Assignment of the signals of the triphenylphosphine carbons is straightforward for all products, and is in accord with assignments given for similar compounds.[3-5]

For compounds **4-7**, assignment of the carbon signals of the substituent R can also directly be made from chemical shifts, C, P coupling constants, and relative intensities. Our data are in complete agreement with those presented earlier.[2]

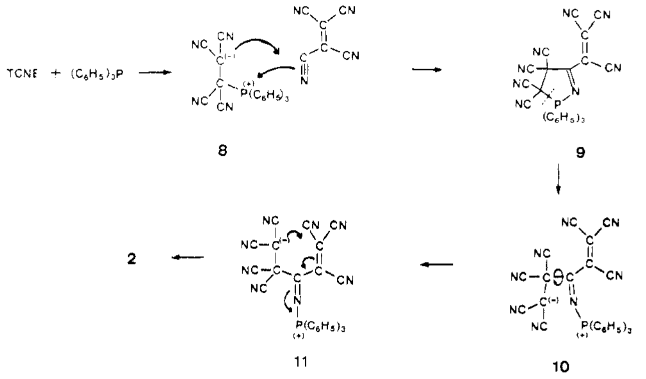
Although not all of the signals of the phosphazene substituent in **2** and **3** can be assigned to individual carbon atoms, the number of signals, their multiplicities, and intensities are fully consistent with the proposed structures. Thus, for compound **2** four signals for CN carbons with an intensity ratio of 1:2:2:2 are observed at 112.2 (CN at C-2), 107.8, 107.6, and 106.4 ppm (the intensities were measured at low pulse angles to avoid saturation).[6] For compound **3**, the CN carbons give rise to five signals of approximately equal intensity between 114.5 and 110.5 ppm. The sp^2 hybridized carbons C-1 and C-2 can directly be identified from their characteristic chemical shifts and C, P coupling constants. The chemical shifts indicate the presence of a strongly polarized double bond. The last of the three sp^3 carbon atoms C-3, C-4, and C-5 can be distinguished from the other two because of its large three-bond C, P coupling constant.

In compound **3**, the carbon signal at 118.2 ppm displays septet structure in the proton undecoupled spectrum, indicating coupling with the protons of two methyl groups (J = 4.2 Hz) as is expected for carbon C-6. That the signal at 158.8 ppm corresponds to a carbon atom with an attached NH$_2$ group is shown by the typical deuterium isotope effect on the chemical shift of this signal;[7] after addition of a 1:1 mixture of H$_2$O/D$_2$O to a Me$_2$SO-d_6 solution of **3**, the signal at 158.8 ppm appears as a triplet with an intensity ratio of 1:2:1 and a splitting of 2.0 Hz (at 25.2 MHZ) in the proton noise decoupled ^{13}C spectrum. The three signals correspond to carbons having a NH$_2$, NHD, and ND$_2$ group attached, displaying an isotope effect of 0.08 ppm/D atom, typical of a two-bond effect.[7]

As has been shown for triphenylphosphoranes,[4] bonding in triphenylphosphazenes can be discussed in terms of valence bond structures **a** to **c**, where the phosphonium saltlike structure **c** is only important for compounds in which the substituent R can stabilize the negative charge by resonance. The ^{13}C spectroscopic parameters in such compounds are expected to be similar to the ones observed in phosphonium salts (chemical shifts and C, P coupling constants or phosphonium salts are reported in the literature[3-5,8]).

From the parameters observed for **2** and **3** (especially chemical shifts of C-s and C-p) and ^1J (C-s, P), it can be concluded that valence bond structure **c** is important for the description of bonding in these compounds. The zwitterionic character in **2** and **3** is also evident from the large chemical shift difference between C-1 and C-2.

Recent investigations point to a completely different explanation for the formation of **2** to that presented earlier.[1]



Tetracyanoethylene and triphenylphosphine form rapidly a 1,3-dipolar intermediate (**8**) which subsequently reacts in a [3 + 2] cycloaddition with one of the cyano groups of TCNE forming a five-membered azaphospholene intermediate of structure **9**.

