Fig. 2. Part of the ^{1}H-NMR spectra (200 MHz, CD_2Cl_2) of a) 6⊕ and b) 6⊕ plus ten equivalents of *Pirkle*'s reagent (S)-(+)-7. Peaks indicated by 7,8, o or o', m, or m' in spectrum (a) (labeling given in Fig. 1) are split in spectrum (b). The signals corresponding to the chiral reagent are marked by a black square.

Those protons might be hidden by the 4-phenyl group and the pentaoxyethylene link so that their chemical shift is not sensitive to the particular environment induced by *Pirkle*'s reagent.

Spectrum 2b indicates that the topological chirality of 6⊕ is accompanied by easy recognition of its enantiomers by a chiral reagent. This observation might be related to the high rigidity of the molecule. Demetalation of 6⊕ (KCN in H_2O/CH_2Cl_2, 78% yield) leads to an extremely flexible system 1, whose two rings can easily glide within one another. The catenane nature of 1 was supported by its mass spectrum (m/z 1284 (M) and 642 (M/2)). Its topological chirality is obvious from the directed nature of the starting compound 2 and the synthetic route followed. In contrast to 6⊕, no clear enantioselective interaction with *Pirkle*'s reagent could be observed in the NMR spectra of 1.

The present templated synthesis of chiral catenands indicates that separation of their enantiomers will be easiest at the stage of their intermediate rigid copper(I) catenates. These enantiomerically pure complexes are expected to show enantioselectivity in both photoinduced electron transfer and interaction with DNA helices.[15]

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Conjugated and Nonconjugated Cyclopentenones by a Reaction Cascade from Methyl 6-Oxo-5-phenyl-1,3,4-oxadiazine-2-carboxylate and 1,3-Butadienes**

By *Joachim Hegmann, Manfred Christl,* *Karl Peters, Eva-Maria Peters,* and *Hans Georg von Schnering*

Five-membered carbocycles are structural components of numerous natural products and therefore attractive synthetic goals.[1] Since synthetic procedures with a broad scope of application are still unknown, new methods are of interest. Herein we report on reactions of the title heterocyclic compound 1 with 1,3-butadienes 2; these reactions, although multistep processes, afford conjugated and nonconjugated cyclopentenones in a one-pot procedure and also allow the annelation of these five-membered rings.
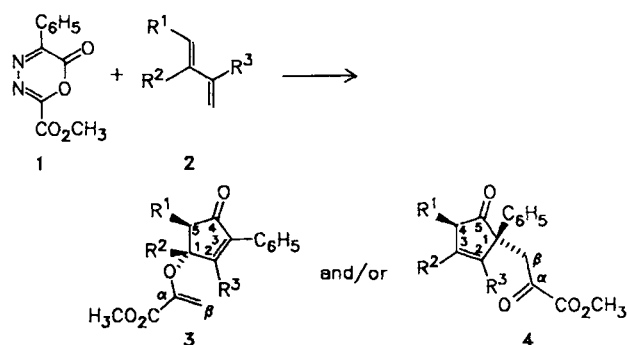
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Table 1. Reaction conditions, yields, and melting points of some products for the reactions of 1 with 2 (50% excess).

2	R¹	R²	R³	Solvent	t_1 [a]	(T [°C])	t_2 [a]	(T [°C])	Product [b]	Yield [%]	M.p. [°C]
a	H	H	H	CCl₄	7	(40)	340	(80)	3a, 4a	20	oil
b	H	CH₃	H	CH₂Cl₂		120 (20)			3b	13	80–82
	H	CH₃	H	} CCl₄	2	(80)	480	(80)	{ 4b	19	oil
	H	H	CH₃						{ 3b'	15	oil
c	H	CH₃	CH₃	CCl₄		240 (20)			3c [c]	11	oil
				CCl₄		3 (80)			4c	51	oil
d [d]	CH₃	CH₃	H	CCl₄	3	(80)	48	(80)	4d	46	oil
e	CH₃	H	CH₃	CCl₄	7	(80)	340	(80)	3e	27	96–97
f	(CH₂)₃		H	CH₂Cl₂	4	(20)	48	(20)	3f	54	60–61
g	(CH₂)₄		H	CCl₄	2	(80)	48	(80)	4g	43	97–100
h	(CH₂)₅		H	CH₂Cl₂		48 (20)			4h	41	61–62

[a] Reaction times in h; t_1 refers to the complete conversion of 1 and t_2 to that of the corresponding γ-oxoketene, e.g., 5 in Scheme 1. [b] The products were isolated by flash chromatography (SiO₂, petroleum ether/ethyl acetate 4 : 1) or by crystallization (3f, 4g, 4h). Their structures are in agreement with the elemental analyses and the spectroscopic data (for several examples see Table 2). [c] Along with 38% of 7, which was separated by crystallization and chromatography. [d] Dimethyl-butadiene 2d (200% excess) was used as a 3 : 1 mixture with its (Z) isomer, which reacts appreciably more slowly.

