only the ribose moiety is left.

(8) Thelander et al.[3] observed a rapid loss of titratable sulfhydryl groups followed by a slower increase in absorbance at 320 nm. These observations are nicely explained by a rapid Michael addition of a sulfhydryl group to the ribose fragment followed by a slow step, perhaps a rearrangement or dehydration to yield the chromophore. For instance, a β-mercapto-α,β-unsaturated ketone might be expected to have a λ_{max} at 320 nm.

(9) NOTE ADDED IN PROOF. It has been demonstrated (Pfitzner, K. E.; Moffatt, J. G. *J. Am. Chem. Soc.* **1965**, *87*, 5661–5670) that oxidation of thymidine 5′-monophosphate to afford the presumed 3′-keto analogue results in the generation of inorganic phosphate, thymine, and unidentified sugars. This chemical model provides strong support for our proposal. Moreover, we have recently found that incubation of RDPR with [^{14}C]-2′-chloro-2′-deoxyaridine 5′-diphosphate (uniformly labeled) effects a covalent labeling of the enzyme concomitant with inactivation. This finding is consistent with the modification of the active site by the ribose fragment.

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An ab Initio SCF Study of the Structure and Vibrational Spectrum of Thiirene

Sir:

Although antiaromatic 4n π systems have received considerable attention over the past few years, thiirene is the only heterocyclic example which has yet been prepared.[1,2] Calculations had predicted thiirene to be an extremely antiaromatic system (REPE = -0.114β),[3] and its instability has been confirmed by experiment.[1,2] Both Krantz and Laureni[1] and Strausz and his co-workers[2,4] have recently reported the isolation and IR spectrum of thiirene at low temperature though they are not in complete agreement on the spectrum, in part due to the presence of other substances in the reaction mixture.

We have now calculated the equilibrium structure and IR spectrum of thiirene using an ab initio single-configuration method and the 4-31G basis of Pople and Hehre.[5] Geometry optimization with an assumed C_{2v} structure gave C—S = 1.9782 Å, C═C = 1.2509 Å, C—H = 1.0556 Å, ∠HCC = 154.94°, and an energy of −473.725 975 hartrees.[6] This is nearly 2 hartrees lower than the best previous ab initio calculation on thiirene.[7] Of interest is the unusually long C—S bond and the short C═C bond. The latter is in accord with the reported high stretching force constant.[4] Together these results do reflect the expected antiaromaticity of thiirene; i.e., they show a tendency of the molecule to minimize conjugation between the sulfur atom and the C═C bond. A similar situation arises in cyclobutadiene where in the rectangle the C—C bond is calculated to be unusually long.[8]

Symmetry-adapted 0.01-Bohr displacements of atoms were then taken singly and in pairs to give a force constant matrix for each vibrational symmetry. These were diagonalized to yield the normal modes and frequencies. Dipole moment changes, and hence related infrared intensities, were computed by displacing the atoms along a normal mode by 0.1 au (this corresponds roughly to one half the classical turning point for high-frequency modes and one quarter this distance for those of low frequency). Calculated IR and Raman frequencies and intensities of the IR active bands of thiirene and dideuteriothiirene are listed in Table I. In Figures 1 and 2 the IR bands are plotted for comparison with those found experimentally by Strausz.[4] Although all lie too high, the computed C—H and C—C stretches are of the correct symmetry and relative intensity and are in the correct order for both compounds. The observed shift on deuteration of C—H stretching intensity from the b$_2$ to the a$_1$ band is reproduced by the calculations.

Table I. Calculated IR and Raman Frequencies and IR Intensities of Thiirene and of Dideuteriothiirene (in Parentheses)

symmetry[a]	frequency, cm^{-1}	rel intensity	type
a$_1$	509 (505)	0.15 (0.30)	ring deformation
	939 (667)	0.01 (0.02)	in-plane C—H bend
	1935 (1779)	0.09 (0.12)	C═C stretch
	3645 (2820)	0.10 (0.21)	C—H stretch
b$_1$	808 (604)	1.00 (1.00)	C—H out-of-plane bend
b$_2$	448 (429)	0.00 (0.00)	ring deformation
	996 (767)	0.36 (0.36)	in-plane C—H bend
	3548 (2606)	0.38 (0.39)	C—H stretch
a$_2$	934 (775)	—	C—H out-of-plane bend

[a] The a$_1$ frequencies are IR active only; the a$_2$ is Raman active only; b$_1$ and b$_2$ appear in both Raman and IR.