The adduct **8** is a new type of highly reactive 1,3-dipolar intermediate[9,10] with phosphorus as one of the terminal centers of a zwitterionic species which represents a reactive type without double bond. Cycloadditions of 1,3-dipolar species on nitrile groups have been reported by several authors[11-13] although the rate of reaction in general appears to be very slow. Reversible cleavage of the P-C bond in **9** gives rise to **10**, whereby further stabilization is enhanced by the dicyano methide group despite the large separation of the ionic centers.[14-16] Rotation about the C-C bond as indicated (**10** → **11**) and subsequent cyclization of the zwitterion leads to the formation of a new C-C bond between C-3 and C-4 yielding **2**.

Experimental Section

Compounds **2-7** were prepared by literature procedures.[1,2] The ^{13}C-NMR spectra were recorded on Varian XL-100/15 (25.2 MHz) and Bruker HX-360 (90.5 MHz) NMR spectrometers in the Fourier mode with either proton noise decoupling, coherent off-resonance decoupling, or gated noise decoupling (for undecoupled spectra or NOE suppression). The numbers of data points and sweep widths were chosen such that an accuracy of 0.05 ppm for chemical shifts and 0.2 Hz for C, P coupling constants was achieved.

Registry No.—**1a**, 17989-88-7; **1b**, 68014-24-4.

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Nucleophilicity of Cycloheptatrienyldiene Generated from a Nitrogen-Free Precursor. Evidence for a Free Carbene in the Decomposition of Tropone Tosylhydrazone Sodium Salt

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Received May 22, 1978

In a previous study of the reactivity of the aromatic carbene cycloheptatrienylidene (**1**) [and/or cycloheptatetraene (**5**)] with substituted styrenes in THF solution, a ρ value of +1.05 ± 0.05 (correlation coefficient 0.982) was determined.[2] From this it was argued that the reacting species has considerable

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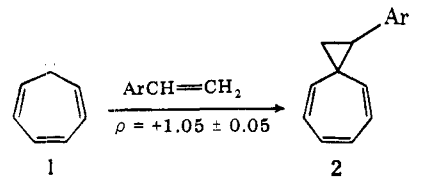
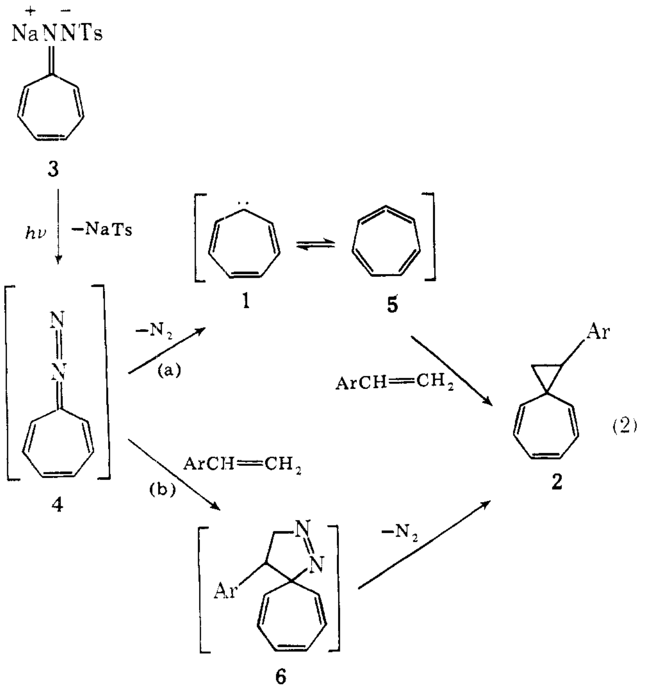


(1)

nucleophilic character, a property that is also consistent with its failure to react with normal alkenes and its facile reaction with electrophilic olefins such as dimethyl fumarate and fumaronitrile.[3]