Thus, treatment of 1 with 1,3-butadiene 2a in tetrachloromethane at 40°C, followed by heating at reflux, gave a 3 : 1 mixture of the conjugated cyclopentenone derivative 3a and the nonconjugated isomer 4a in a yield of ca. 20%. Products analogous to 3a were formed from (E)-2-methyl-1,3-pentadiene 2e, 1-vinylcyclopentene 2f, 2,3-dimethyl-1,3-butadiene 2c (at 20°C), and, in part, from isoprene 2b. On the other hand, the reactions of 1 with (E)-3-methyl-1,3-pentadiene 2d, 1-vinylcyclohexene 2g, 1-vinylcycloheptene 2h, 2,3-dimethyl-1,3-butadiene 2c (at 80°C), and, in part, with isoprene 2b afforded nonconjugated cyclopentenone derivatives 4. The results are summarized in Table 1 and selected spectroscopic data are collected in Table 2. The relative configurations of C-1 and C-5 indicated in the formula were confirmed for 3f by NOE experiments and are therefore plausible for the other compounds 3 as well. From those and from mechanistic considerations (see below) the relative configurations of C-1 and C-4 of compounds 4 were derived.

The reaction cascades presumably begin with the cycloaddition of a CC double bond of 2 to the diazabutadiene system of 1. In the case of the nonsymmetric butadienes 2, the unsubstituted vinyl group is expected to be the more reactive and the orientation should correspond to that observed in the addition of styrene to 1.[2] As found for normal reactions of olefins with 1,[2] the Diels–Alder adducts could not be observed. However, the products

Scheme 1.

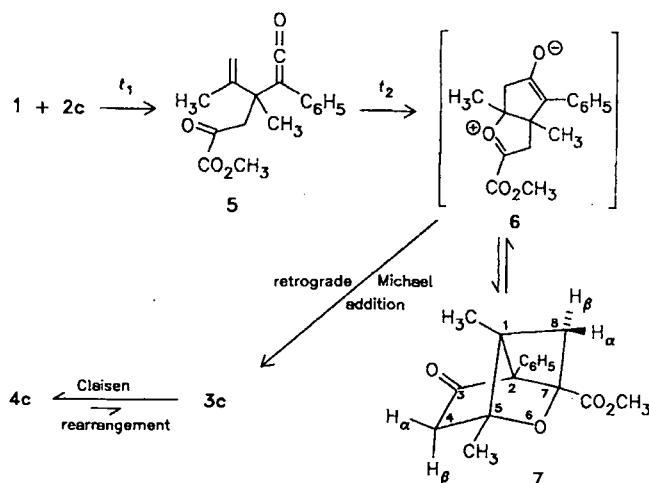Table 2. Selected spectroscopic data for 3a, 3c, 4c, and 7: NMR (CDCl₃, δ values, coupling constants in Hz).

3a: IR (CCl₄): $\tilde{v}=1750$ (sh), 1738, 1728 (ketone and ester carbonyl), 1629 cm⁻¹ (C=C)

3c: ¹H-NMR: 1.71 and 2.19 (each s; 1-CH₃, 2-CH₃), 2.64 and 3.16 (each d, $J_{5,5}=18.5$; 5-H₂), 3.80 (s; OCH₃), 4.70 and 5.55 (each d, $J_{8,8}=2.5$; β-H₂), 7.31 (o-H), 7.36 (p-H), 7.42 (m-H).—¹³C-NMR: 12.4 (q; 2-CH₃), 24.7 (lq; 1-CH₃), 45.7 (t; C-5), 52.4 (q; OCH₃), 83.7 (s; C-1), 100.8 (t; C-β), 140.9 (s; C-3), 147.5 (s; C-α), 164.0 (s; CO₂CH₃), 171.1 (s; C-2), 201.4 (s; C-4), 128.3 (especially strong signal, d; m-C, p-C), 129.1 (d; o-C), 130.6 (s; ipso-C)

4c: IR (CCl₄): $\tilde{v}=1753$, 1734, 1710 cm⁻¹ (C=O).—¹H-NMR: 1.54 (tq, J with 3-CH₃≈1.0, J with 4-H₂≈2.0; 2-CH₃), 1.90 (sext, J with 4-H₂≈1.0; 3-CH₃), 2.96 and 3.06 (each dqq, $J_{4,4}=22.5$; 4-H₂), 3.70 and 3.75 (each d, $J_{8,8}=18.5$; β-H₂), 3.84 (s; OCH₃), 7.21–7.26 (o-H, p-H), 7.32 (m-H).—¹³C-NMR: 10.7 and 14.0 (each q; 2-CH₃, 3-CH₃), 43.2 and 46.4 (each t; C-β, C-4), 53.1 (q; OCH₃), 61.9 (s; C-1), 131.0 (s; C-3), 132.7 (s; C-2), 160.8 (s; CO₂CH₃), 190.9 (s; C-α), 214.7 (s; C-5), 126.2 (d; o-C), 127.4 (d; p-C), 128.9 (d; m-C), 138.5 (s; ipso-C)

