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	Ace-naphthyl-ene re-covered, 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.

(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.

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.

(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)

(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).

have served as the electron-donating groups this anticipated effect has manifested itself in an inertness to typical alkenes but reactivity with a wide variety of electrophiles.

A second mechanism for delocalizing electrons into the vacant p orbital of a singlet carbene and thereby accentuating its nucleophilicity is its incorporation into a conjugated ring in such a way as to make the vacant orbital an integral part of an aromatic system. The simplest example of this type of system, the two-π-electron cyclopropenylidene (1), has defied standard techniques for generating carbenes[4,5] but has been suggested as a possible intermediate in the reaction of a substituted cyclopropenyl carbamate with base. The evidence for this as an intermediate consists simply of the fact that it gives spiropentenes with electrophilic olefins[6] and no reaction with simple alkenes.[4]

1

2
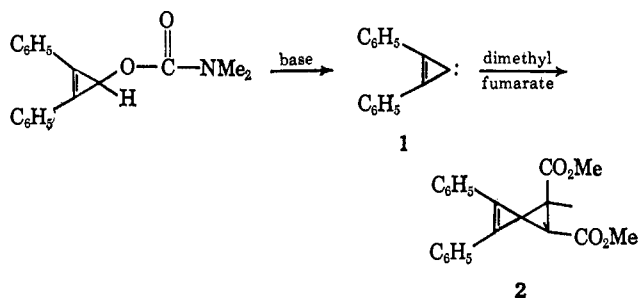
At this time we wish to report the results of our attempts to generate a potentially nucleophilic carbene in which the vacant p orbital is an integral part of a six-π-electron aromatic system—cycloheptatrienylidene[7] (3).

3
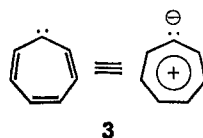
As a potential precursor to this species, tropone tosylhydrazone was synthesized in high yield from tropone via 7,7-dichlorocycloheptatriene. The tosylhydrazone was converted to its sodium salt (a muddy brown solid) with sodium hydride in tetrahydrofuran. Photolysis of the salt in tetrahydrofuran in the presence of typical alkenes gave the salt of p-toluenesulfinic acid and up to 50% of a photolytically unstable, almost black crystalline solid, but no indication of the spirononatriene adduct that would result from carbene addition to the alkene double bond. The dark solid was identified as heptafulvalene (5) by comparison of its properties with those reported for an authentic sample.[9]

(4) Unpublished results from these laboratories.
(5) R. Breslow and L. J. Altman (*J. Am. Chem. Soc.*, **88**, 504 (1966)) have pointed out that perhaps one factor contributing to the acidity of the ring hydrogen of n-propylcyclopropenone is contribution of a cyclopropenylidene resonance form.


(6) W. M. Jones and M. E. Stowe, *Tetrahedron Letters*, 3459 (1964).
(7) Generation of di- and triannelated cycloheptatrienylidenes has been recently reported by Murahashi, Moritani, and Nishino.[8] In view of the involvement of the aromatic rings in the conjugated systems of these intermediates, it is not surprising that their chemical properties resemble typical aryl-substituted alkylidenes.
(8) *Cf.* S. Murahashi, I. Moritani, and M. Nishino, *J. Am. Chem. Soc.*, **89**, 1257 (1967).

4

5   6
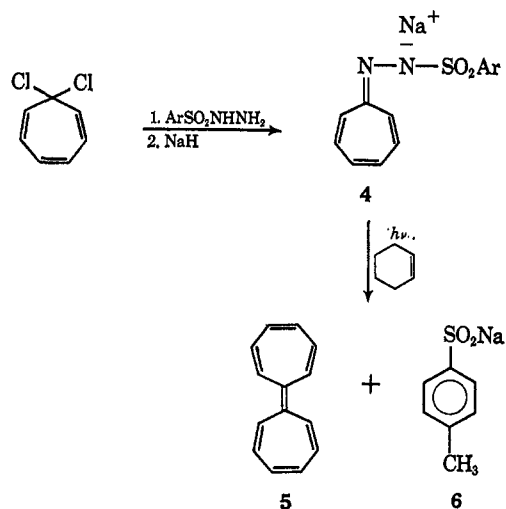
Even in the presence of electron-rich alkenes (*e.g.*, enamines) there was observed none of the spiro adduct but, again, only the dimer and sodium p-toluenesulfinate. However, when the photolysis was carried out in the presence of the electrophilic olefin, dimethyl fumarate, there was isolated, in addition to the sulfinate salt and the dimer, a 47% yield of the spirononatriene 7 which, formally, would arise from addition of cycloheptatrienylidene to the fumarate double bond.