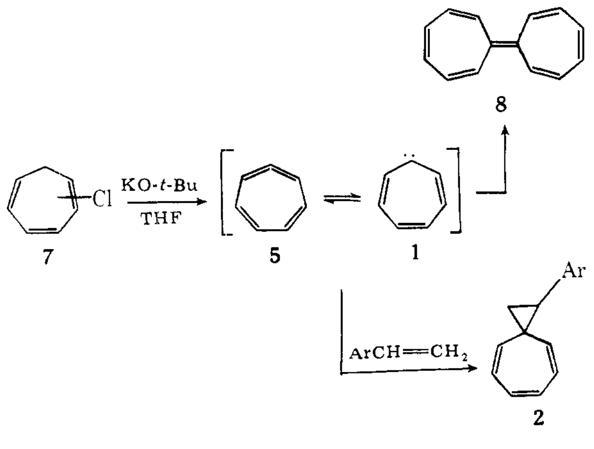
However, in that study, the tosylhydrazone sodium salt of tropone (**3**) was used as the progenitor of the reacting intermediate, which introduced the possibility that the intermediate might, in fact, be diazocycloheptatriene (**4**) rather than the carbene. This was of particular concern in this case because cycloadditions of diazoalkanes to substituted styrenes are known to give positive ρ values of about this magnitude.[4]



(2)

We therefore undertook to determine the ρ value of cycloheptatrienylidene–cycloheptatetraene generated from a nitrogen-free precursor. In this paper we report the results of our study.

It has been known for some time that the reaction of KO-*t*-Bu with a mixture of 1-, 2-, and 3-chlorocycloheptatrienes (**7**) gives, in almost quantitative yield, heptafulvalene (**8**).[5] Furthermore, in the presence of styrene, the same reaction yields the spirononatriene, **2** (Ar = Ph).[5] From this it appears that reaction of **7** with base gives an intermediate which shows the same properties as that derived from **3**. We therefore carried out a Hammett study of the addition of this intermediate to substituted styrenes.



(3a)

(3b)

Table I

X in p-$XC_6H_4CH{=}CH_2$	registry no.	k_X/k_H
CH_3O	637-69-4	0.49
CH_3	622-97-9	0.76
H	100-42-5	1.00
F	405-99-2	1.07
Cl	1073-67-2	1.60
Br	2039-82-9	1.88

The relative reactivities of the styrenes (k_{rel}) were calculated from the equation:

$$k_{rel} = k_X/k_H = (P_X/P_H)(S_H/S_X)$$

where P_X and P_H are the moles of substituted and unsubstituted products (**2**), respectively, and S_X and S_H the initial moles of substituted and unsubstituted styrenes.[6] With the exception of k_{CH_3}, all k_{rel} were determined by direct comparison with k_H, and were the average of two runs. The value for k_{CH_3}/k_H was obtained indirectly by measuring k_{CH_3}/k_{Cl} (average of three runs) and multiplying it by k_{Cl}/k_H (average of two runs).

The relative rate constant data (Table I) correlate well with the Hammett equation using σ values. The ρ value computed from a least-squares analysis is +1.02 ± 0.10 with a correlation coefficient of 0.982. This is essentially identical with that obtained from the tosylhydrazone salt, **3** (+1.05 ± 0.05), and leads to the conclusion that both precursors, **3** and **7**, give the same intermediate.[7] Since the intermediate from **7** cannot contain nitrogen, the common reactive species cannot be diazocycloheptatriene (**4**) and therefore must be the free carbene, **1** (and/or its allene isomer, **5**), via eq 2a and 3b.

