

Thermal Behavior of Spiroozonides from Formaldehyde-*O*-oxide and Tropones Derivatives: A Coarctate Reaction

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In memory of Rudolf Criegee

Spiroozonides generated from cyclopropanones and cyclopropanones already fragment at temperatures below -80°C to give alkenes and alkynes, respectively, carbon dioxide, and formaldehyde.^[1] The surprisingly low activation barrier is explained by stabilization of the transition state by *coarctate* Möbius aromaticity.^[2,3] The spiro geometry of the starting materials and transition states is consistent with the stereochemical rules of coarctate reactions. We have included the thermal behavior of the spiroozonides from tropones and **1** in our investigations of this class of reactions. In analogy to the cyclopropane derivatives^[1] the valence isomeric spiroozonides with a norcaradiene structure should undergo spontaneous fragmentation to give carbon dioxide, formaldehyde, and benzene derivatives. The driving force of the reaction is increased over that of the parent system because an aromatic ring is formed as a product.

Under ozone-free conditions^[1,4] the spiroozonides are accessible by [3+2] cycloaddition of **1** and tropones (Scheme 1). The spiroozonides **3**, **7**, **11**, **15**, **19**, **23**, **27**, **31**, **35**, **39**, **43**, **47** from the tropones **2**, **6**, **10**, **14**, **18**, **22**, **26**, **30**, **34**, **38**,

42, and **46**, respectively, and formaldehyde-*O*-oxide (**1**) were unambiguously characterized by low-temperature ^1H NMR spectroscopy. The decomposition kinetics were determined by ^1H NMR spectroscopy following literature methods^[5] for 1,2,3-trioxolanes. Spiroozonides and 1,2,3-trioxolanes decompose according to a first-order rate law. The quantitative evaluation of suitable, temperature-dependent ^1H NMR signals allows the determination of the half-lives $t_{1/2}$ of all spiroozonides at a given temperature ($t_{1/2}$ varies between 9 min at -56°C for **11** and 38 min at $+72^{\circ}\text{C}$ for **47**). The kinetic parameters of decomposition $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and ΔE_a of all spiroozonides except **23**, **31**, and **35** were experimentally determined. The results and product yields are summarized in Table 1.

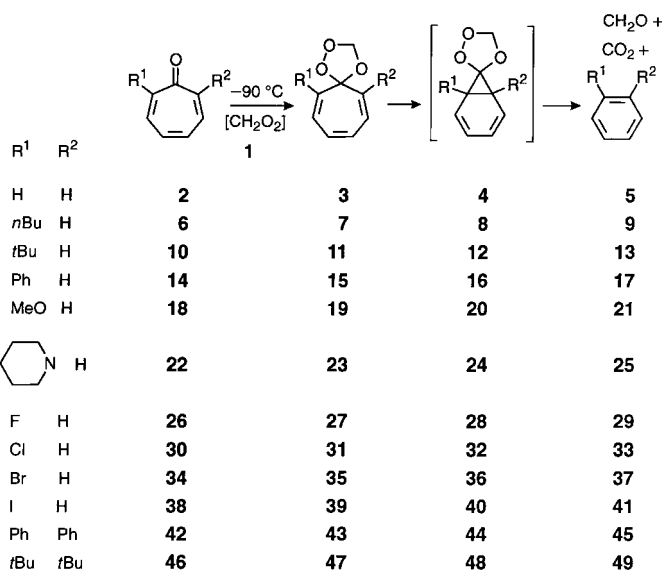
Table 1. Kinetic data and product yields of the decomposition of the spiroozonides generated from **1** and tropones.

