Thus, dianion **5** was titrated with 1 equiv of water in THF-hexane and the ^{1}H NMR of the resulting reaction mixture was recorded on a 60-MHz spectrometer using TMS as an external standard. Interestingly, the resulting spectrum was found to be identical with that of the enolate monoanion **4** (Scheme I) described earlier. These results strongly suggest that, while alkylations of the 1-phenyl-2-propanone dianion **5** occur predominately at the methine site, protonation occurs exclusively at the terminal methylene position.

The alkylation reactions of the 1,1-diphenyl-2-propanone dianion were next examined. This dianion was generated from the corresponding ketone by the method described earlier in connection with the 1-phenyl-2-propanone dianion **5** (Scheme I).

Treatment of the 1,1-diphenyl-2-propanone dianion with a variety of alkyl halides again showed that the site of electrophilic attack was substantially dependent upon the reactivity of the alkylating agent (Table I).

The mode of alkylation of the 1-phenyl-2-propanone dianion **5** outlined in the present communication closely parallels that described in the literature for the allylbenzene anion. Thus, numerous studies[10] have shown that alkylations of this anion, under a variety of experimental conditions, occurred largely at the carbon adjacent to the benzene ring. Terminal alkylation products were also formed during these reactions, but in smaller quantities.[10b,c] It was further shown that the amount of terminal alkylation products formed was largely dependent upon the reactivity of the alkyl halide used, the more reactive halides producing larger quantities of terminal alkylation products.[10c]

The close similarity in the alkylation patterns of dianion **5** and the allylbenzene anion is very much in line with the close structural similarity of these two intermediates suggested earlier on the basis of their NMR spectra.

The higher reactivity of the carbon atom adjacent to the benzene ring in both intermediates can be best explained by recognizing that the presence of the benzene ring will cause the accumulation of a higher electron density on C_1 relative to C_3.[10d,11-13] As a result of this, even though C_1 is more sterically hindered than C_3, alkyl halides of low reactivity (high selectivity) will preferentially react at the more reactive methine site. On the other hand as the reactivity of the alkyl halides is made increasingly higher, their selectivity will be lowered, and steric effects will begin to favor alkylation at the less hindered terminal site.

Reaction of dianion **5** with *p*-anisaldehyde at the terminal position rather than the site adjacent to the benzene ring also parallels the reaction patterns observed earlier in connection with the allylbenzene anion and related systems. Steric effects have been considered to be at least partly responsible for the observed regioselectivity of these reactions,[14] although a number of alternative mechanisms have also been proposed to explain the reactions of allylic anions with carbonyl compounds.[15]

The mode of protonation of dianion **5** is not entirely understood at this point. Initial proton attack at C_1 to give the less stable terminal enolate intermediate, followed by fast equilibration of the latter to the more stable enolate **4**, seems unlikely in view of the results of the alkylation–silylation experiment described earlier. It is noteworthy to mention that protonation of the allylbenzene anion is also not entirely understood.[10d] In the latter case the site of proton attack appears to be highly dependent on the reaction solvent. Thus, protonation under *kinetically controlled conditions* with a variety of proton donors in liquid ammonia, afforded propenylbenzene in excess of 90%,[10c,d] while protonation in less polar solvents gave largely allylbenzene.[10c,d]

Inspection of Table I clearly shows that the alkylation reactions of the 1,1-diphenyl-2-propanone dianion follow a pattern quite similar to that observed in the case of dianion **5**. In the former case, however, more severe steric crowding around C_1 has caused an increase in terminal alkylation.

A more detailed investigation of the two dianions described herein and related systems is currently underway.

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An Approach to Biradical-like Species. Spectroscopy of *o*-Xylylene in Argon Matrix

Sir:

The reactive intermediate, *o*-xylylene (**1**), and its simple derivatives have been the subject of considerable interest.[1]

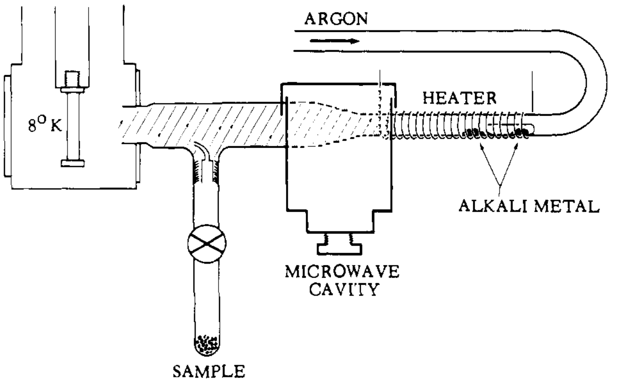


Figure 1. Excited alkali atom-dihalide reaction and deposition chamber. The glowing region is dashed.

