that the effect of the substituent on the NH shift parallels the profound influence that these substituents are known to have on the base strengths in these systems. Studies are in progress to measure the nitrogen-15 chemical shifts in these compounds.

Finally, the $J(^{14}NH)$ in pyrrole has been variously reported to be 55,[12] 60,[13] and 69.5 Hz.[14] These values correspond to a ^{15}N–H coupling constant of 77, 84, and 97.4 Hz, respectively.[15] Our findings for the indoles are consistent with this latter value and with the contention that the nitrogen atom is sp^2 hybridized.[3] This conclusion is further supported by microwave studies[16] and the recently reported[17] investigation of 2,5-di-*tert*-butylpyrrole-^{15}N.

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Isomerization of Conjugated Dienes *via* Photolysis of Metal Carbonyl–Diene Complexes

Sir:

Interest has been shown in the photochemistry of metal carbonyls, especially as photosubstitution reactions provide a synthetic tool for preparing new metal carbonyl–olefin complexes.[1–3] Many molybdenum and tungsten carbonyl–olefin complexes have been reported, and the photochemistry is known to proceed as in eq 1 and 2.[1,4,5] Subsequent photolysis of the metal carbonyl–olefin complexes has received

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_6{}^* \longrightarrow M(CO)_5 + CO \quad (1)$$

$$M(CO)_5 + \text{olefin} \longrightarrow [M(CO)_5(\text{olefin})] \quad (2)$$

relatively little attention. Photoexchange reactions have been reported,[1,6–8] and dimerization of norbornadiene *via* photolysis of norbornadiene–chromium tetracarbonyl has recently been reported.[9] We have initiated a study of the photochemistry of tungsten, molybdenum, and chromium hexacarbonyls and their olefin derivatives and wish to report here our preliminary results with the tungsten carbonyl–conjugated diene system.

We have observed that irradiation of solutions containing $W(CO)_6$ and either of the isomeric 1,3-pentadienes (piperylenes) or the isomeric 2,4-hexadienes leads to cis–trans isomerization.[10] The quantum yields are time dependent, first increasing and then gradually declining. The cis → trans quantum yields are generally much higher than the trans → cis reactions. We have observed net isomeric conversion of more than five molecules of piperylene per molecule of $W(CO)_6$ present in the system.

In Table I we report cis → trans quantum yields for the piperylene system in three solvents and for two irradiation times. In Table II we present quantum yield data for the isomers of 2,4-hexadiene. The quantum yields vary only slightly with changes in diene concentration over the range 0.01–0.1 *M*.

Table I. Quantum Yields for 0.05 *M* *cis-* → *trans*-Piperylene Conversion

Solvent	Irradiation time, min	[*trans*] formed, *M*	$\Phi_{c\rightarrow t}$
Pentane	180	1.90×10^{-3}	0.082
	460	4.16×10^{-3}	0.070
Dodecane	180	1.52×10^{-3}	0.066
	460	3.42×10^{-3}	0.058
Hexadecane	180	1.97×10^{-3}	0.085
	460	3.90×10^{-3}	0.066

Table II. Quantum Yields for 0.088 *M* 2,4-Hexadienes in Pentane

Irradiation time, min	$\Phi_{tt\rightarrow ct}$	$\Phi_{tt\rightarrow cc}$	$\Phi_{cc\rightarrow ct}$	$\Phi_{cc\rightarrow tt}$	$\Phi_{ct\rightarrow tt}$	$\Phi_{ct\rightarrow cc}$
175	0.038	*a*	0.053	0.019	0.046	0.005
460	0.026	*a*	0.085	0.019	0.065	0.010

[a] $\Phi_{tt\rightarrow cc}$ is less than 0.002.

