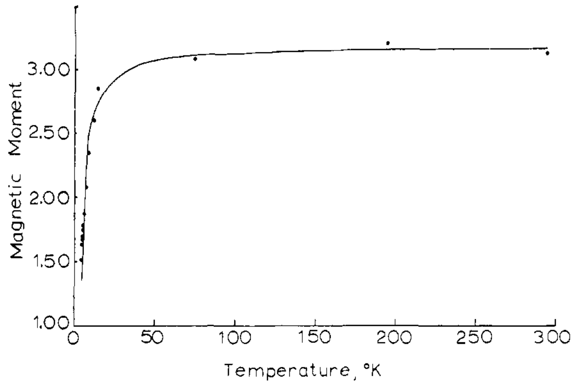

Figure 1. The temperature variation of the observed (●) and the calculated (—) magnetic moments of tetrabutylammonium bis(toluene-3,4-dithiolato)cobaltate.

unique, being the first example of a high-spin square-planar transition metal complex with a triplet ground state. However, the Weiss constant of 14°K reported by Balch, Dance, and Holm[2] is somewhat high for magnetically dilute $^3B_{1g}$ states, and further study on this compound was indicated.

We have extended the magnetic susceptibility measurements to 4.2°K using a Foner-type vibrating sample magnetometer[3] operated at a field strength of 10,000 Oe and calibrated with a sample of very pure nickel metal and with $HgCo(NCS)_4$.[4] Temperature measurements were obtained with a precision germanium resistor and a high-impedance ac resistance bridge. The experimentally determined susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[5]

The dramatic feature of the low-temperature magnetic data is a pronounced maximum of the magnetic susceptibility near 8°K. This behavior of the magnetic susceptibility indicates that the ground electronic state is of singlet multiplicity with only a small energy difference existing between this state and the paramagnetic triplet state. The temperature variation of the magnetic moment is shown in Figure 1.

With the assumption that these two electronic states (singlet ground state and low-lying triplet state) are sufficiently separated from other excited states such that the Van Vleck equation (eq 1)[6,7] applies, we have compared the data to the equation and find, from the best fit of experimental and calculated susceptibilities as determined by the minimum least-squares deviation, that $\Delta E = 8.5 \text{ cm}^{-1}$. Thus, while the bis(toluene-3,4-dithiolato)cobaltate ion does not have a triplet ground state, it remains a unique compound, since it is apparently the only known monomeric dithiolato square-planar complex with a singlet ground state and a low-lying triplet state, with configurations of $(\pi_2)^2$ and $(\pi_2)(\pi_1)$, respectively.

$$\chi_m = \frac{2g^2N\beta^2}{3kT}[1 + (1/3)\exp(+\Delta E/kT)]^{-1} \qquad (1)$$

Although the structure of $(n\text{-Bu}_4\text{N})[\text{Co(tdt)}_2]$ has not been reported, in the triphenylmethylarsonium salt,[8] the cobalt ions are separated by 10.21 Å. This observation, coupled with the absence of the characteristic behavior associated with the supercooling of substances with lattice antiferromagnetism and with the triplet-state electron spin resonance spectrum which was obtained,[9] discounts the possibility of pairwise or longer range ordering of the magnetic ions as explanations for the magnetic properties.

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(10) NSF Trainee, 1968–1971.

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Photocycloaddition of Arylazirenes with Electron-Deficient Olefins

Sir:

Previous reports on the photoreductive dimerization of acyclic aryl *N*-alkylimines showed that the reaction did not involve the excited state of the imine at all, but was the result of a ground-state reaction of the imine with a ketyl radical.[1,2] The ketyl radical was derived from carbonyl compounds present in starting material as an impurity, an added sensitizer, or as a photogenerated species. The low photoreactivity of the imine chromophore was attributed to facile deactivation of the excited state as a consequence of rotation about the C–N double bond.[1] In rigid systems, this mode of energy dissipation would not be available and these molecules would have maximum opportunity to undergo reaction from an electronically excited state. In this communication we wish to report that the rigid arylazirene system readily undergoes photochemical addition to electron-deficient olefins.