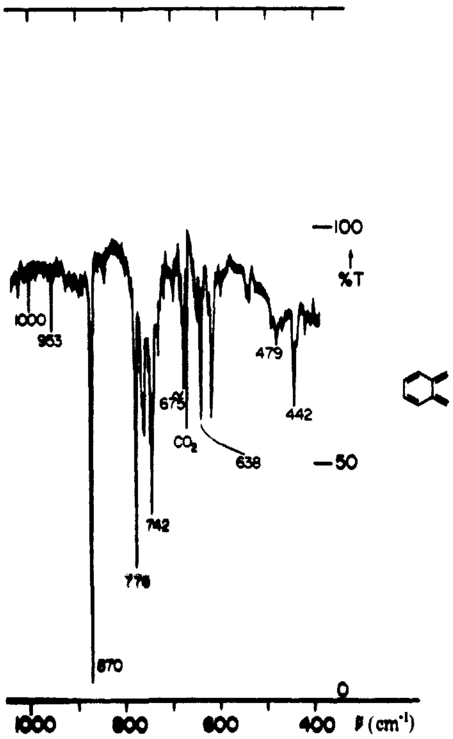


Figure 2. IR spectra of **1** and **2** in argon matrix in the C–H out-of-plane bending and C–Br stretching regions (on the same scale, but shifted vertically).

Direct observation of **1** in an organic matrix by fluorescence, fluorescence excitation, and UV absorption spectroscopy has been reported,[2,3] and, recently, better resolved spectra were obtained in a Shpolskii matrix.[4] The methods used did not lend themselves to the study of vibrational spectra.

We now wish to report that **1** can be generated in gas-phase reaction of $\alpha\alpha'$-dibromo-*o*-xylene (**2**) with sodium or potassium vapor and collected in an argon matrix (8–30 K) in the apparatus shown in Figure 1, permitting the first measurement of its IR (Figure 2) and Raman (Figure 3) spectra and providing improved resolution in UV, fluorescence, and fluorescence excitation spectra (Figure 4). Halogen abstraction reactions of alkali metal atoms with organic halides in gas phase,[5] as well as in the surface,[6] and, with photoactivation, in the bulk,[7] of a rare gas matrix are well known.

An important option in the method, which greatly increases the degree of conversion **2** → **1** under otherwise similar conditions, is the use of microwave discharge to excite the alkali metal vapor–argon mixture prior to reaction. Then the reaction occurs inside an intensely glowing gas stream and most likely involves excited alkali atoms. The high degree of conversion achieved can be judged from the IR spectra of Figure 2. It

