enes to serve as model systems for cyclopropanation.[4] In an effort to find a less stable and more reactive metal–carbene complex, we recently synthesized (diphenylcarbene)pentacarbonyltungsten(0)[5] (1) a carbene complex not stabilized by electron donating heteroatoms attached directly to the carbene carbon atom.[6] Here we report several interesting reactions of 1 with alkenes that may bear upon the mechanism of cyclopropanation and olefin metathesis reactions.

Since even relatively stable metal–carbene complexes such as $(CO)_5WC(OCH_3)C_6H_5$ react with vinyl ethers,[4] we first studied the reaction of 1 with ethyl vinyl ether. Heating a solution of 1 in ethyl vinyl ether at 37° for 3 hr gave 65% 1-ethoxy-2,2-diphenylcyclopropane, 11% 1,1-diphenylethylene, ~45% $W(CO)_6$, and no 1. When 1 was heated to 100° for 2.5 hr with the unactivated alkene isobutylene, a 76% yield of 1,1-diphenylethylene was obtained in addition to 45% $W(CO)_6$ and approximately 10% 1,1-dimethyl-2,2-diphenylcyclopropane.
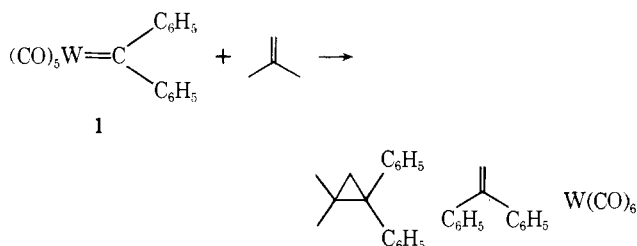
To determine the source of the methylene fragment in 1,1-diphenylethylene in these unusual reactions, we studied the reaction of trans-2-butene with 1. When 1 was heated to 50° for 4 hr in trans-2-butene, a 54% yield of 1,1-diphenyl-1-propene was obtained in addition to 41% $W(CO)_6$ and a trace of 1,2-dimethyl-3,3-diphenylcyclopropane. These experiments demonstrate the scission of the carbon–carbon double bond of the alkene and the combination of a methylene fragment with the diphenylcarbene group of 1.

We considered the possibility that the second fragment from the alkene scission reaction might be incorporated as the carbene ligand in a new metal carbene complex. The reaction of 1 with 1-methoxy-1-phenylethylene was studied since the expected new carbene complex $(CO)_5WC(OCH_3)C_6H_5$ is stable under the reaction conditions. When 1 was heated to 32° for 6 hr with 1-methoxy-1-phenylethylene, a 24% yield of $(CO)_5WC(OCH_3)C_6H_5$ was obtained in addition to 26% 1,1-diphenylethylene, 13% 1, $W(CO)_6$, and a trace of 1-methoxy-1,2,2-triphenylcyclopropane. Thus in the alkene scission reaction, one fragment of the alkene is incorporated into 1,1-diphenylethylene while the other fragment is incorporated into a new metal-carbene complex.[7]
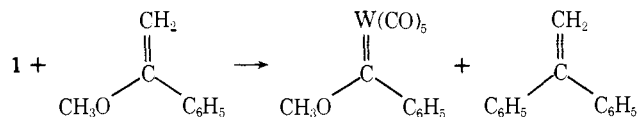
Both the cyclopropanation and alkene scission reactions of 1 can be explained in terms of the mechanistic scheme (Scheme I) shown below. The metallocyclobutane 2 formed by rearrangement of a metal complex containing both a carbene and an alkene ligand is the key intermediate in these reactions. 2 can undergo a reductive elimination to give a cyclopropane or can undergo cleavage to give a metal complex containing both a coordinated 1,1-diphenylethylene and a new carbene ligand.