Spiro- ozonide	$t_{1/2}$ (T) [min] [$^{\circ}\text{C}$]	$\Delta G^{\ddagger}$ (T) [kcal · mol $^{-1}$] [K]	$\Delta H^{\ddagger}$ [kcal · mol $^{-1}$]	$\Delta S^{\ddagger}$ [cal K $^{-1}$ · mol $^{-1}$]	ΔE_a [kcal · mol $^{-1}$]	Product/ Yield [%]
3 ^[a]	32 (−22)	19 (257)	16	−12	16	5 / >90 ^[f]
7 ^[a]	11 (−24)	18 (245)	17	−1	18	9 / >90 ^[f]
11 ^[a]	9 (−56)	16 (222)	7	−37	8	13 / >90 ^[f]
15 ^[a]	18 (−25)	18 (253)	13	−21	13	17 /65 ^[g]
19 ^[a]	16 (+25)	22 (294)	11	−37	11	21 / >90 ^[f]
23 ^[a]	32 (−24)	— ^[e]	— ^[e]	— ^[e]	— ^[e]	25 /43 ^[g]
27 ^[a]	49 (+5)	21 (278)	16	−17	17	29 ^[h]
31 ^[a]	34 (−5)	— ^[e]	— ^[e]	— ^[e]	— ^[e]	33 ^[h]
35 ^[a]	33 (−15)	— ^[e]	— ^[e]	— ^[e]	— ^[e]	37 ^[h]
39 ^[a]	22 (−15)	19 (248)	14	−18	15	41 ^[h]
43 ^[a]	35 (+14)	21 (283)	14	−27	14	45 /75 ^[g]
47 ^[b]	35 (+25)	22 (309)	23	2	23	49 /66 ^[g]
47 ^[c]	34 (+40)	23 (308)	19	−15	19	49 ^[e]
47 ^[d]	38 (+72)	26 (349)	43	49	44	50 /60 ^[g]

[a] Fragmentation in $[\text{D}_{10}]$ diethyl ether/ CD_2Cl_2 5:1. [b] Fragmentation in CD_3OD . [c] Fragmentation in CDCl_3 . [d] Fragmentation in $[\text{D}_{12}]$ cyclohexane. [e] Not determined. [f] Yield in the raw product. [g] Yield for the isolated product. [h] ^1H NMR spectrum exhibits only product and no signals for the starting materials.

Spiroozonides of tropones with suitable structures undergo spontaneous fragmentations. Besides the aromatic leaving groups **5**, **9**, **13**, **17**, **21**, **25**, **29**, **33**, **37**, **41**, **45**, **49**, carbon dioxide and formaldehyde are formed. The qualitative detection of carbon dioxide by passing a stream of nitrogen through the reaction mixture and then through a solution of barium hydroxide is temperature-dependent (see Experimental Section). Formaldehyde cannot be detected by ^1H NMR spectroscopy. However, convincing evidence of its intermediacy was provided by the thermal treatment of the crystalline spiroozonide **47** in CD_3OD . The increase of the ^1H NMR signals of *o*-di-*tert*-butylbenzene (**49**) is accompanied by the growth of a singlet at $\delta = 4.6$, which can be assigned to the methylene protons of the semiacetal $\text{CD}_3\text{OCH}_2\text{OD}(\text{H})$.

The spontaneous fragmentation is an example of a coarctate reaction. At the spiro-C atom two bonds are made (two $\text{C}=\text{O}$ bonds in CO_2) and two bonds are broken (two $\text{C}-\text{C}$ bonds in the three-membered ring) simultaneously. With eight electrons involved, the reaction has to proceed via a coarctate



Scheme 1. [3+2] cycloaddition of **1** and tropones derivatives.

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Möbius transition state, which must have a spiro geometry. The suitable stereoelectronic prerequisites are realized in the spiro geometry of the starting material and the reaction therefore is favored.

We performed density functional theory calculations^[6] with the B3LYP^[7,8] combination of functionals and the 6-31G* basis set to obtain quantitative information on the parent system (Figure 1 and Table 2).^[9] According to these calculations the rate-determining step of the reaction is not the

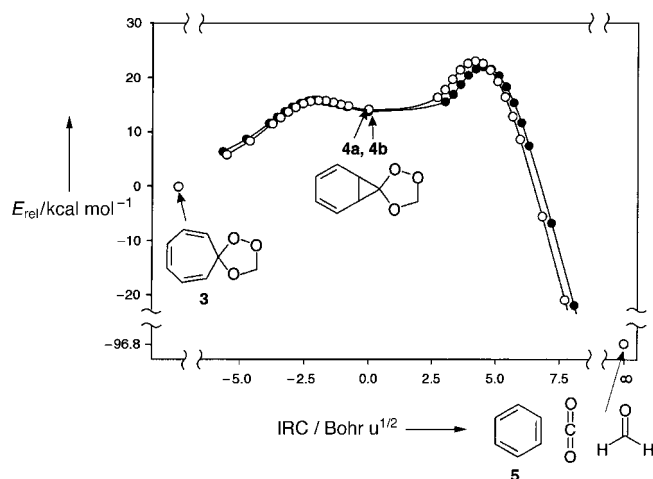


Figure 1. Relative energies E_{rel} in the course of the fragmentation of the spiroozonide **3** calculated at the B3LYP/6-31G* level (IRC = intrinsic reaction coordinate). The values of the IRC are relative to the norcaradiene intermediates **4a** and **4b**.