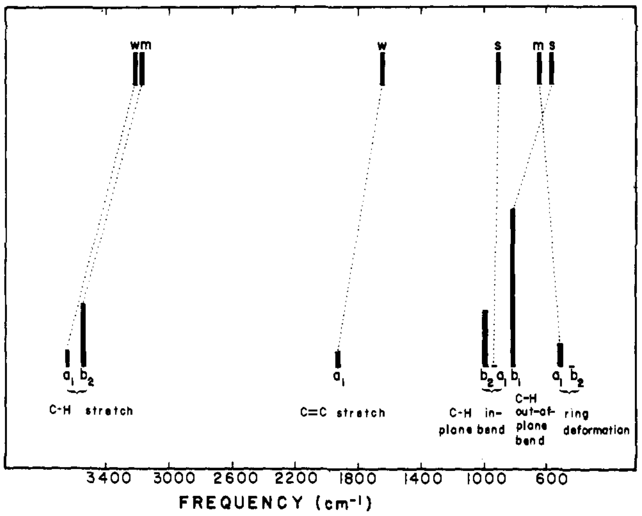

Figure 1. Comparison of observed and computed IR spectra of thiirene. The observed bands (from ref 4) are shown at the top of the figure with relative intensities indicated by strong (s), medium (m), or weak (w). Calculated bands are at the bottom of the figure with relative intensities shown by the height of the lines.

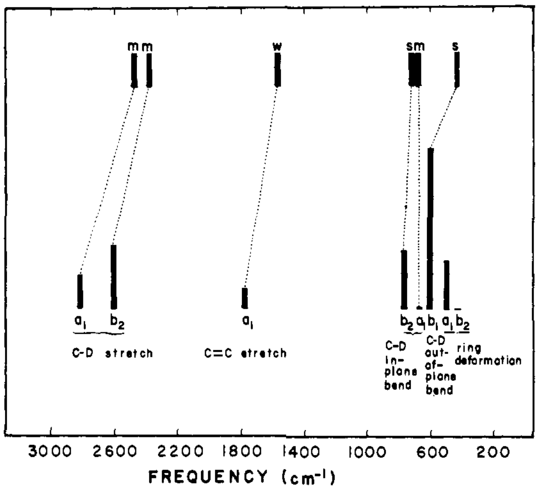

Figure 2. Comparison of observed and computed IR spectra of dideuteriothiirene. See legend of Figure 1.

The strong absorption of C_2H_2S seen at 910 cm^{-1} has been assigned[4] to the a$_1$ in-plane C—H bend, but, from the calculated intensities, it seems more likely to be the b$_2$ in-plane bend.[9] (We take the plane perpendicular to the molecular plane to be that distinguishing a from b symmetry.) This would make the bands of third-lowest frequency in C_2H_2S and C_2D_2S

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correspond. There seems to be no way to bring our remaining low frequency lines into agreement with those observed by Strausz.[4] Our frequencies for the a_1 ring deformation and the b_1 C—H bend are inverted with respect to his in C_2H_2S, and our calculated intensity for the a_1 CH bend in C_2D_2S is much lower. However, in a very recent paper, Krantz and Laureni[10] question the assignment of the observed 657-cm^{-1} band of thiirene which Strausz has assigned to an a_1 ring deformation. Such a band exists, but, because the spectrum is complicated in this region, its rate of appearance, and hence whether or not it is an absorption of thiirene, is difficult to determine. Removing this band, and what might be the corresponding band (in spite of a shift of 24 cm^{-1} to higher frequency) at 681 cm^{-1} in C_2D_2S, would give spectra for both compounds that are now in good agreement, in intensity and frequency, with our calculated results. In both cases the two strongest of the low-frequency absorptions have been observed. Of the remaining bands, that of predicted highest intensity is the a_1 ring deformation, which should lie at lower frequency than the observed bands.

Our best thiirene wave function is still many thousands of reciprocal centimeters too high in energy. Nevertheless, similar wave functions for ethylene and cyclobutadiene have been shown to give useful predictions of vibrational spectra.[8] Individual calculated frequencies may be in error by as much as 400 cm^{-1}, but the overall agreement, in frequency and intensity, between calculated and experimental patterns is strikingly good. While these computed spectra certainly can be helpful, they must not be taken as definitive.

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References and Notes

(1) (a) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1977,** *99*, 4842. (b) Krantz, A.; Laureni, J. *Ber. Bunsenges. Phys. Chem.* **1978,** *82*, 13.
(2) Torres, M.; Clement, A.; Bertie, J. E.; Gunning, H. E.; Strausz, O. P. *J. Org. Chem.* **1978,** *43*, 2490.
(3) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1973,** *95*, 3907.
(4) Torres, M.; Safarik, I.; Clement, A.; Bertie, J. E.; Strausz, O. P. *Nouv. J. Chim.* **1979,** *3*, 365.
(5) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1970,** *54*, 724. (b) Hehre, W. J.; Lathan, W. A. *Ibid.* **1972,** *56*, 5255.
(6) We have used the values of the fundamental constants recommended by Cohen, E. R.; Taylor, B. N. *J. Phys. Chem. Ref. Data* **1973,** *2*, 663. With these 1 hartree = 627.5092 kcal/mol; 1 Bohr = 0.5291 7706 Å.
(7) Strausz, O. P.; Gosavi, R. K.; Bernardi, F.; Mezey, P. G.; Goddard, J. K.; Csizmadia, I. G. *Chem. Phys. Lett.* **1978,** *53*, 211.
(8) Schaad, L. J.; Hess, Jr., B. A.; Ewig, C. S. *J. Am. Chem. Soc.* **1979,** *101*, 2281.
(9) In a private communication, Professors Bertie, Strausz, and Torres say they now do favor the assignment of b_2 symmetry to this band.
(10) Krantz, A.; Laureni, J. *J. Org. Chem.* **1979,** *44*, 2730.