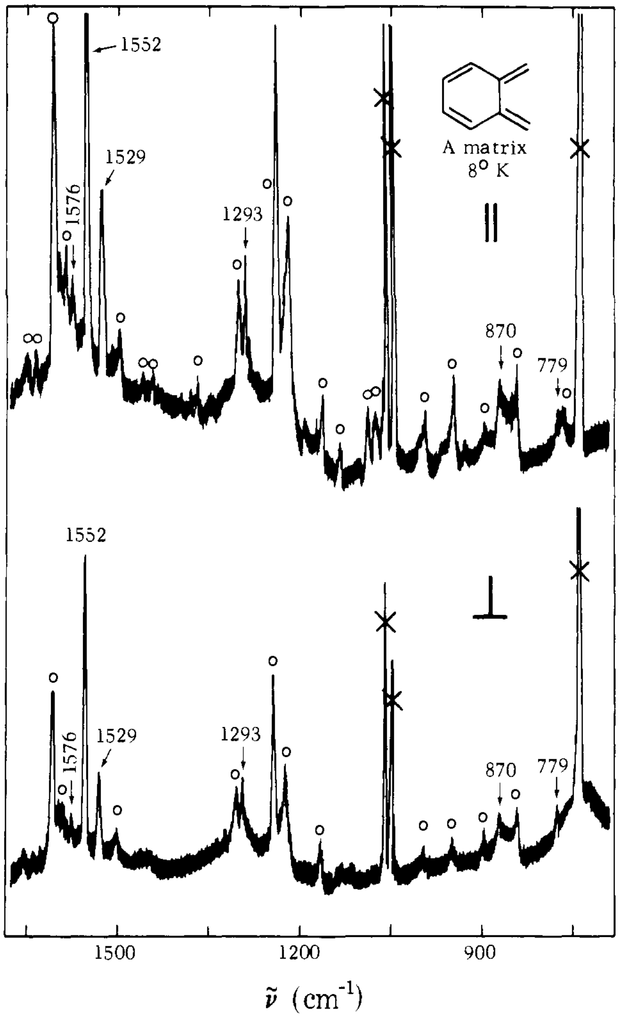


Figure 3. The Raman spectrum of **1** in argon matrix (top, parallel, bottom, perpendicular polarization; 20 491-cm⁻¹ line of an argon ion laser, 110 mW). The stronger among the lines were also observed with a weaker 19 436-cm⁻¹ line of the laser, 40 mW. Circles indicate bands which are due to **2** and to background. Crosses indicate laser plasma lines.

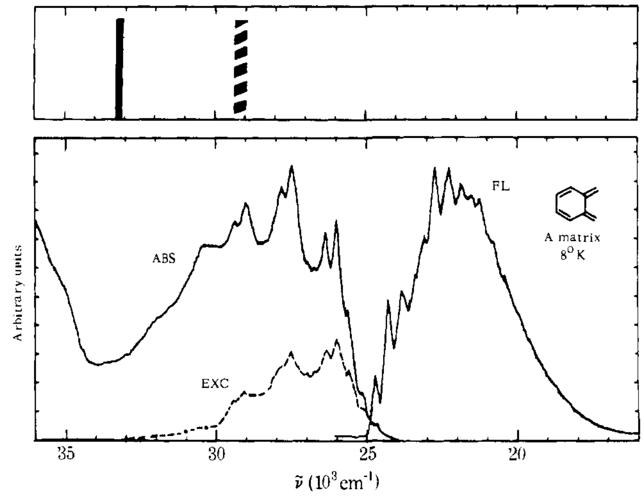
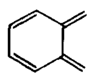


Figure 4. Absorption, fluorescence, and excitation (dashed, uncorrected) spectra of argon-matrix isolated **1**. On top, calculated transition energies (dashed, short-axis polarized; full, long-axis polarized; thick, strong; thin, weak).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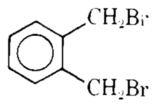

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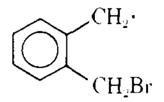

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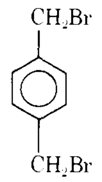

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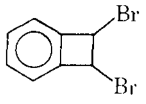

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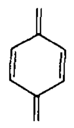
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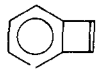
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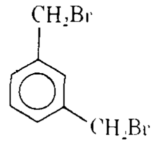

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decreases with decreasing distance of the dihalide inlet from the cold window, indicating that the bulk of the reaction occurs in the gas phase. If the alkali metal vapor is omitted in the experiment, no **1** is formed, and the IR spectrum reveals only **2** and a generally increased background, presumably due to partial indiscriminate destruction of **2** by metastable argon atoms (these appear to be completely quenched in the presence of metal atoms).

In a large number of spectra obtained under various conditions and with varying degrees of conversion, we have observed little if any evidence for the monoradical **3**. However, when the dihalide inlet is placed very near the microwave cavity, a product different from **1** is formed. Its structure has not been elucidated so far (radical anion of **1**?).

The identification of **1** is based on comparison with its known UV, fluorescence, and excitation spectra (Figure 4).[2-4] The calculations shown were performed using selected[8] singly and doubly excited configurations and appropriate[9] parameter values. They account for the observed spectra and support the previous belief[3] that an unobserved transition to a doubly excited state, presumably involved in the known photochemical conversion of **1** to benzocyclobutene, is buried under the intense first transition.