coarctate fragmentation but the electrocyclic ring closure to give the norcaradiene.^[10,11] Interestingly, the spiroozonide **3** has a planar seven-membered ring^[12,13] in contrast to cycloheptatriene and most of its derivatives. Two diastereomeric forms **4a** and **4b** are possible for the nonplanar structure of the intermediate norcaradiene, which both fragment to give the same products. The activation enthalpy for the electrocyclic ring closure of **3** to **4a** and **4b** is 14.7 kcal mol⁻¹ in both cases. The norcaradienes **4a** and **4b** are flat minima that isomerize back to the cycloheptatrienes with an activation barrier of 1.3 and 0.9 kcal mol⁻¹ or fragment to give the products benzene, carbon dioxide, and formaldehyde with a barrier of 6.6 and 7.1 kcal mol⁻¹. Figure 1 shows the relative

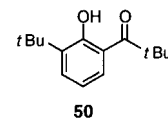
energies of the structures along the intrinsic reaction coordinate (IRC)^[14,15] of the reaction.^[16]

The remarkable dependency of the activation parameter on the substitution of the cycloheptatriene ring is inter alia attributed to steric effects that affect the cycloheptatriene/norcaradiene isomerization and not the subsequent coarctate fragmentation. Semiempirical PM3^[17] calculations indicate that the *tert*-butyl-substituted cycloheptatriene **11** is more sterically hindered than the corresponding norcaradiene **12**, whereas the situation in the di-*tert*-butyl-substituted systems **47** and **48** is reverse. Norcaradiene **48** exhibits strong sterical interactions between the neighboring *tert*-butyl groups. Consequently, in the first case the activation barrier is lowered and in the second case the barrier is raised. The PM3 calculations correctly reproduce this trend qualitatively (Table 3).

Table 3. PM3-calculated energies [kcal mol⁻¹] of the stationary points (minima and transition states) of the fragmentation of the spiroozonides **3**, **11**, and **47**.

Compound	R ¹	R ²	Cycloheptatriene derivative	TS1	Norcaradiene derivative	TS2	Products
3	H	H	0.0	22.7	8.1	26.0	–92.7
11	<i>t</i> Bu	H	0.0	20.9	6.9	24.7	–99.4
47	<i>t</i> Bu	<i>t</i> Bu	0.0	26.3	21.8	40.4	–88.8

The reactivity of **47** is solvent-dependent. In CD₃OD and CDCl₃ at different temperatures *o*-di-*tert*-butylbenzene (**49**), carbon dioxide, and formaldehyde are formed. In cyclohexane (80 °C/1 h), **49**, **46**, and 2-hydroxy-3-*tert*-butylpivalophenone (**50**) in a ratio of 1:1.2:2 were detected. In methylcyclohexane (100 °C/1 h) the product ratio is 1.5:1:6. The maximum yield of **50** is 60%. The formation of **50** can be explained by the intermediacy of the isomeric 2,7-di-*tert*-butyltropone-*O*-oxide. In contrast to the thermolysis of **47** that of the spiroozonide **27** is only weakly dependent on the solvent polarity.



Interestingly, the observations are not transferable to the next higher homologue of **1**: acetaldehyde-*O*-oxide^[4] does not react with the tropone derivatives **18** and **46**.^[18] Colchicines belong to the tropone derivatives. The fragmentation of the

Table 2. Density functional theory (B3LYP/6-31G*) calculated energies of the stationary points (minima and transition states) of the fragmentation of the spiroozonide **3** to benzene, carbon dioxide, and formaldehyde. Absolute energies (E_{abs}) and zero-point energies (ZPE) in Hartree per particle, NIMAG = number of imaginary frequencies according to a normal coordinate analysis, $\tilde{\nu}$ = wavenumber [cm⁻¹] of the imaginary frequency, E_{rel} = relative energy of the stationary points relative to the starting material **3**.