7: IR (KBr): $\tilde{v}=1745$ cm⁻¹ (ketone and ester carbonyl).—¹H-NMR: 1.30 and 1.51 (each s; 1-CH₃, 5-CH₃), 2.20 (d, $J_{8,8}=8.5$; 8α-H), 2.63 (d; $J_{4,4}=17.5$; 4α-H), 2.64 (dd, $J_{4\beta,8\beta}=1.3$; 8β-H), 2.87 (dd, 4β-H), 3.73 (s; OCH₃), 7.12 (o-H), 7.27–7.38 (m-H, p-H).—¹³C-NMR: 11.8 and 16.4 (each q; 1-CH₃, 5-CH₃), 40.4 and 51.7 (each t; C-4, C-8), 52.5 (q; OCH₃), 59.0 (s; C-1), 77.4 (s; C-2), 85.7 and 86.4 (each s; C-5, C-7), 167.1 (s; CO₂CH₃), 208.2 (s; C-3), 127.6 (d; p-C), 128.4 and 129.0 (each d; o-C, m-C), 131.7 (s; ipso-C)

formed from them, γ-oxoketenes such as 5, could be detected in every case owing to an IR band of the reaction mixture at ca. 2100 cm⁻¹.

In the case of 2,3-dimethylbutadiene 2c, we were able to identify a second intermediate in addition to the γ-oxoketene 5 (Scheme 1). This intermediate could be isolated (67% yield, m.p. = 133–136°C) when the reaction was carried out in dichloromethane at 20°C (1 d). According to the X-ray structure analysis, it is the tricyclic compound 7. The bonds C1-C2 and C2-C7 (159.8 and 160.5 pm) in the four-membered ring are significantly lengthened, whereas the lengths of all other endocyclic CC bonds lie between 151.2 and 154.1 pm.[3] Heating of 7 in tetrachloromethane at 80°C resulted in the formation of 4c, with 3c being observed as an intermediate.

The zwitterion 6 appears to be a logical intermediate for the conversion of 5 into 3c and 7. Intramolecular addition of the enolate group to the carbenium-oxonium moiety would lead to 7. This reaction is apparently reversible at elevated temperatures, so that 6 can undergo a retrograde Michael addition generating the more stable 3c. Claisen rearrangement of 3c then gives rise to 4c.

Whether the reactions at 80°C lead to the pyruvic ester enol ethers 3 or to the pyruvic esters 4 presumably de-

pends on their relative thermodynamic stability. We draw this conclusion from the finding that alkyl substituents R^2 favor the formation of 4 in each case, at least at 80°C. The exception, 3f, might be due to the fact that it has a lower strain energy than 4f, since the latter contains a CC double bond to a bridgehead.

The reaction 5→6 is an electrophilic attack of the ketene functionality at the α-vinyl group with participation of the γ-oxo oxygen atom. Out of a number of conceivable alternatives, the reaction times t_2 (Scheme 1, Table 1) lead us to prefer a two-step process involving a zwitterionic intermediate whose five-membered ring contains a carbocationic center in addition to the enolate moiety. In the second step, the oxo group acts as a nucleophile toward the cationic center. The slow conversion of the ketene intermediate for $R^2 = H$ (compare t_2 in Table 1 for 2a, b, e) and its rapid disappearance for $R^2 = $ alkyl (compare t_2 for 2c, d, f–h) indicate that secondary and tertiary carbocationic centers, respectively, are generated.

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[3] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-52845, the names of the authors, and the journal citation.

μ-Hydroxo- and μ-Oxobis(μ-acetato)diruthenium Complexes with Weak Intramolecular Ru···Ru Interactions**

By Peter Neubold, Karl Wieghardt,* Bernhard Nuber, and Johannes Weiss

The electron-spectroscopic, magnetic, and electrochemical properties of binuclear transition-metal complexes containing the structural unit $[M_2^{III}(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2]^{2\oplus}$ are the subject of intensive investigation, in particular because the complexes of iron and manganese are model complexes for metalloproteins in which the metal centers are held together by μ-oxo and μ-hydroxobis(μ-carboxylato) bridges.[1, 2] We recently showed that, in the case of the analogous molybdenum(III) complexes, a Mo≡Mo bond $(\sigma^2\pi^4)$ is formed when a μ-hydroxo-bridged complex is deprotonated, giving $[Mo_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2]^{2\oplus}$.[3] The mixed-valence Mo^{III}-Mo^{IV} complex, which we also prepared, contains a weaker Mo–Mo bond with a bond order of 2.5 $(\sigma^2\pi^3)$.[3b] It was therefore of interest to investigate the corresponding chemistry of ruthenium, since, in this case, only a Ru^{III}-Ru^{III} single bond $(\sigma^2\pi^4\pi^{*4})$ is expected and oxidation to the Ru^{III}-Ru^{IV} complex should result in an increase in the bond order to 1.5 $(\sigma^2\pi^4\pi^{*3})$.