Experimental Section

In a typical run, ~100–120 mg of **7** in 3 mL of dry THF was added via syringe over a 3-min period to a rapidly stirred solution of a 7- to 11-fold excess of a mixture of two styrenes plus 1.5 equiv of KO-*t*-Bu in dry THF. After stirring 2.5–3.0 h at room temperature (21–26 °C), the mixture was quenched with 10 mL of water and extracted with ether (3 × 20 mL). The combined ether extracts were washed with water (3 × 50 mL), then with 50 mL of saturated aqueous Na_2SO_4, and dried over $MgSO_4$. After evaporation of the solvent, most of the excess styrenes were removed at room temperature by bulb-to-bulb vacuum distillation. Product ratios were then determined by integrating the triplets in the NMR (at about δ 2.0) due to the benzylic cyclopropane hydrogens. The chemical shifts of these protons were sensitive enough to solvent to make it possible, by judicious choice of the mixture of $CDCl_3$ and C_6D_6, to effect a clean separation of the triplets, enabling direct product integration.

Except for that obtained from *p*-fluorostyrene, all products could be identified in the NMR by comparison to spectra of previously characterized spirononatrienes.[2] In the case of **2**, Ar = *p*-C_6H_4F, an authentic sample was prepared by reaction of **7** with KO-*t*-Bu in the presence of *p*-fluorostyrene using the procedure described above. Stirring of a $CHCl_3$ solution of the crude products in the air for a few hours to destroy the heptafulvalene, followed by column chromatography (silica gel/pentane), gave the spirononatriene as a light yellow oil: NMR ($CDCl_3$) δ 1.21 and 1.25 (overlapping d, J = 7.3 and 8.0 Hz, 2, cyclopropyl methylene), 2.08 (t, J = 7.6 Hz, 1, cyclopropyl methine), 5.02 and 5.39 (both d, both J = 9.4 Hz, 1 each, H_4 and H_9), 5.9–6.5 (m, 4, H_5, H_6, H_7, H_8), 6.94 (d, J_{HF} = 3.0 Hz, 2, H ortho to F), 7.07 (s, 2, H meta to F); IR (neat) 3017 (s), 1601 (m), 1506 (s), 1442 (m), 1222 (s), 1156 (m), 1100 (w), 836 (s), 745 (w), 705 (s) cm^{-1}; mass spectrum m/e (rel intensity) 212 (82), 211 (41), 197 (100), 196 (71), 116 (64), 115 (56), 91 (51), 90 (49), 89 (47); exact mass spectrum m/e 212.0992 (calcd for $C_{15}H_{13}F$, 212.1000). Elemental analysis was not attempted due to the tendency of the compound to decompose at room temperature.

Acknowledgment. This research was supported by the National Science Foundation, to whom the authors express grateful appreciation.

Registry No.—2, Ar = *p*-C_6H_4F, 67711-71-1; 1-chlorocycloheptatriene, 32743-66-1; 2-chlorocycloheptatriene, 34896-79-2; 3-chlorocycloheptatriene, 55619-05-1.

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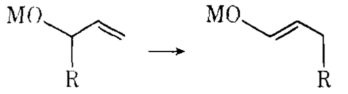
(6) The validity of this equation depends on the constancy of the ratio S_H/S_X. This was checked indirectly by weighing the final products, calculating the total amounts of styrenes consumed in the reaction (assuming all of the products were spirocyclopropanes, **2**), and determining the net change in the S_H/S_X ratio at the end of the reaction. In no case was the change >3%.
(7) This is barring the coincidence that **3** and **7** give two different intermediates that have the same ρ value, which cannot be excluded.