A solution of phenylazirene[3] (**1**) (0.5 g) in excess methyl acrylate (200 ml) was irradiated under a nitrogen atmsophere using an internal water-cooled mercury arc lamp (450 W) equipped with a Vycor filter. The usual work-up and distillation gave the 1:1 adduct, 2-phenyl-4-carbomethoxy-Δ^1-pyrroline (**2a**), in good yield (80%). The spectral data were in accord with the assigned structure:[4] mass *m/e* 203 (parent), 144,

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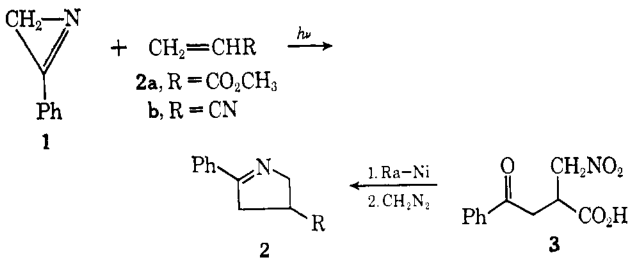
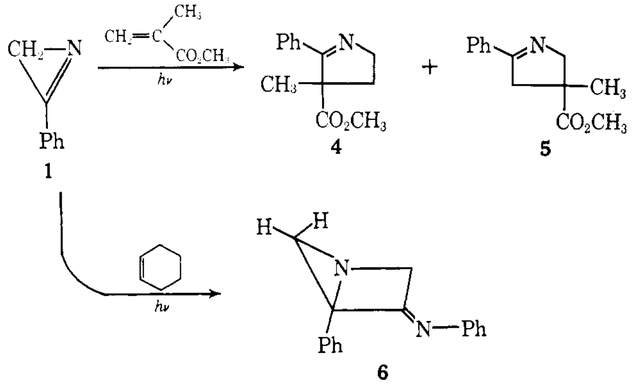
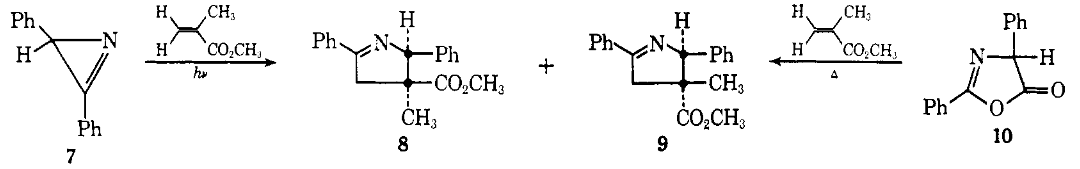
(4) All compounds analyzed satisfactorily. Complete spectroscopic and degradative details will be given in our full publication.



117 (base); ir (neat) 5.75 (C=O) and 6.17 μ (C=N); uv (95% ethanol) 243 mμ (ε 14,000); nmr ($CDCl_3$) τ 6.80 (3 H, m), 6.38 (3 H, s), 5.80 (2 H, m), and 2.65 (5 H, m). Structure **2a** was further confirmed by its unequivocal synthesis from 3-benzoyl-2-nitromethylpropionic acid[5] (**3**) by Raney nickel (W2) reduction followed by esterification with diazomethane. Similarly, when acrylonitrile or tetracyanoethylene was used as substrate, Δ^1-pyrroline **2b** (mp 95–96°; 70%) and 2-phenyl-3,3,4,4-tetracyano-Δ^1-pyrroline (**2c**) (mp 191–192°; 95%) were formed in high yield.[4]

The photoaddition of phenylazirene to methyl methacrylate produced two major photoadducts shown to be 2-phenyl-3-methyl-3-carbomethoxy-Δ^1-pyrroline (**4**, clear oil, 40%) and 2-phenyl-4-methyl-4-carbomethoxy-Δ^1-pyrroline (**5**, mp 41–43°, 60%). The analytical and spectral data support the formulation of these compounds as Δ^1-pyrrolines.[4] A choice between the alternative 3,3- and 4,4-disubstituted Δ^1-pyrrolines can be readily made on the basis of their characteristic nmr spectra.[6] The 60-MHz nmr spectrum of **4** ($CDCl_3$) showed singlets at τ 8.55 (3 H) and 6.40 (3 H), and had multiplets at τ 7.85 (2 H), 5.97 (2 H), and 2.71 (5 H). Structure **5** had singlets at τ 8.72 (3 H) and 6.38 (3 H), two AB quartets at τ 6.90 and 5.91 (J = 15 Hz), and a multiplet at τ 2.70 (5 H). Irradiation of phenylazirene in the presence of excess cyclohexene produced no photoadduct but instead gave 4-phenyl-3-phenylimino-1-azabicyclo[2.1.0]pentane (**6**).[10]