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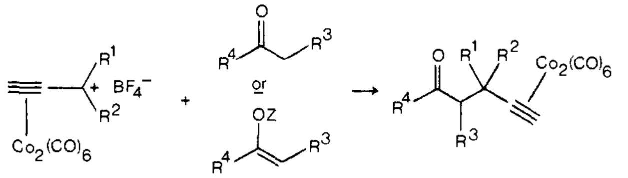
Synthetic Applications of Transition-Metal-Stabilized Carbenium Ions. Selective Alkylation of Ketones and Ketone Derivatives with (Propargyl)dicobalt Hexacarbonyl Cations[1]

Sir:

The selective alkylation of carbonyl compounds has been a long sought goal in organic synthesis. Accordingly, several approaches to this end have been developed, with varying success, to overcome the frequently encountered problems of polyalkylation, competing aldol condensation, and lack of regio- and stereoselectivity.[2] Most of these methods ultimately involve alkylation of the carbonyl-derived *enolate anion*—e.g., use of α-blocking groups and α-activating groups, cleavage of trimethylsilyl enol ethers and enol acetates, and kinetic enolate generation with strong bases. On the other hand, very few useful alkylation procedures are known which combine the ketone directly as its *enol tautomer* or an enol derivative with a suitable alkylating agent. Examples of this latter type include the Mannich reaction,[3] enamine alkylations,[4] and some recently reported additions to silyl enol ethers.[5] The paucity of such reactions probably is due in part to the limited availability of sufficiently electrophilic and flexible alkylating agents.

We have been interested in the alkylating potential of the cobalt-complexed propargyl cations **1**, representatives of a long-recognized but synthetically little-utilized group of highly stable carbenium ions flanked by organotransition metal moieties.[6] Previously, these electrophilic species, conveniently prepared from propargyl alcohols,[7] have been found to C-alkylate aromatics[8] and β-dicarbonyl compounds[1] with great facility and without formation of allenic byproducts. We now report that these same cationic complexes *alkylate ketones regiospecifically as well as trimethylsilyl enol ethers and enol acetates* (**1** → **2**).



1

2

Z = SiMe$_3$, COMe

a: $R^1 = R^2 = H$
b: $R^1 = H, R^2 = Ph$
c: $R^1 = R^2 = CH_3$

Simple dissolution of the complexes **1** in an excess of the dry ketone at 0 °C results in a rapid reaction (30–90 min) from which the α-alkylated products, dark red oils or low melting solids, are easily isolated upon addition of solid $NaHCO_3$ and $MgSO_4$, filtration, evaporation of excess substrate, and chromatography over silica gel.[9] Results with some representative ketones are presented in Table I. The key features to be noted are (1) the generally good yields of exclusively *mono*alkylated products which are obtained and (2) the remarkable regioselectivity found in reactions with unsymmetrical ketones. The only other organometallic products isolated were the alcohols $(R^1C{\equiv}CCR^2R^3OH)Co_2(CO)_6$ and ethers, $[Co_2(CO)_6(R^1C{\equiv}CCR^2R^3)]_2O$, resulting from competing reaction with residual water in the ketones. The specificity towards monoalkylation, while not unexpected considering the high ketone/complex ratio (~100:1) employed, is still nonetheless significant in view of the substantial amounts of polyalkylation obtained in many enolate alkylations, despite controlled addition of alkyl halide to preformed enolate.[10]

The regioselectivity observed is qualitatively as expected for attack of the electrophilic complex on the thermodynamically favored, more highly substituted enol. The degree of selectivity ($\geqslant$95%)[11] is exceptional, however, when compared with that of most other acid-catalyzed α-substitution reactions of ketones such as deuteration,[12] halogenation,[12-14] and the Mannich reaction.[15] Further experiments are planned which will test the limits of this regiospecificity and attempt to establish its origin.

The use of the ketone as solvent is an obvious limitation of this alkylation procedure, making impractical its application to solid or precious substrates. Thus far our initial efforts to carry out these reactions stoichiometrically in a solvent have

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