The use of infrared spectroscopy for structural characterization in such systems has been demonstrated.[2–5] Irradiation of solutions of the piperylene and $W(CO)_6$ results in appearance of the new carbonyl peaks tabulated in Table III. The positions of the

Table III. Ir Data for $W(CO)_6$–Piperylene Irradiations

Starting material	Band (intensity), cm^{-1}		
cis-Piperylene	2080 (w)	1967.9 (s)	1950.2 (s)
trans-Piperylene	2080 (w)	1965.5 (s)	1949.0 (s)
70% *trans*-, 30% *cis*-piperylene	2080 (w)	1966.8 (s)	1949.2 (s)

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(10) Irradiations were carried out at 313 nm in a merry-go-round apparatus[11] at 27°. The samples were thoroughly degassed, and aliphatic hydrocarbon solvents were used with diene concentrations of 0.05–0.10 *M* and a $W(CO)_6$ concentration of 2.3×10^{-3} *M*. Conversion was generally less than 5%. Light intensity was measured by benzophenone-sensitized isomerization of *cis*-piperylene.[12] Dienes were analyzed by vpc on a 25-ft × 1/8 in. β,β'-ODPN column at 50°. The ir data were obtained using a Perkin-Elmer 225 grating infrared spectrophotometer. Quantum yields were ±10%.

(11) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

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maxima are close to those reported for [$\mathrm{W(CO)_5}$-(butadiene)].[2] Further irradiation results in other infrared bands, but *no shifting of the three primary product bands is observed.* Prolonged irradiation results in a decline of all carbonyl absorptions. The infrared bands observed in experiments with the 2,4-hexadiene are similar. The peaks due to primary photoproducts disappear thermally at very slow rates, and this may be partially due to the sensitivity of the intermediates to air. Slow regeneration of the $\mathrm{W(CO)_6}$ is also observed when irradiations are carried out in sealed infrared cells. The disappearance of $\mathrm{W(CO)_6}$ has been monitored starting with *cis*- and *trans*-piperylene; Figure 1 shows typical results as well as the per cent isomerization in the experiment with *cis*-piperylene. The quantum yield of disappearance of $\mathrm{W(CO)_6}$ at time zero is 0.20, indicating significant recombination of $\mathrm{W(CO)_5}$ and CO.[13] The initial rates of disappearance of $\mathrm{W(CO)_6}$ and of appearance of the primary photoproducts are the same with *cis*- or *trans*-piperylene. The decrease in the rate of disappearance is attributed to competing absorption by the photoproduct, which is yellow. Ultraviolet spectra indicate, for example, that the $\mathrm{W(CO)_6}$ is absorbing only ∼50% of the incident irradiation after an irradiation time of 60 min.

We propose that cis–trans isomerization of the dienes is the result of the photolysis of the diene–tungsten pentacarbonyl initially formed. Photoexchange reactions have been observed in these systems, but reactions of the ligands themselves have not been studied.[1,6-8] We have shown by following the ir spectra that 2,4-hexadiene exchanges with isopropylene when [$\mathrm{W(CO)_5}$-(isopropylene)] is produced photolytically. The exchange occurs rapidly at room temperature. A reasonable mechanism is outlined in eq 3–9. The

$$\mathrm{W(CO)_6} \xrightarrow{h\nu} \mathrm{W(CO)_6}^* \longrightarrow \mathrm{W(CO)_5} + \mathrm{CO} \tag{3}$$

$$\mathrm{W(CO)_5} + cis\text{-diene} \longrightarrow [\mathrm{W(CO)_5}(cis\text{-diene})] \tag{4}$$

$$\mathrm{W(CO)_5} + \mathrm{CO} \longrightarrow \mathrm{W(CO)_6} \tag{5}$$

$$[\mathrm{W(CO)_5}(cis\text{-diene})] \xrightarrow{h\nu} [\mathrm{W(CO)_5}\cdots(cis\text{-diene})]^* \tag{6}$$

$$[\mathrm{W(CO)_5}\cdots(cis\text{-diene})]^* \longrightarrow \alpha[\mathrm{W(CO)_5}(cis\text{-diene})] + (1-\alpha)[\mathrm{W(CO)_5}(trans\text{-diene})] \tag{7}$$

$$[\mathrm{W(CO)_5}(trans\text{-diene})] + cis\text{-diene} \longrightarrow [\mathrm{W(CO)_5}(cis\text{-diene})] + trans\text{-diene} \tag{8}$$

$$[\mathrm{W(CO)_5}(cis\text{-diene})] \xrightarrow{h\nu} \text{further substitution} \tag{9}$$

isomerization occurs in step 7 *via* the excited complex. The possibility of photoexchange exists but the production of free, electronically excited dienes can be ruled out. The free triplet is excluded because our attempt to dimerize isopropylene under these conditions failed.[14] The singlet excited state of the diene can be eliminated, since we have shown that the *cis,cis*-2,4-hexadiene can be converted to the trans,trans isomer in one step. This does not occur in the singlet excited state.[15] Step 9 is included because of the known further substitution and our observations concerning ultimate disappearance of absorption in the carbonyl stretching region of the infrared spectrum.