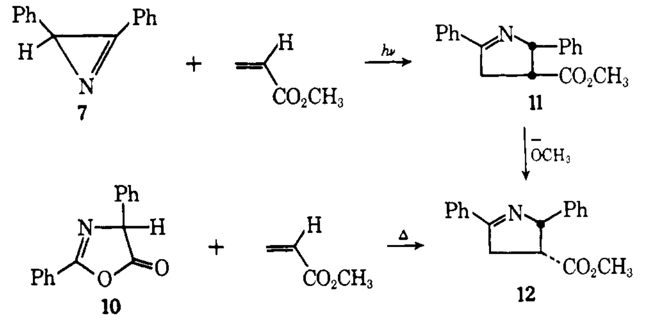




The photochemical reaction of 2,3-diphenylazirene[11] (**7**) with methyl methacrylate was also investigated. Under the standard irradiation conditions the reaction proceeded readily and afforded a mixture of 2,5-diphenyl-4-methyl-4-carbomethoxy-Δ^1-pyrrolines **8** (40%) and **9** (60%). The stereochemical relationship of photoadducts **8** and **9** is apparent from the similar spectral data (uv, ir, m/e) of the two compounds. The basis for the assignment of geometry rests on the nmr data. Compound **8** has a signal attributable to the methyl group at τ 8.45 whereas the methyl group of **9** appeared at τ 9.27. The strong upfield shift of the methyl signal of **9** can be attributed to shielding by the π electrons of the neighboring phenyl ring. The same two adducts were prepared by heating 2,4-diphenyl-Δ^2-oxazolin-5-one (**10**) with methyl methacrylate in xylene.[12] Similar cycloaddition using tetracyanoethylene and acrylonitrile as substrates furnished related photoadducts in high yield.

Irradiation of a mixture of **7** and methyl acrylate led to an especially clean photoaddition process giving 2,5-diphenyl-*cis*-4-carbomethoxy-Δ^1-pyrroline (**11**) as the only photoadduct (mp 101–102°, 95%). In contrast, heating **10** with methyl acrylate afforded the isomeric *trans*-pyrroline **12**. Control experiments demonstrated that **11** was stable to the thermal conditions. Proof of the cis relationship of the groups in **11** was obtained by base-catalyzed epimerization of **11** to **12**.

The photocycloaddition of arylazirenes with electron-deficient olefins to produce Δ^1-pyrrolines can be rationalized by the assumption that the electronically excited state of the azirene opens to give a nitrile ylide intermediate **13**. As a 1,3-dipole, **13** can be intercepted with suitable dipolarophiles to form five-membered rings.[13] The difference in product stereochemistry from the reactions of **7** and **10** with methyl acrylate suggests the absence of a common intermediate. The 1,3-dipolar cycloaddition of azlactones such as **10** has been suggested to proceed by tautomerization to a



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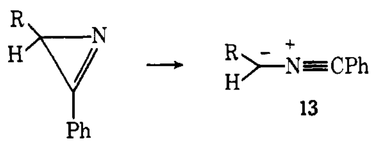

13

1, R = H
7, R = Ph

mesoionic oxazolium 5-oxide which then combines with the dipolarophile.[12] Formation of the less thermodynamically stable *cis*-Δ^1-pyrroline **11** may be the result of preferred geometrical or electronic factors operative in the transition state for cycloaddition. The orientation of the groups in the Δ^1-pyrrolines is similar to that observed by Huisgen in related 1,3-dipolar additions.[14] It is interesting to note that Huisgen has reported that diarylazirenes do not undergo thermal cycloaddition with dipolarophiles.[9]

Irradiation of a mixture of **7**, a dipolarophile, and xanthone, under conditions where xanthone absorbs $>95\%$ of the light (3660 Å), gave no photoadduct. This result tentatively suggests that the cycloaddition proceeds *via* the excited singlet state of **7**. Additional studies are currently in progress to further elucidate the nature of the excited state and the mechanistic implications of the above observations.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (Grant No. CA 12195-04).