	3	[3 → 4a][‡]	4a	[4a → Prod.][‡]	[3 → 4b][‡]	4b	[4b → Prod.][‡]	Prod.
E_{abs}	–535.17585	–535.15072	–535.15397	–535.14082	–535.15073	–535.15336	–535.13918	–535.33007
ZPE	0.148084	0.146351	0.147524	0.144865	0.146455	0.147529	0.144675	0.139171
NIMAG	0	1	0	1	1	0	1	0
$\tilde{\nu}$	–	–405	–	–506	–399	–	–512	–
E_{rel}	0.0	14.7	13.4	20.0	14.7	13.8	20.9	–102.4

spiroozonides from **1** and colchicines provides an elegant access to the class of allocolchicines.^[19]

Experimental Section

Procedure for trapping formaldehyde-*O*-oxide **1** with tropones:

Ketene diethylacetal (1.20 mmol) in ether (5 mL) was treated with ozone at -116°C until the solution started to turn blue. After removal of the ozone in a stream of nitrogen, a cold solution of the tropone (0.30 mmol) in ether/dichloromethane (2:1, 5 mL) was added. The solvent was removed at room temperature in a rotatory evaporator at 300 mbar. The less volatile benzene derivatives **17**, **25**, **45**, and **49** could be isolated after purification by chromatography. The physical data of the benzene derivatives are in agreement with authentic samples. The yields of the volatile benzene derivatives **5**, **9**, **13**, and **21** were determined by ^1H NMR spectroscopy relative to an inert standard.

Procedure for the low-temperature ^1H NMR measurements:^[1]

Ketene diethylacetal (0.20 mmol) was dissolved in $[\text{D}_{10}]$ diethyl ether (0.40 mL) and thoroughly ozonized in an NMR tube at -116°C by using a capillary. After ozonization a precooled stream of nitrogen was passed through the NMR tube until a moistened KI starch paper remained colorless. Then a precooled solution of the tropone (0.050 mmol) in $[\text{D}_{10}]$ diethyl ether/ CD_2Cl_2 (2:1; 0.40 mL) was added. The tube was immediately introduced into the precooled ^1H NMR measuring cell. The reaction temperature was determined by using the $\Delta\delta$ -value of methanol.^[20]

Results: a) ^1H NMR data of the spiroozonides; signals whose decrease is monitored are marked with the symbol †. The spiroozonides **7**, **15**, **23**, and **43** exhibit ^1H NMR signals for the substituents that are almost identical with those of the products **9**, **17**, **25**, and **45**; b) value of the temperature range for the qualitative detection of CO_2 ; c) half-lives $t_{1/2}$ for different temperatures.

2 + 1: a) 1,2,4-Trioxaspiro[4.6]undeca-6,8,10-triene (**3**): ^1H NMR (500 MHz, -22°C): $\delta = 5.20$ (s, 2H, OCH_2OO), 5.83 (d, 2H, $J = 10.5$ Hz, olefin. H), 6.50–6.59 (m, 4H, olefin. H)†; b) -22 to -15°C ; c) 33 min (-22°C), 16 min (-16°C), 8.3 min (-11°C).

6^[21] + 1: a) 6-*n*-Butyl-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene (**7**): ^1H NMR (500 MHz, -34°C): $\delta = 2.35$ –2.52 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 5.09 (s, 1H, OCH_2OO), 5.50 (s, 1H, OCH_2OO), 5.74 (d, 1H, $J = 10.7$ Hz, olefin. H), 6.41 (d, 1H, $J = 6.8$, olefin. H)†, 6.43–6.49 (m, 1H, olefin. H)†, 6.51–6.61 (m, 2H, olefin. H)†; b) -21 to -15°C ; c) 51 min (-34°C), 27 min (-28°C), 11 min (-24°C).

