom solvents were used in a study of the type II photoelimination reactions of aliphatic ketones,[3] nor was an effect observed in the photodimerization of coumarin.[4] Both of these systems contain n–π* excited states. El-Sayed[5] has pointed out that in carbonyl compounds the spin–orbit perturbation due to the carbonyl group is comparable to or larger than an internal heavy-atom perturbation due to halogen substitution on the carbonyl-containing molecule. In addition, the internal heavy-atom perturbation is expected to be much larger than the external perturbation due to a heavy-atom solvent.

In this note we wish first to present evidence to document the heavy-atom solvent effect on the photodimerization of a system not containing n–π* states and second to show that in the two cases easily com-

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[1] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949); M. Kasha, *ibid.*, **20**, 71 (1952); S. P. McGlynn, T. Azumi, and M. Kasha, *ibid.*, **40**, 507 (1964); R. F. Borkman and D. R. Kearns, *Chem. Commun*, 446 (1966).

[2] A. R. Horrocks, T. Medinger, and F. Wilkinson, *Photochem. Photobiol.*, **6**, 21 (1967); S. P. McGlynn, J. Daigre, and F. J. Smith, *J. Chem. Phys.*, **39**, 675 (1963); S. Siegel and H. S. Judeikis, *ibid.*, **42**, 3060 (1965).

[3] P. J. Wagner, *ibid.*, **45**, 2335 (1966).

[4] H. Morrison, H. Curtis, and T. McDowell, *J. Am. Chem. Soc.*, **88**, 5415 (1966).

[5] M. A. El-Sayed, *ibid.*, **41**, 2462 (1964).

pared that the effect is proportional to the square of the spin–orbit coupling factor (ζ^2).

It has been shown[6,6a] that the *cis* and *trans* dimers from the photolysis of acenaphthylene arise from two distinct excited states. The *cis* dimer is formed predominantly *via* an excited singlet state or more probably from a singlet excimer, while the *trans* dimer is formed *via* the triplet state. Since the probability of a singlet–triplet transition resulting from spin–orbit coupling depends inversely upon the square of the energy separation between the two states, one would expect a greater probability of crossing from a perturbed excited singlet to the triplet state than from the triplet to the ground state. Therefore, in the acenaphthylene system an increased triplet yield should result in an increased conversion to the *trans* isomer. The results of our experients are shown in Table I. All photolyses were carried out using the apparatus and analytical procedure previously described.[6] As can be seen in Table I, both the total conversion to products and the relative amount of the *trans* dimer produced are markedly affected by the presence of a heavy atom in the solvent. For example, a change from pure cyclohexane to cyclohexane containing 10 mole % ethyl iodide increased, by a factor of 2, the total conversion and produced an 11-fold increase in the amount of *trans* dimer formed.[7] The amount of *trans* produced in propyl bromide solvents was found to be linearly dependent upon the mole per cent of propyl bromide for percentages where the total amount of conversion did not appreciably affect the probability of bimolecular reaction.

Table I. Heavy-Atom Solvent Effect on Photodimerization of Acenaphthylene

Solvent[a]	Total amount of dimer formed, g	Acenaphthylene recovered, g	*trans*, g	*cis*, g
Cyclohexane	6.51	8.40	1.09	5.42
Benzene	9.62	5.27	2.82	6.80
n-Butyl chloride	7.14	7.76	2.12	5.02
n-Propyl bromide in cyclohexane				
10 mole %	5.98	9.05	3.45	2.53
25 mole %	8.03	7.01	5.03	3.00
50 mole %	10.99	4.05	7.49	3.50
100 mole %	14.07	0.84	10.01	4.06
10% Ethyl iodide in cyclohexane	13.74	1.14	10.96	2.78

[a] All determinations were made with 15.2 g of acenaphthylene in 150 ml of solvent; irradiation time 15 hr.