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(16) NDEA trainee, 1969–1970.

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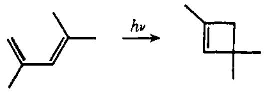
Absolute Rate of the Photochemical Valence Isomerization of a Conjugated Diene

Sir:

It has been demonstrated that the rates at which stereoisomers of a linear, 1,3-diene photoisomerize to cyclobutenes are distinctly different.[1,2] However, the absolute rate of each of these reactions was slower than the rate at which the diene isomerized stereochemically. These studies[1] also indicated that (i) stereoisomerization in these compounds cannot be a simple, elementary reaction which occurs in the same electronically excited state as cyclobutene formation, and (ii) very little can be inferred about the absolute rate of the valence isomerization from these results.

It was considered desirable to obtain the rate of cyclobutene formation from a diene relative to some other process whose rate can be estimated, *e.g.*, a collisional quenching process. Such a measurement would give a fundamental rate in the singlet photochemistry of conjugated dienes and would help to calibrate the rates of the other reactions in these systems. Hitherto, this was not possible because the linear 1,3-dienes which were known to isomerize to cyclobutenes did so with maximum efficiency in solution.

We now wish to report that we have discovered an example of a linear 1,3-diene which photoisomerizes to the corresponding cyclobutene in the gas phase but not in solution. 2,4-Dimethyl-1,3-pentadiene when irradiated at 253.7 nm in the gas phase isomerizes cleanly to 1,3,3-trimethylcyclobutene. The latter was identified from its molecular weight (mass spectrum, parent peak at m/e 96), infrared spectrum (C=C at 1640 cm^{-1}), and nmr spectrum [(CCl_4 solution, TMS as internal reference) δ 1.13 (6 H, singlet), 1.65 (3 H, multiplet), 2.08 (2 H, multiplet), 5.68 (1 H, multiplet)] and from its ready isomerization to 2,4-dimethyl-1,3-pentadiene on pyrolysis to 190° in the vapor phase.[3] It is noteworthy that earlier attempts[1a,5] to bring about reaction 1 in solution in solvents such as isooctane, diethyl ether, and cyclohexane yielded negative results.



(1)

In order to establish the activation process that allows (1) to occur in the gas phase only, inert gases such as argon, carbon dioxide, or ethane were added to the system. Typical results which were obtained with ethane are given in Table I. The increase in the quantum yields for the cyclobutene on the addition of small amounts of ethane parallels the effect that has been observed in other systems[6] in which a thermally labile product is formed in a photochemical reaction in the vapor phase. It can be attributed to the stabilization of the product by the removal of its excess vibrational energy in quenching collisions. At an ethane pressure of 1 atm this process is overtaken by the deactivation of the excited state of the diene. The latter effect can be only due to the removal of vibrational energy from the excited molecule, as it seems unlikely that electronic energy transfer can occur to molecules as diverse as the three quenchers used here. A reaction scheme which takes into account these effects is as follows (D = diene, C = cyclobutene, M = any molecule; superscript = excited electronic level, subscript = excited vibrational level)

Table I. Relative Quantum Yields for Reaction 1 in Vapor Phase[a]

Ethane pressure, Torr	0	54.50	192.5	382.5	718.5	1440
Cyclobutene,[b] μmol/min × 10	0.95	1.15	1.60	1.90	2.16	1.56

[a] Medium-pressure mercury arc; DDDP = nickel sulfate filter; room temperature; $I = 2.75 \times 10^{16}$ quanta/sec; volume = 560 ml; diene pressure = 13.5 Torr. [b] These rates are estimated to be precise to ±3%.

$$D + h\nu \longrightarrow D_m{}^1 \qquad (2)$$

$$D_m{}^1 + M \longrightarrow D_0{}^1 + M \qquad (3)$$

$$D_m{}^1 \longrightarrow C_n \qquad (4)$$

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(1) (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962); (b) *ibid.*, **91**, 7557 (1968); (c) S. Boué and R. Srinivasan, *ibid.*, **92**, 3226 (1970).
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