7

47%

+ 5 + 6
10%
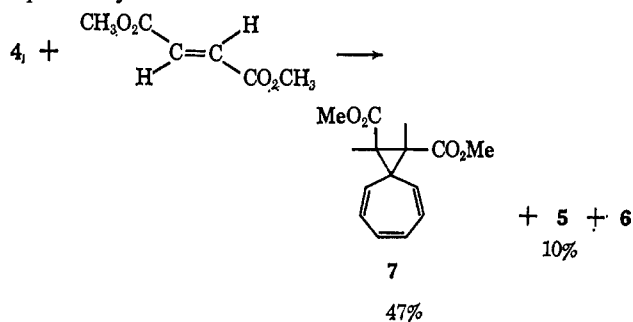
Both analyses[10] and spectra support the interesting structure assigned to 7. In the infrared it showed a single carbonyl absorption at 1720 cm^{-1}, in the ultraviolet it showed a single maximum at 262 mμ (ϵ 2800), and in the nmr it showed single peaks at τ 7.65 (cyclopropyl hydrogens) and 6.32 (methyl hydrogens), a doublet at τ 4.59 (*ortho* ring hydrogens), and a multiplet at τ 3.52 (remaining cycloheptatriene ring hydrogens), with areas in the ratio 2:6:2:4, respectively. Additional support for the assigned structure resides in its facile conversion under acidic conditions to the corresponding heptafulvene 8. For example, 1% HCl

8

9
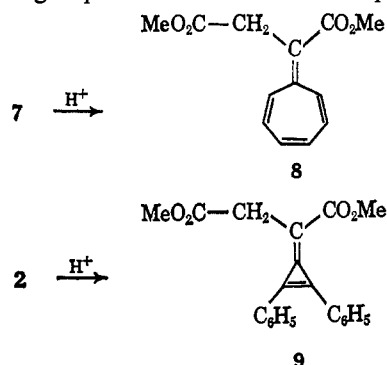
(9) W. von E. Doering in "Theoretical Organic Chemistry. The Kekule Symposium," Academic Press Inc., New York, N. Y., 1959, p 44.
(10) All new compounds gave acceptable analyses.

in ethanol effects complete conversion in 30 min, acid alumina causes rapid isomerization, etc. Both analyses and spectra confirm the assigned structure. This reaction finds analogy in the highly facile acid-induced ring opening of the spiropentene **2** to the triafulvene **9**.[6]

The nature of the intermediate(s) that leads to heptafulvalene and spirononatriene is, of course, questionable.[11] However, whatever its structure, the products that it gives rise to are those anticipated for a carbene (dimer formation) of low electrophilicity (no reaction with alkenes) and relatively high nucleophilicity (reaction with electrophilic double bonds).

Acknowledgment. The authors gratefully acknowledge the support of this research by the U. S. Army Research Office, Durham.

(11) Reaction of heptafulvalene with dimethyl fumarate in a reaction analogous to that proposed by Lemal[3] to explain the products of reaction of electrophiles with tetraaminoethylenes was independently excluded as the source of the spirononatriene.

(12) (a) Alfred P. Sloan Fellow, 1963–1967. (b) Gulf Oil Fellow, 1966–1967.

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Reversible Combination of Molecular Nitrogen with a Cobalt Complex. Exchange Reactions of Nitrogen–Tris(triphenylphosphine)cobalt with Hydrogen, Ethylene, and Ammonia

Sir:

Previously we reported that molecular nitrogen combines with a cobalt complex in the reaction of cobalt acetylacetonate, diethylaluminum monoethoxide, and triphenylphosphine carried out in an atmosphere of nitrogen.[1] We wish to report now on some exchange reactions of the isolated complex, nitrogen–tris(triphenylphosphine)cobalt (I), with molecular hydrogen, ethylene, and ammonia. Recently, ruthenium[2,3] and iridium[4] complexes, which are combined with molecular nitrogen, have been reported, but no report has been made, as far as we know, on the reaction of a nitrogen-coordinated complex with these gases.