Communications

Potassium Alkoxide Promoted 1,3 Shifts of Dithianes

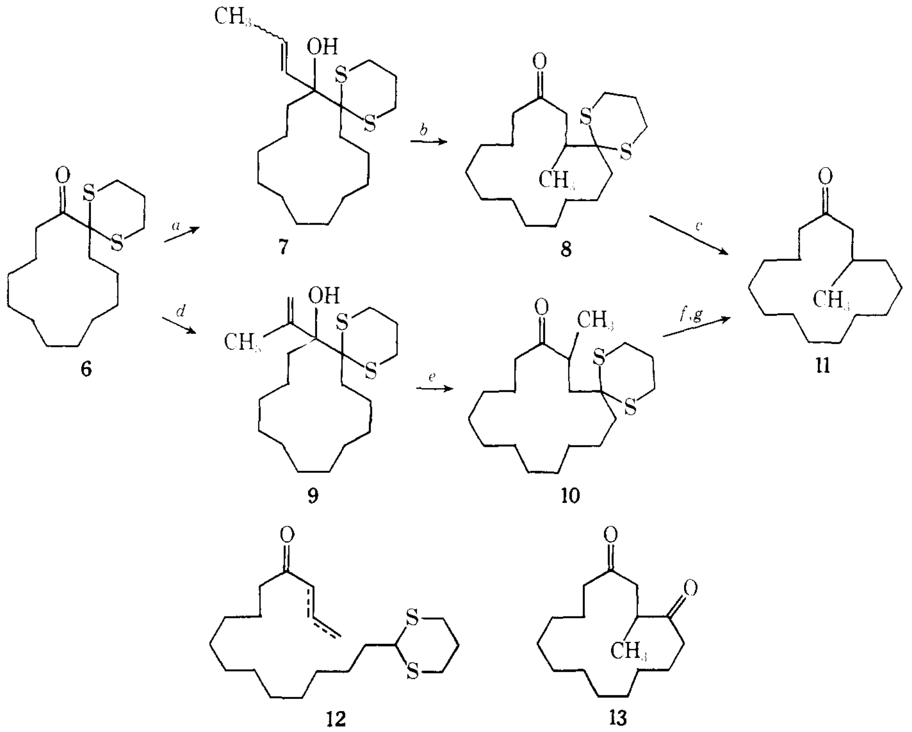
Summary: Applications of alkoxide-promoted 1,3 shifts to 1,4-dicarbonyl synthesis gives a new ring expansion route to *d,l*-muscone.

Sir: Sigmatropic rearrangements have found a wide variety of uses in organic synthesis.[1] Therefore, the report by Evans[2] that the oxy-Cope [3,3] sigmatropic rearrangement[3] can be *strongly accelerated as the potassium salt* appeared to us to have significant synthetic consequences. A number of subsequent reports on alkoxy counterparts to [3,3][4] and [1,3][5] rearrangement processes have since appeared. The [1,3] rearrangement depicted in eq 1 is of course a well-known process, the retro-1,2-carbonyl addition/1,4-Michael addition process.[6] Although not normally considered in these terms, the overall process is the result of a [1,3] sigmatropic shift. The alkoxide substituent on the crucial C–C bond which is breaking in the transition state can promote the requisite first step of the rearrangement process, i.e., reversal of the 1,2 addition.[7] Thus, the use of highly dissociated metal alkoxides in polar aprotic solvents should promote isomerization of 1,2 adducts, such as **1a** (mp 40–41 °C),[11,12] to the corresponding 1,4 adducts. This has proved to be the case. The *potassium salt* of **1a** isomerized to **2a** in 80% HMPA/THF solution (2 h, 25 °C) in 53% isolated yield.[13] The corresponding cyclohexenone adduct **1b** isomerized to **2b** in 23% yield,[14] whereas **1c** (mp 62–63 °C) gives none[14] of the desired **2c**, indicating steric hindrance at the newly forming C–C bond cannot be tolerated. The sodium and lithium salts of **1b** yielded mostly recovered starting material under similar conditions,[15,16] while the po-



(1)

Scheme I



^{a} $CH_3CH{=\!=}CHLi$ (3 recycles); 48% (+48% recovered **2**). ^{b} KH, TPPA/THF; 21%. ^{c} Ra-Ni/EtOH; 40%. ^{d} $CH_3C(Li){=\!=}CH_2$ (5 recycles); 51%. ^{e} KH, HMPA/THF; 28%. ^{f} NH_2NH_2, KOH; 41%. ^{g} HgO, $BF_3 \cdot OEt_2$/aq THF; 72%.