10: 2-*tert*-Butyltropone (**10**) was prepared analogously to the literature procedure^[21] by using *tert*-butyllithium (16.0 mmol, 10 mL of a 1.6M solution in pentane) and tropolone (7.0 mmol, 0.86 g in ether). The by-products were separated from **10** by chromatography on silica gel with pentane/ether (40:1). Compound **10** was eluted with ether. After microdistillation (70°C ; $p = 0.5$ mbar) **10** was obtained as a colorless oil. Yield: 96 mg (12%). ^1H NMR (250 MHz, CDCl_3): $\delta = 1.31$ (s, 9H, $\text{C}(\text{CH}_3)_3$), 6.71–6.92 (m, 4H, olefin. H), 7.19 (d, 1H, $J = 9.1$ Hz, olefin. H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 29.87$, 37.98, 130.89, 131.83, 132.92, 132.93, 138.33, 160.46, 188.80; IR (KBr): $\tilde{\nu} = 1458$, 1588, 1632, 2956, 3002 cm^{-1} ; UV/Vis (*n*-hexane): λ_{max} (lg ϵ) = 205.0 (4.01), 230.0 (4.21), 297.0 nm (3.71); HRMS calcd. for $\text{C}_{11}\text{H}_{14}\text{O}$: 162.1045; found 162.1057.

10 + 1: a) 6-*tert*-Butyl-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene (**11**): ^1H NMR (500 MHz, -56°C): $\delta = 1.30$ (s, 9H, $\text{C}(\text{CH}_3)_3$), 4.95 (s, 1H, OCH_2OO), 5.47 (s, 1H, OCH_2OO), 5.71 (d, 1H, $J = 10.4$ Hz, olefin. H), 6.36–6.41 (m, 1H, olefin. H)†, 6.51 (d, 1H, $J = 7.1$ Hz, olefin. H)†, 6.57–6.67 (m, 2H, olefin. H)†; b) -42 to -32°C ; c) 9.2 min (-56°C), 7.3 min (-52°C), 3.7 min (-46°C).

14^[21] + 1: a) 6-Phenyl-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene (**15**): ^1H NMR (500 MHz, -16°C): $\delta = 4.95$ (s, 1H, OCH_2OO), 5.17 (s, 1H, OCH_2OO), 5.96 (d, 1H, $J = 10.9$ Hz, olefin. H)†, 6.56–6.62 (m, 2H, olefin. H), 6.64–6.70 (m, 1H, olefin. H); b) -16 to -12°C ; c) 18 min (-25°C), 13 min (-20°C), 6 min (-15°C).

18^[22] + 1: a) 6-Methoxy-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene (**19**): ^1H NMR (500 MHz, $+25^{\circ}\text{C}$): $\delta = 3.69$ (s, 3H, OCH_3), 5.14 (s, 1H, OCH_2OO), 5.26 (s, 1H, OCH_2OO), 5.71 (d, 1H, $J = 10.9$ Hz, olefin. H), 5.80 (d, 1H, $J =$

8.3 Hz, olefin. H), 6.28–6.32 (m, 1H, olefin. H)†, 6.50–6.56 (m, 2H, olefin. H); b) $+8$ to $+12^{\circ}\text{C}$; c) 26 min ($+18^{\circ}\text{C}$), 23 min ($+21^{\circ}\text{C}$), 16 min ($+25^{\circ}\text{C}$).

22^[22] + 1: a) 1-(1,2,4-Trioxaspiro[4.6]undeca-6,8,10-trien-6-yl)piperidine (**23**): ^1H NMR (500 MHz, -30°C): $\delta = 5.17$ (s, 1H, OCH_2OO), 5.40 (s, 1H, OCH_2OO), 5.56 (d, 1H, $J = 10.0$ Hz, olefin. H), 5.91 (d, 1H, $J = 8.1$ Hz, olefin. H)†, 6.36–6.48 (m, 2H, olefin. H), 6.57–6.62 (m, 1H, olefin. H); b) -30 to -24°C ; c) 50 min (-30°C), 32 min (-24°C).

26^[22] + 1: a) 6-Fluoro-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene (**27**): ^1H NMR (400 MHz, $+10^{\circ}\text{C}$): $\delta = 5.24$ (s, 1H, OCH_2OO), 5.37 (s, 1H, OCH_2OO), 5.87 (dd, 1H, $J = 11.4$, 6.8 Hz, olefin. H)†, 6.31–6.49 (m, 3H, olefin. H)†, 6.62 (dd, 1H, $J = 11.7$, 7.3 Hz, olefin. H)†; b) -2 to $+4^{\circ}\text{C}$ (methanol), $+4$ to $+10^{\circ}\text{C}$ (diethyl ether/dichloromethane), $+7$ to $+12^{\circ}\text{C}$ (toluene); c) 49 min ($+5^{\circ}\text{C}$), 25 min ($+10^{\circ}\text{C}$), 17 min ($+15^{\circ}\text{C}$).