The mechanistic scheme proposed here explains Fischer's observation of 1-methoxy-1-phenylethylene in the reaction of $(CO)_5CrC(OCH_3)C_6H_5$ with ethyl vinyl ether[4] and with

Scheme I
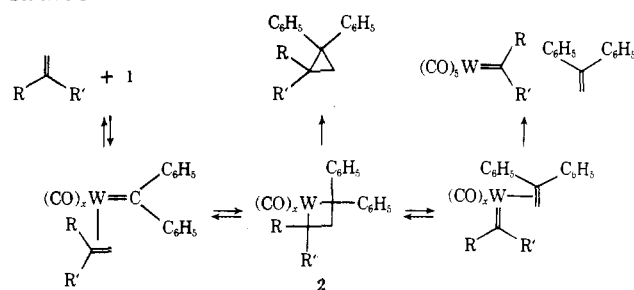
1-vinyl-2-pyrolidone.[8] Previously, Lappert has observed related exchange reactions of tetraaminoethylenes and bisnitrogen substituted carbene–metal complexes.[9] A metallocyclobutane intermediate similar to 2 was recently proposed by Noyori in the bis(1,5-cyclooctadiene)nickel(0) catalyzed reaction of bicyclobutanes with electron deficient olefins.[10]

It should be noted that the equilibrium between a metallocyclobutane and a metal complex containing both an alkene and a carbene ligand provides a sufficient mechanism for olefin metathesis. Such a scheme has previously been proposed by Chauvin.[11] A related equilibrium between a metallocyclopentane and a metallocyclobutane containing a carbene ligand has been proposed by Grubbs to explain olefin metathesis.[12]

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Baluchistanamine. A Novel Type Dimeric Isoquinoline Alkaloid[1]

Sir:

It has been adumbrated that the isoquinolone alkaloids (1)[2] originate in plants from the oxidation of simple benzylisoquinolines. A parallel assumption is that the alkaloid her-

nandaline (2) is formed by oxidation of a thalicarpine type aporphine-benzylisoquinoline.[3] We wish herewith to report the isolation and characterization of the first known isoquinolone-benzylisoquinoline alkaloid, baluchistanamine (3), which strongly supports the aforementioned hypotheses.

1
6. R = CH$_3$;
   R$_1$ = H

2
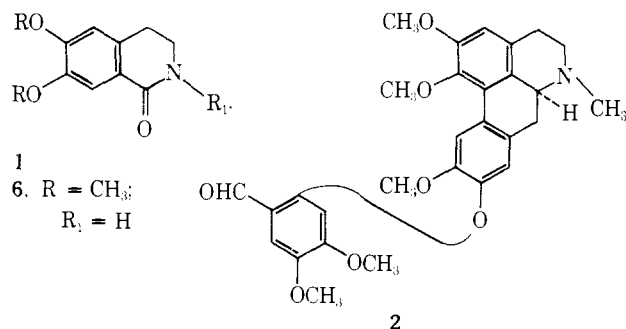
Examination of the basic extracts of *Berberis baluchistanica* Ahrendt (Berberidaceae) yielded the crystalline and colorless free base baluchistanamine (3), mp 122–124° (cyclohexane–benzene), λ_{max}(EtOH) 224, 260, 270, 282 sh, 294 sh, and 305 sh nm (log ϵ 4.57, 4.05, 4.06, 3.97, 3.90, and 3.80), with a bathochromic shift in base due to the presence of a phenolic function: ν_{max}(CHCl$_3$) 1640 (conjugated tertiary δ-lactam) and 1720 cm^{-1} (conjugated aldehyde); CD (methanol) (concn = 0.5 mg/ml) $[\theta]_{290}$ = 0, $[\theta]_{263}$ = +2560, $[\theta]_{253}$ = 0, $[\theta]_{231}$ = −14,000, and $[\theta]_{220}$ = 0.