The probability of a radiationless transition is proportional to the square of the perturbing operator in an expectation value equation involving the two states between which the transition is occurring. For transitions between states of different multiplicity, vibronic and/or spin–orbit perturbation operators are important. However, if there is strong electronic coupling of the excited states with the heavy-atom solvent states, the most important operator may generally be the spin–orbit operator.[8]

The probability then of an intersystem crossing from a singlet to a triplet state may be directly related to the square of the spin–orbit coupling factor ζ, the values of which are known for atoms. Since the coupling is related to the atomic number of the perturbing nucleus, the relative magnitude of coupling may be approximated by using the coupling factor for the heaviest atom in the solvent. Thus, to a first approximation, the relative probability of intersystem crossing in proceeding from *n*-PrBr to EtI would be given by $(\zeta_I/\zeta_{Br})^2$. Using the values $\zeta_I = 5060$ and $\zeta_{Br} = 2460$,[9] this ratio becomes equal to 4.2. Using the data for the formation of *trans* dimer in Table I (10% *n*-PrBr, EtI) and correcting for the amount of *trans* formed in pure cyclohexane, the ratio $trans_{EtI}/trans_{PrBr}$ is equal to 4.18. The agreement between these two ratios is excellent. Investigations of the effect of other heavy-atom solvents as well as a comparison of external and internal heavy-atom effects on the photodimerization are currently in progress.

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[6] D. O. Cowan and R. L. Drisko, *Tetrahedron Letters*, 1255 (1967); D. O. Cowan, "Photochemistry: Recent Developments and Applications," Symposium, Houston, Texas, Feb 17, 1967; R. Livingston and K. S. Wei, *J. Phys. Chem.*, **71**, 541 (1967).

[6a] Note Added in Proof. All solvents were essentially transparent at the wavelengths used (>3300 A).

[7] A discussion of the *cis* dimer production is deferred until publication of the full paper since we have shown that the *cis* dimer arises from more than one excited state.

[8] S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

[9] E. V. Condon and G. H. Shortley, "Theory of Atomic Spectra," Cambridge University Press, London, 1959.

[10] Du Pont Postgraduate Teaching Fellow, 1965–1967.

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Formation of Spirononatriene and Heptafulvalene from an Attempt to Generate Cycloheptatrienylidene

Sir:

If the normal electrophilicity[1] of a singlet carbene is sufficiently suppressed by delocalization of electrons into its vacant p orbital, its behavior should resemble that of a nucleophile as a result of the nonbonded pair of electrons on the carbene carbon. In a number of cases[2] where adjacent heteroatoms (oxygen, nitrogen)

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[1] *Cf.* J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964, p 43; W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 164.

[2] Although the question of the actual intermediacy of nucleophilic carbenes in many cases has been clouded by the fact that the carbene dimers (*e.g.*, tetraaminoethylenes) give the same products with electrophiles[3] as would be expected from the carbene itself, there are still a number of cases that probably do indeed involve intermediate carbene formation (including, in fact, reactions of the dimer with electrophiles[3]). For examples of these as well as lead references to earlier work, see: D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966); R. W. Hoffmann and H. Hauser, *Tetrahedron*, **21**, 1891 (1965); H. Quast and S. Hunig, *Chem. Ber.*, **99**, 2017 (1966); *Angew. Chem. Intern. Ed. Engl.*, **3**, 800 (1964); H. Balli, *ibid.*, **3**, 809 (1964); H. Quast and E. Frankenfeld, *ibid.*, **4**, 691 (1965); H. W. Wanzlick and A. Hanns, *Chem. Ber.*, **99**, 1580 (1966); H. W. Wanzlick and H. J. Kleiner, *Angew. Chem. Intern. Ed. Engl.*, **3**, 65 (1964). For an excellent review of earlier work in this area, see H. W. Wanzlick, *ibid.*, **1**, 75 (1962). For the first example of an intermediate of this type, see R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

[3] D. M. Lemal, R. A. Lovald, and K. I. Kawano, *ibid.*, **86**, 2518 (1964); H. E. Winberg, J. E. Carnahan, D. D. Coffman, and M. Brown, *ibid.*, **87**, 2055 (1965); N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3000 (1963).