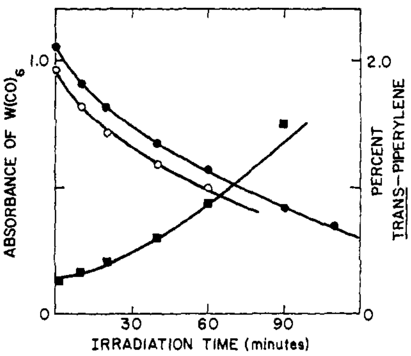
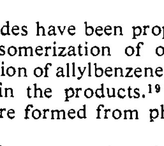


Figure 1. Disappearance of $\mathrm{W(CO)_6}$ by ir starting with *cis*-, ●, and *trans*-piperylene, ○, and per cent *trans*-piperylene, ■, formed from *cis*-piperylene; $\mathrm{W(CO)_6}$ concentration = 2×10^{-3} *M*, piperylene concentration = 0.1 *M*.

The competing absorption of light by the [$\mathrm{W(CO)_5}$-(diene)], the thermal isoprene–hexadiene exchange, and the time dependency of the isomerization quantum yields all support the mechanism proposed.[16] It seems highly probable that nearly all electronically excited species arrive at the lowest energy triplet configuration, either by direct S → T absorption or by very rapid nonradiative decay mediated by the heavy tungsten atom. The excited state of $\mathrm{W(CO)_6}$ itself is short lived, as evidenced by our inability to observe strong emission or chemical quenching by known triplet quenchers. Although short lived, this excited state must be highly energetic and reactive, because unimolecular decay to a pentacarbonyl intermediate occurs with nearly unit efficiency. Since monoolefin pentacarbonyl species are known to undergo further photolytic substitution,[1] their excited states must have enough energy to facilitate cis–trans isomerization of a weakened carbon–carbon double bond coordinated to the metal.[17] Interconversion of cis and trans olefins in the electronic excited state cannot be ruled out. The direct conversion of *cis,cis*-2,4-hexadiene to the trans,trans isomer is known to occur *via* the triplet state.[20,21] The likely configuration of the diene attached to the metal is s-cis as in I.[22] Triplet s-cis dienes decay largely to trans



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[13] The production of $\mathrm{W(CO)_5}$ when $\mathrm{W(CO)_6}$ is irradiated has approximately unit efficiency when the CO is removed from the system.[1]

[14] See, for example, R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

[15] J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

[16] We have obtained data for $\mathrm{W(CO)_6}$-assisted photoisomerization of simple alkenes which indicate a similar mechanism. Isomerization of the olefins does occur thermally under our conditions only after photolysis and the thermal contribution is small (<10%) compared to the photochemical reaction.

[17] Metal π-allyl hydrides have been proposed as the intermediates in the $\mathrm{Fe(CO)_5}$-assisted isomerization of olefins.[18] However, $\mathrm{DCo(CO)_4}$-catalyzed isomerization of allylbenzene did not result in significant deuterium incorporation in the products.[19] If the hydrides are important at all here, they are formed from photolysis of the [$\mathrm{W(CO)_5}$-(diene)] complex.

[18] See, for example, T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

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[21] J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969).

[22] N. A. Clinton and C. P. Lillya, *ibid.*, **92**, 3058 (1970).

geometry about the double bonds,[23] and a similar preferred direction of decay might be expected for the excited complex I. We have observed substantial selectivity for the formation of trans dienes. In summary, the evidence suggests that the isomerization of the dienes occurs *via* the triplet excited state of the $[W(CO)_5(diene)]$ due to direct absorption of light by the complex. Further studies of the structure and reactivity of this complex are in progress.

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(23) This has been confirmed experimentally by selective triplet transfer to *s-cis,trans*-piperylene: J. Saltiel, L. Metts, and M. Wrighton, unpublished results.