30^[21] + 1: a) 6-Chloro-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene (**31**): ^1H NMR (400 MHz, -5°C): $\delta = 5.19$ (s, 1H, OCH_2OO), 5.40 (s, 1H, OCH_2OO), 5.86 (pseudo-d, 1H, olefin. H)†, 6.45–6.53 (m, 1H, olefin. H)†, 6.59–6.65 (m, 2H, olefin. H)†, 6.86 (d, 1H, $J = 7.8$ Hz, olefin. H)†; b) -5 to 0°C ; c) 34 min (-5°C).

34^[21] + 1: a) 6-Bromo-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene (**35**): ^1H NMR (400 MHz, -15°C): $\delta = 5.17$ (s, 1H, OCH_2OO), 5.41 (s, 1H, OCH_2OO), 5.85 (d, 1H, $J = 10.7$ Hz, olefin. H)†, 6.41–6.47 (m, 1H, olefin. H)†, 6.58–6.70 (m, 2H, olefin. H)†, 7.11 (d, 1H, $J = 7.8$ Hz, olefin. H); b) -15 to -10°C ; c) 33 min (-15°C).

38^[21] + 1: a) 6-Iodo-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene (**39**): ^1H NMR (400 MHz, -15°C): $\delta = 5.17$ (s, 1H, OCH_2OO), 5.41 (s, 1H, OCH_2OO), 5.77 (d, 1H, $J = 11.0$ Hz, olefin. H)†, 6.31–6.37 (m, 1H, olefin. H)†, 6.56–6.72 (m, 2H, olefin. H), 7.40 (d, 1H, $J = 7.6$ Hz, olefin. H); b) -20 to -15°C ; c) 72 min (-25°C), 57 min (-20°C), 22 min (-15°C).

42^[23] + 1: a) 6,11-Diphenyl-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene (**43**): ^1H NMR (500 MHz, $+10^{\circ}\text{C}$): $\delta = 5.00$ (s, 2H, OCH_2OO), 6.59–6.66 (m, 2H, olefin. H)†, 6.73–6.78 (m, 2H, olefin. H)†; b) $+8$ to $+12^{\circ}\text{C}$; c) 50 min ($+10^{\circ}\text{C}$), 35 min ($+14^{\circ}\text{C}$).

46^[24] + 1: 2,7-Di-*tert*-butyltropone (**46**) (60 mg, 0.28 mmol) in pentane (5 mL) was added to the primary ozonide generated from ketene diethylacetal (160 mg, 1.38 mmol) dissolved in pentane (5 mL) at -110°C . The reaction mixture was allowed to warm up to 0°C , the solution was decanted from the polymeric peroxides and then concentrated. Compound **47** was obtained as colorless crystals (55 mg, 76%). a) 6,11-Di-*tert*-butyl-1,2,4-trioxaspiro[4.6]undeca-6,8,10-triene **47**: m.p. (pentane) 78 – 79°C (decomp), ^1H NMR (250 MHz, $+20^{\circ}\text{C}$, CDCl_3): $\delta = 1.37$ (s, 18H, $\text{C}(\text{CH}_3)_3$), 5.26 (s, 2H, OCH_2OO), 6.45–6.63 (m, 4H, olefin. H); ^{13}C NMR (100.6 MHz, CDCl_3): $\delta = 32.36$, 37.66, 93.95, 110.22, 123.20, 128.42, 144.71; IR (KBr): $\tilde{\nu} = 743$, 987, 1053, 1117, 1250, 1357, 1370, 1463, 1481, 2903, 2956 cm^{-1} ; UV/Vis (ether): λ_{max} (lg ϵ) = 271.6 nm (3.85); HRMS calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_3$: 264.1725, found 264.1695; C,H analysis for $\text{C}_{16}\text{H}_{24}\text{O}_3$: calcd. C 72.69, H 9.15; found C 72.24, H 8.67, b) not measured, c) in CD_3OD : 35 min ($+25^{\circ}\text{C}$), 15 min ($+32^{\circ}\text{C}$), 7.6 min ($+36^{\circ}\text{C}$), 5.8 min ($+40^{\circ}\text{C}$); in CDCl_3 : 57 min ($+35^{\circ}\text{C}$), 34 min ($+40^{\circ}\text{C}$), 21 min ($+45^{\circ}\text{C}$); in $[\text{D}_{12}]$ cyclohexane: 38 min ($+72^{\circ}\text{C}$), 25 min ($+76^{\circ}\text{C}$), 8.9 min ($+80^{\circ}\text{C}$).