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Hydrolysis of $LRuCl_3 \cdot H_2O$ (L = N,N',N''-trimethyl-1,4,7-triazacyclononane) in aqueous NaOAc solution results in the formation of a deep violet solution, which, after addition of $NaPF_6$, affords violet crystals of 1 in 85% yield. Complex 1 undergoes protonation in 2 M hydrochloric acid, yielding dark green microcrystals of 2. Dissolution of 2 in H_2O results in deprotonation and quantitative re-formation of 1. The dissociation constant of 1 at 20°C ($pK_a = 1.9$) was determined spectrophotometrically.

1 $[L_2Ru_2^{III}(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2][PF_6]_2 \cdot 0.5 H_2O$

2 $[L_2Ru_2^{III}(\mu\text{-OH})(\mu\text{-CH}_3\text{CO}_2)_2][PF_6]_3$

3 $[L_2Ru^{III}Ru^{IV}(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2][PF_6]_3$

Complex 1 was oxidized in aqueous solution with $Na_2S_2O_8$ to the mixed-valence $Ru^{III}Ru^{IV}$ dimer 3, which was isolated as the orange-brown $PF_6^{\ominus}$ salt. The electronic spectra of the new complexes are shown in Figure 1.
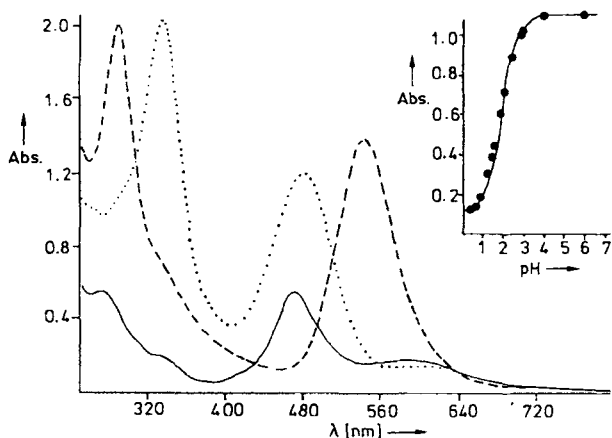

Fig. 1. Electronic spectra of 1 (H_2O), 2 (5M HCl) and 3 (H_2O). ([1]=2.15 × 10⁻⁴M (----); [2]=2.15 × 10⁻⁴M (——); [3]=2.15 × 10⁻⁴M (·····); 1-cm cuvette); the inset shows the absorption of 1 at 540 nm as a function of pH.

The cyclovoltammogram of 1 in CH_3CN (0.1 M nBu_4NPF_6; Pt electrode) shows a reversible electron transfer at $E_{1/2} = +0.59$ V versus the normal hydrogen electrode $(NHE)^{[4]}$ as well as an irreversible reduction at -0.88 V versus NHE. Coulometry gave 1.0 ± 0.1 electron/dimer for the reversible transition.

Measurement of the molar magnetic susceptibility between 100 and 293 K using the Faraday method showed that 1 is diamagnetic, whereas 2 has a temperature-dependent magnetic moment per dimer of $\mu_{eff} = 0.68 \mu_B$ (98 K) and 1.82 μ_B (293 K). Complex 2 exhibits intramolecular, antiferromagnetic coupling of the two low-spin Ru^{III} centers ($H = -2JS_1S_2$, $S_1 = S_2 = 1/2$, $J = -218$ cm⁻¹, $g = 2.4(1)$). For 3, a weak temperature-dependent moment of $\mu_{eff} = 1.85 \mu_B$/dimer (98 K) and 2.04 μ_B (293 K) was found, as expected for a $Ru^{III}Ru^{IV}$ complex containing one unpaired electron per dimer.

Figures 2 and 3 show the structures of the complex cations in 1 and 3 as determined by X-ray crystal structure analysis.[5] Important structural parameters of complexes containing $[M_2(\mu\text{-OH})(\mu\text{-CH}_3\text{CO}_2)_2]^{n\oplus}$ and $[M_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2]^{m\oplus}$ frameworks are collected in Table 1. The structures of the cations in 1 and 3 are similar. Two Ru