The mass spectrum of baluchistanamine (3) shows a small molecular ion peak m/e 638 (C$_{37}$H$_{38}$N$_2$O$_8$) cleaving to give a base peak m/e 411 (C$_{23}$H$_{27}$N$_2$O$_5$). Other important fragments are m/e 365 (C$_{21}$H$_{21}$N$_2$O$_4$), 227 (C$_{14}$H$_{11}$O$_3$), 206 (C$_{12}$H$_{16}$NO$_2$), 204 (C$_{12}$H$_{14}$NO$_2$), and 120 (C$_7$H$_4$O$_2$). Consistent with the presence of one nonbas-

ic amidic nitrogen in the alkaloid, no doubly charged ion derived from the base peak m/e 411 is present.

The nmr spectrum of 3 in CDCl$_3$ contains two N-methyl singlets at δ 2.35 (amine) and 3.10 (amide), three methoxyl singlets at δ 3.62, 3.85, and 3.90, a complex pattern representing ten aromatic protons with peaks at δ 6.55, 6.73, 6.90, 7.05, 7.20, 7.36, 7.48, and 7.61, and finally an aldehyde proton downfield at δ 9.76.

Since other alkaloids present in *B. baluchistanica* include the known oxyacanthine (4) and obaberine (5), as well as the isoquinolone corydaldine (6),[4] it was considered a definite possibility that baluchistanamine (3) was derived biogenetically from oxidation of oxyacanthine (4). In order to emulate this process *in vitro*, obaberine (5) was oxidized at room temperature with dilute KMnO$_4$ in acetone.[5] The main oxidation product, formed in 35% yield, proved to be the isoquinolone-benzylisoquinoline dimer 7, C$_{38}$N$_{40}$N$_2$O$_8$, mp 105–108° (cyclohexane–benzene), whose uv spectrum (λ_{max}(EtOH) 226, 262, 270, 283 sh, 292 sh, and 305 sh nm (log ϵ 4.58, 4.12, 4.10, 3.99, 3.85, and 3.77)) and CD curve in methanol (concn = 0.45 mg/ml: $[\theta]_{290}$ = 0, $[\theta]_{263}$ = +2020, $[\theta]_{253}$ = 0, $[\theta]_{231}$ = −14,900, and $[\theta]_{220}$ = 0) are very close to those for alkaloid 3. Similarly, the nmr spectrum of 7 bears a direct resemblance to that of 3 except for the presence, in the former, of an extra methoxyl singlet at δ 3.90; while in the mass spectrum, the m/e 227 ion of 3 is now replaced by a m/e 241 ion. Treatment of baluchistanamine (3) with ethereal CH$_2$N$_2$ then furnished O-methylbaluchistanamine, identical with 7 in terms of tlc R_f values, CD curves, and uv and mass spectra.

Aiming to synthesize the alkaloid itself, oxyacanthine (4) was oxidized under the same conditions as obaberine (5). The oxidation product was obtained in only 5% yield, but proved to be identical with baluchistanamine (3) in terms of tlc R_f values, and uv and mass spectra.