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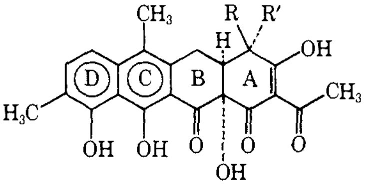
Structure of Chelocardin, a Novel Tetracycline Antibiotic

Sir:

Chelocardin, a broad-spectrum antibiotic produced by *Nocardia sulphurea*, was first described in 1962.[1] Based on further work, we conclude that chelocardin is 2-decarboxamido-2-acetyl-4-dedimethylamino-4-epi-amino-9-methyl-5a,6-anhydrotetracycline (**1a**), a new member of the tetracycline family. This structure contains several features which are not commonly encountered among the tetracyclines but which are readily accommodated biogenetically.[2] Chelocardin, $C_{22}H_{21}NO_7$[3] ($M^+ = 411$, $M - H_2O = 393.1273$), possesses a typical anhydrotetracycline absorption spectrum[4] (λ_{max}^{MeOH} 226, 276, and 437 nm (log ϵ 4.51, 4.70, and 3.91)). Subtraction of the uv spectrum of 2-acetylnaphthalene-1,8-diol leaves a difference curve characteristic of the 2-acetyl-1,3-dione system[5] present in ring A. This finding is consistent with the presence of a single nitrogen atom, isolatable as ammonia on strong alkaline treatment, and the presence of ir carbonyl absorption at 1684 cm^{-1}.[6] The antibiotic gives naphthacene and anthracene derivatives on zinc dust distillation, establishing the carbon framework.



1a, R = NH_2; R' = H
b, R = H; R' = NH_2
c, R = $NHCOCH_3$; R' = H
1d, R = H; R' = $NHCOCH_3$
e, R = NMe_2; R' = H
f, R = H; R' = NMe_2

The pmr spectrum (60 MHz) of chelocardin hydrochloride in dimethyl-d_6 sulfoxide solution further emphasizes the similarity of chelocardin to model anhydrotetracyclines:[7,8] δ 2.56 (s, $COCH_3$, partly obscured by solvent resonance), 2.34 (s, 6-CH_3), 2.28 (s, 9-CH_3), 4.87 (d, H_4), 2.5–3.8 (m, H_{4a}, H_5, and $H_{5'}$), and 7.31 and 7.57 ppm (AB d, J = 8.0 Hz, ArH_2). The pmr spectrum (100 MHz) of **1c** in acetone-d_6 was much more clearly defined and allowed determination of chemical shifts and coupling constants: δ 2.10 (s, N–$COCH_3$), 2.31 (s, 6-CH_3), 2.34 (s, 9-CH_3), 3.08 (d of t, H_{4a}, $J_{4,4a}$ = 4.2 Hz, $J_{4a,5}$ = 12.3 Hz, $J_{4a,5'}$ = 4.4 Hz), 2.72 (d of d, H_5, $J_{5,5'}$ = 16.4 Hz), 3.53 (d of d, $H_{5'}$), 5.79 (d, H_4), 7.32 (d, H_7, $J_{7,8}$ = 8.5 Hz), 7.50 (d, H_8), and 2.50 ppm (s, C–$COCH_3$).

These assignments were confirmed by appropriate spin-decoupling experiments. Complete analysis of the spectrum affords corroboration of the structure, assignment of the relative stereochemistry, and establishment of the solution conformation (to be discussed in our full paper).

The occurrence of tetracyclines with an acetyl function at C-2 in place of the more common carboxamido group[5,6,9] and a primary amino function at C-4[10] has precedent, whereas the presence of a second aromatic *C*-methyl group is novel in this class of antibiotics. The position of the aromatic methyl group was ascertained from the ortho coupling of the two aromatic protons and the discovery that each aromatic proton is proximate to an aromatic methyl group. The latter was clearly demonstrated by a nuclear Overhauser effect[11] observed with derivative **1c**. Simultaneous irradiation of both aromatic methyl resonances results in a significant increase in the integrated intensity of both aromatic proton resonances (H-7, 16.5%; H-8, 11.5%) compared to the integrated intensity when the irradiation is off resonance.

Application of the method of aromatic-solvent-induced chemical shift differences in pyridine[12] fails with chelocardin derivatives. Neither the methyl nor the proton resonances associated with rings C and D in derivative **1c** move with respect to their positions in chloroform. Rules derived from studies with simple, monofunctional models may be unsatisfactory on occasion when dealing with complex substrates having

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