The IR (Figure 2) and Raman (Figure 3) spectra also fit the structure well. IR bands occur at 436 (w, shoulder), 442 (m), 638 (m), 675 (m), 737 (m), 742 (m), 776 (s), *779* (w, sh), *866* (w, sh), *870* (s), 953 (w), 1000 (w), 1158 (w), 1303 (w), 1333 (w), 1427 (w), 1465 (w), 1471 (w), 1490 (w), 1542 (w), *1552* (m), *1576* (w), 1741 (w), 2950 (w), *3045* (w), 3070 (w), and 3105 (w) cm^{-1}. Raman bands occur at *779* (w), *866* (w), *870* (w, 0.6), 1293 (m, 0.5), 1529 (m, 0.48), *1552* (s, 0.45), *1576* (w, 0.3) and *3045* (w) cm^{-1} (depolarization ratios in parentheses, frequencies common to the two spectra are italicized). The fluorescence spectrum can be analyzed in terms of two vibrational spacings, ~450 and ~1550 cm^{-1}, and we identify these with the 442- and 1552-cm^{-1} frequencies observed in the vibrational spectra. The spectra are independent of whether sodium or potassium was used in the reaction.

As numerous organic halides are easily available, the present approach to organic biradicaloid and similar reactive species promises to be widely applicable. Preliminary experiments with α,α'-dibromo-*p*-xylene (**4**) and 1,2-dibromobenzocyclobutene (**5**) produced argon-matrix isolated *p*-xylylene[10] (**6**) and benzocyclobutadiene[11] (**7**), identified by comparison of UV and IR spectra with those published previously. The use of α,α'-dibromo-*m*-xylene (**8**) produced only small amounts of organic material in the matrix using the apparatus of Figure 1, and it appears that shorter lived biradicals will have to be prepared closer to the matrix surface.

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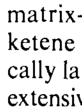
A Methodology for the Preparation and Characterization of Three-Membered, Potentially Antiaromatic Molecules. Preparation of Matrix-Isolated Thiirene and Selenirene

Sir:

Because of their strain and putative electronic destabilization, three-membered heterocycles[1] possessing a cyclic array of 4π electrons offer a considerable challenge to synthesis. Such molecules are expected to be both unimolecularly and bimolecularly reactive, if they exist at all as energy minima.[2] Thiirene (**1**) and its kindred systems, oxirene (**2**), azirene (**3**), and selenirene (**4**) are of interest because of their theoretical significance as prototypes of antiaromatic species.[3] To date, neither the parent nor a single derivative of these heterocyclic molecules has been prepared and characterized.[4]



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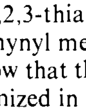

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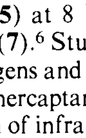

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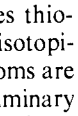

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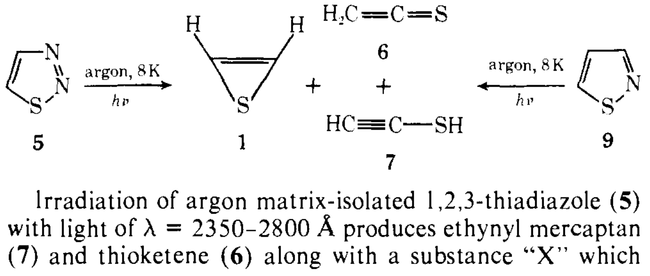
We wish to report the preparation and chacterization of thiirene (**1**). Strausz and co-workers[5] implicated thiirene as a transient in the gas-phase photodecomposition of 1,2,3-thiadiazole (**5**). We have previously noted that irradiation of matrix-isolated 1,2,3-thiadiazole (**5**) at 8 K produces thioketene (**6**) and ethynyl mercaptan (**7**).[6] Studies with isotopically labeled **5** show that the hydrogens and carbon atoms are extensively randomized in ethynyl mercaptan (**7**). Preliminary evidence for thiirene (**1**) in the form of infrared data has been presented by us.[7]



Irradiation of argon matrix-isolated 1,2,3-thiadiazole (**5**) with light of λ = 2350–2800 Å produces ethynyl mercaptan (**7**) and thioketene (**6**) along with a substance "X" which