3. R = H
7. R = CH$_3$

m/e 411

m/e 365

m/e 227

m/e 206 and 204

m/e 120

4, R = H
5. R = CH$_3$

8
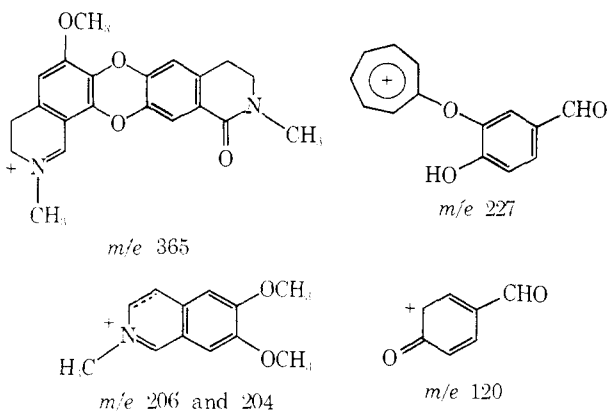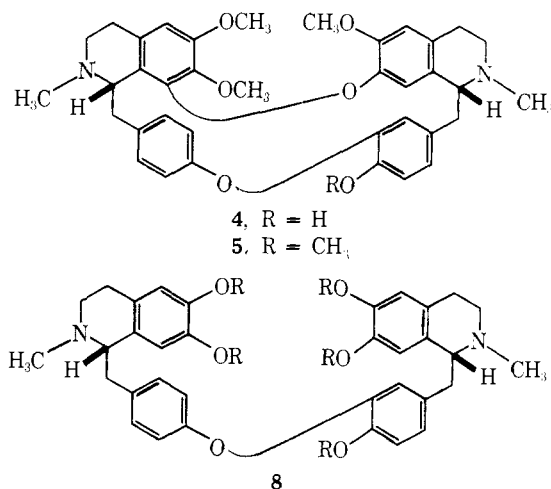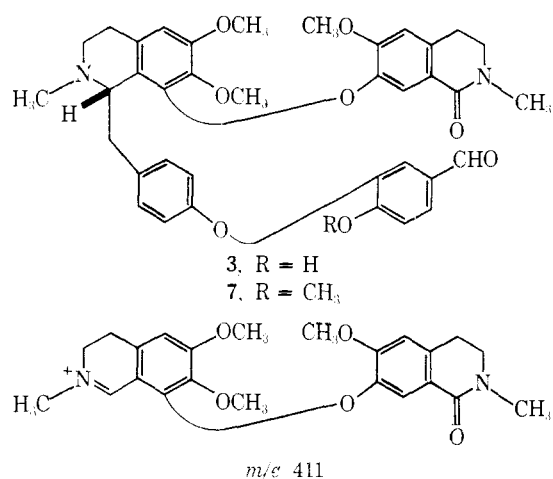
Within the intricate mosaic of isoquinoline alkaloids, it can be stated that the dimerization of two enantiomeric N-methylcoclaurine units can lead to a bisbenzylisoquinoline of the dauricine type (8). At this stage, either of two different phenolic oxidative pathways can prevail. One leads to proaporphine-benzylisoquinoline dimers of the pakistanamine type which can undergo dienone-phenol rearrangement to furnish aporphine-benzylisoquinolines such as pakistanine.[6] The alternate phenolic oxidative route will produce bisbenzylisoquinolines with two diaryl ether bridges, *e.g.*, oxyacanthine (4), which can be subject to oxidative cleavage to produce isoquinolone-benzylisoquinoline dimers. It is self-evident that the *in vivo* oxidation of an oxyacanthine type alkaloid to an isoquinolone-benzylisoquino-

line dimer, as well as that of a simple monomeric benzyliso-quinoline to an isoquinolone, is an intrinsic part of the general alkaloid catabolic process within *B. baluchistanica*.[7]

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Singlet–Triplet Transformation in the Dimeric Association of Pyridinyl Radicals

Sir:

Three kinds of radical pairs, A_S, A_T, and B_T, have been postulated for the association of pyridinyl radicals **1** in 2-methyltetrahydrofuran (MTHF) glass, and the generation of the triplet dimer B_T from the diamagnetic dimer A_S by light irradiation was demonstrated in a previous esr study.[1] A further study on the association has now revealed that the transformation of A_S into B_T occurred probably through the charge-transfer excitation of the diamagnetic dimer. The spectroscopic study will be reported.
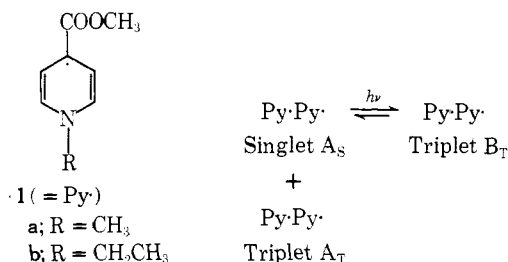
The esr study disclosed that the triplet B_T species can be generated by irradiating the radical solution at 77°K with the light of 420–500 nm, which was selected by the use of three Toshiba glass filters, VY-42, VY-50, and VV-44. However, the radical solution does not show any characteristic absorption band in this region at 77°K.[2] It was then thought that the specimen had been irradiated with the light enough to convert A_S into B_T. Thus, the following careful examination of the radical spectra was carried out.