Warming of **47** in methylcyclohexane: Compound **47** (446 mg, 1.69 mmol) was warmed to 100°C in methylcyclohexane (3 mL) for 1 h. From the crude product 1,2-di-*tert*-butylbenzene (**49**) (19 mg, 6%) and 2-hydroxy-3-*tert*-butylpivalophenone (**50**)^[25] (240 mg, 60%) were separated by chromatography with pentane as eluant. If the eluting solvent was changed to pentane/ether (5:1), 2,7-di-*tert*-butyltropone (**46**) (48 mg, 13%) was isolated.

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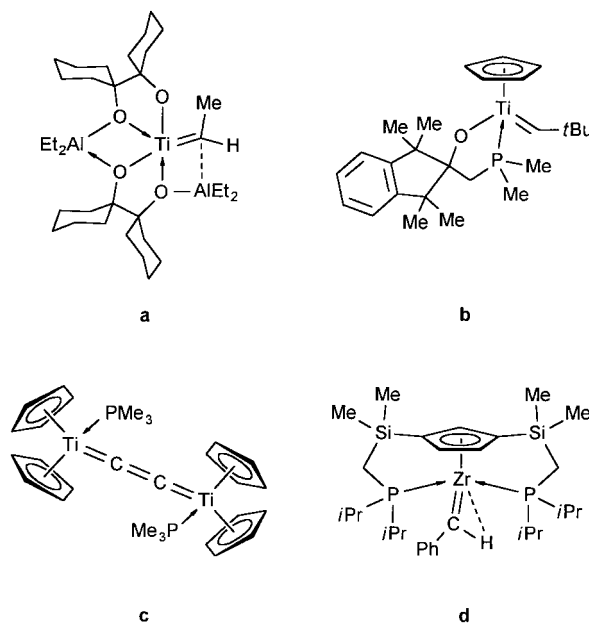
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α -Hydrogen Elimination from (1-Aza-1,3-diene)titanium Complexes: Synthesis of Metallacyclic Titanium–Alkylidene Complexes**

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Alkylidene–metal intermediates play a key role in several important reactions such as transition metal catalyzed olefin and alkyne polymerization, olefin metathesis, or olefination of carbonyl compounds. Therefore there is a great deal of interest in model studies with defined and isolable alkylidene complexes, and several methods for the synthesis of such compounds have already been developed.^[1] Among the alkylidene–metal complexes of the titanium group, the methylidene titanocene [$\text{Cp}_2\text{Ti}=\text{CH}_2$] has gained special significance. Its application in organic synthesis^[2] is attributed to the fact that it is relatively readily generated in situ from different compounds such as bis(cyclopentadienyl)titanacyclobutane complexes,^[3] dimethyltitanocene,^[4] or [$\text{Cp}_2\text{TiCH}_2 \cdot \text{Me}_2\text{AlCl}$] (Tebbe reagent).^[5] To date, however, very few alkylidene–metal complexes of the titanium group have been isolated and characterized by X-ray structure analysis (Scheme 1).^[6–9]



Scheme 1. Selected, structurally characterized alkylidene complexes of titanium and zirconium complexes. **a**: Ti–C 1.933(6) Å, $\delta(\text{Ti}=\text{C}) = 202.1$ (main components);^[6] **b**: Ti–C 1.911(3) Å, $\delta(\text{Ti}=\text{C}) = 278.1$;^[7] **c**: Ti–C 2.051(2) Å, $\delta(\text{Ti}=\text{C}) = 258.1$;^[8] **d**: Zr–C 2.024(4) Å, $\delta(\text{Zr}=\text{C}) = 229.4$.^[9]

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