When a benzene solution of nitrogen–tris(triphenylphosphine)cobalt (I) is swept or shaken with purified hydrogen gas, the original red color changes to yellow with a loss of molecular nitrogen from the complex, as proved by infrared and mass spectrometry. The sharp strong band at 2088 cm^{-1} assigned to the stretching vibration of the coordinated nitrogen molecule disappears rapidly with the appearance of new bands at about 1940 and 1760 cm^{-1}. Sweeping the benzene solution of I with argon gas does not affect the original spectrum at all. On concentrating the yellow benzene solution, light yellow crystals are isolated which can be recrystallized from toluene. *Anal.* Calcd for $C_{54}H_{47}P_3Co$ (II): C, 76.50; H, 5.59. Found: C, 76.72; H, 6.00; N, 0. Thermal decomposition of the yellow complex II releases hydrogen and benzene. On sweeping the yellow

(1) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967).
(2) A. D. Allen and C. V. Senoff, *ibid.*, 621 (1965).
(3) A. E. Shilov, A. K. Shilova, and Yu. G. Borodko, *Kinetika i Kataliz*, 7, 768 (1966).
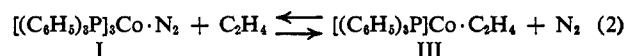(4) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, 88, 3459 (1966); 89, 169 (1967); 89, 844 (1967).

solution of II with nitrogen, the ν_{N_2} band at 2088 cm^{-1} resumes the original intensity and the solution regains its initial red color. The cycle can be repeated many times, showing a reversible equilibrium.

$$[(C_6H_5)_3P]_3Co\cdot N_2 + H_2 \rightleftarrows [(C_6H_5)_3P]_3CoH_2 + N_2 \quad (1)$$
$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$
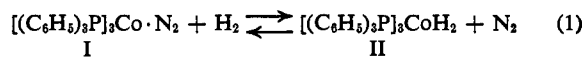
On sweeping the benzene solution of I with deuterium, a band is observed at 1260 cm^{-1} which may be assigned to a Co–D stretching vibration which is shifted from the band of Co–H stretching vibration at 1760 cm^{-1} by a factor of 1.4. The band at 1940 cm^{-1} was not observed in the spectrum of the benzene solution swept with deuterium, but no corresponding new band due to deuterium substitution appeared. The origin of the band at 1940 cm^{-1} is not clear at the moment.

When a benzene solution of I is swept with purified ethylene, the original red color darkens with the loss of the coordinated nitrogen molecule. The ν_{N_2} band at 2088 cm^{-1} disappears and new bands, which may be assigned to the C–H stretching vibration of the coordinated ethylene molecule, appear at about 2950 and 2850 cm^{-1}. Similar bands are observed in the spectrum of $[(C_6H_5)_3P]_2Ni\cdot C_2H_4$ prepared according to Wilke and Hermann.[5] On passing nitrogen through the solution, these bands disappear and the ν_{N_2} band resumes the original intensity, suggesting a reversible exchange reaction of the type

$$[(C_6H_5)_3P]_3Co\cdot N_2 + C_2H_4 \rightleftarrows [(C_6H_5)_3P]Co\cdot C_2H_4 + N_2 \quad (2)$$
$$\text{I} \qquad\qquad\qquad\qquad\qquad \text{III}$$

Tris(triphenylphosphine)cobalt coordinated with ethylene (III) can be isolated by the reaction of cobalt acetylacetonate, triphenylphosphine, and diethylaluminum monoethoxide in an argon atmosphere.[6] Combination of nitrogen with cobalt also takes place in the reaction of tris(triphenylphosphine)methylcobalt[1] with nitrogen gas.

Analogous reversible reaction of the nitrogen–cobalt complex is observed with ammonia as indicated by the reversible change of the ν_{N_2} band. The complex reacts irreversibly, however, with carbon monoxide and carbon dioxide. The details will be reported later.

(5) G. Wilke and G. Hermann, *Angew. Chem.*, 74, 693 (1962).
(6) Unpublished results.

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Reaction of Benzyne with Benzene. Effect of Silver Ion

Sir:

The decomposition of suspensions of benzenediazonium-2-carboxylate (1) in excess benzene at 45° is reported[1] to yield benzobarrelene (2), benzocyclooctatetraene (3), and biphenyl (4) (*cf.* run 8, Table I). The products were postulated to occur by 1,4 addition,[1] 1,2 addition (followed by valence bond isomerism),[1] and insertion[2a] reactions of benzyne (from 1) on benzene, respectively. These are the "accepted" prod-

(1) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, 85, 1798 (1963).