1-Methyl-4-methoxycarbonylpyridinyl (**1a**) was purified by distillation under vacuum. The radical solution in MTHF at 77°K exhibited the spectrum shown in Figure 1 (b and c), which was taken before the solution at 77°K was exposed to any light except the dispersed light of a Cary 14 spectrophotometer for the measurement.[3] This spectrum has a significant absorption band at 437 nm. Irradiation of the solution with a light beam from the near-infrared source
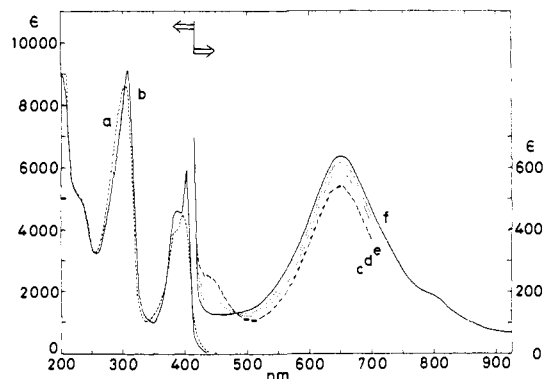

Figure 1. Absorption spectrum of 1-methyl-4-methoxycarbonylpyridinyl in MTHF: (a) 6.7×10^{-3} M, at room temperature; (b) 8.3×10^{-3} M, at 77°K; (c) 6.3×10^{-2} M, at 77°K before irradiation; (d) after 10-sec irradiation with a W-lamp; (e) after 20-sec irradiation; (f) after sufficient irradiation.
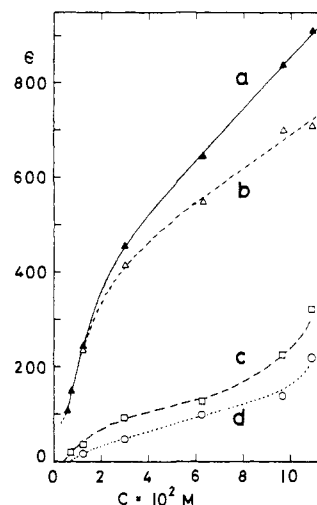

Figure 2. Concentration dependences of the absorption intensities of 1-methyl-4-methoxycarbonylpyridinyl at 77°K: (a) $\epsilon(653$ nm) after irradiation; (b) $\epsilon(653$ nm) before irradiation; (c) intensity increase at 675 nm with irradiation; (d) intensity decrease at 437 nm with irradiation.

(GE-CPR W-lamp) of the spectrometer for 10 sec changed the spectrum into that of Figure 1d. Further irradiation with the light for 10 sec gave the spectrum of Figure 1e, and then the spectrum of Figure 1f was finally shown after sufficient irradiation. It was thus clearly observed that the light irradiation causes the disappearance of the band at 437 nm, being accompanied by the increase of the broad absorption in 500–800 nm with the maximum increase at 675 nm. Wavelength specificity to the spectral change was the same as that shown in the esr study.[1] The change of the green color into a blue on irradiation was also seen. The spectral change is observed when the solution was moderately concentrated, implying that the change is directly related to the transformation in the radical associations. The concentration dependences of the intensity changes at two wavelengths are shown in Figure 2, together with the dependence of ϵ (at 653 nm) on the radical concentration.[4]

A similar phenomenon was observed for 1-ethyl-4-methoxycarbonylpyridinyl (**1b**) in MTHF glass. The spectrum is shown in Figure 3, in which the disappearance of the absorption at 440 nm on irradiation accompanied the spectral change in the region of 500–750 nm.

The absorption at around 440 nm coincides in wavelength with the light specific to the generation of the B_T species observed in the esr study. Since the intensity de-

COOCH₃

Py·Py· $\overset{h\nu}{\rightleftarrows}$ Py·Py·
Singlet A_S Triplet B_T

+

Py·Py·
Triplet A_T

1 (= Py·)
a; R = CH₃
b; R = CH₂CH₃