Relative Reactivities of Carbonyl and Thiocarbonyl Groups toward Dimethoxycarbene: Two New Dimethoxythiiranes

Małgorzata Dawid,[a] Grzegorz Mloston,[b] and John Warkentin*[a]

Dedicated to Professor Aleksandra Skowronska on the occasion of her 70th birthday

Abstract: Reaction of dimethoxycarbene (DMC), generated by thermolysis of a 2,5-dihydro-1,3,4-oxadiazole, with 2,2,4,4-tetramethyl-3-thioxocyclobutanone afforded primarily 2,2-dimethoxy-3,3,5,5-tetramethyl-4-thioxocyclopentanone from ring expansion by overall insertion into the C–CO bond. 4,4-Dimethoxy-2,2,5,5-tetramethyl-3-thioxocyclopentanone, from overall insertion into a C–CS bond, was a minor product. Thus the carbene had reacted preferentially at the carbonyl group, rather than the thiocarbonyl group of the four-membered ring. However, the minor product reacted with DMC at the thiocarbonyl group to afford a dimethoxythiirane. A product from a corresponding reaction at the carbonyl group could not be found. A rationale for the apparent reversal of relative reactivities of the carbonyl and thiocarbonyl groups is offered, with supporting evidence.

Keywords: carbenes · dimethoxycarbene · nucleophilic addition · thiirane · thiocarbonyl

Introduction

Recently we reported ring expansions of a number of anhydrides[1] and small-ring carbonyl compounds[2] by insertion (overall) of the nucleophilic dimethoxycarbene (DMC) into a bond between the carbonyl carbon and an atom in the α-position. Similar ring expansions by reactions of nucleophilic carbenes with thiocarbonyl compounds have not been reported. Thiocarbonyl compounds do react with electrophilic carbenes, such as dichlorocarbene or difluorocarbene, but the attack is at sulfur to generate the appropriate thiocarbonyl ylides.[3] Thus, reactions of the carbonyl and thiocarbonyl groups appear to depend strongly on the attacking carbene's nucleophilicity, as expected.

It was therefore of interest to compare the reactions of DMC with a carbonyl and a thiocarbonyl group in similar or identical environments. The thiocarbonyl double bond is longer (ca. 1.617 versus 1.200 Å),[4] weaker (ca. 127.6 versus 188.9 kcal mol^{-1})[4] and less polar (1.65 in $H_2C{=}S$ versus 2.33 D in H_2CO)[5] than the carbonyl double bond and might be expected to be more reactive in many processes. For example, it is a powerful dipolarophile[6] as well as a reactive 2π-component in Diels–Alder reactions.[7] We now report that the thiocarbonyl group in 2,2,4,4-tetramethyl-3-thioxocyclobutanone (a four-membered ring) was found to be *less* reactive toward dimethoxycarbene than the carbonyl group in the same ring. On the other hand, the thiocarbonyl group in 4,4-dimethoxy-2,2,5,5-tetramethyl-3-thioxocyclopentanone (a five-membered ring) was found to be *more* reactive toward that carbene than the carbonyl group in the same ring, but the reaction was thiirane formation instead of ring expansion. The apparent reversal of relative reactivities is accounted for in terms of group polarities and neighbouring substituents that could interact with the attacking agent at the transition state.

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Results and Discussion

DMC (**2**), generated by thermolysis of 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (**1**),[8, 9] (also known as 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline) reacted with 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**3**) to afford ring expansion product **4** in 50% yield. That product must have arisen from attack of **2** at the carbonyl group of the ketone and subsequent (or concurrent) ring expansion.[2] An isomer (**5**) from analogous attack at the thiocarbonyl group was obtained in about 5% yield (Scheme 1). A third product (**6**) must have arisen from attack of DMC at the thiocarbonyl group of **5**. Isolation of **5** and treatment with **2** gave **6** in 50% yield. Isolation of **4** and analogous treatment with **2** gave only very small amounts (ca. 1% each) of three products of higher

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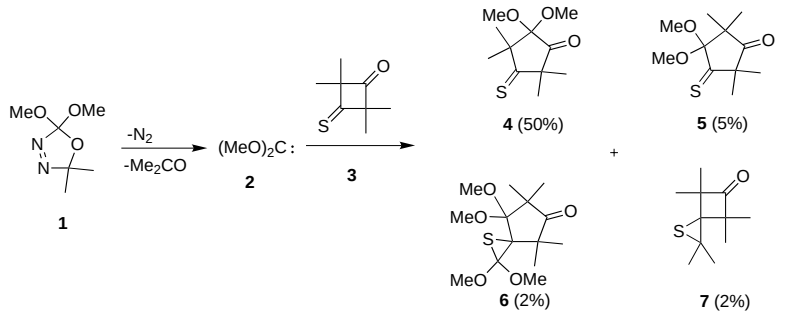
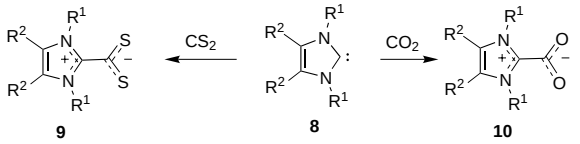


Scheme 1.

molecular weight. Although these were not identified, it is clear that **5** is much more reactive than **4** towards **2**. The fourth product was the known thiirane **7**[10] from reaction of **3** in the presence of **1**. It is presumably formed from cycloaddition of 2-diazopropane (minor co-product of thermolysis of **1**) to the C=S bond and subsequent loss of N_2.

The structures of **4** and **5** were established by means of NMR spectroscopy (^{1}H, ^{13}C and three-bond correlations), IR spectroscopy, and mass spectrometry. In the IR spectra of **4** and **5** there were absorptions indicating the presence of a carbonyl group. The ^{1}H NMR spectrum of **4** in C_6D_6 consisted of two singlets (each 6H) in the methyl region and one singlet (6H) in the methoxy region while the ^{13}C NMR spectrum was composed of eight signals. One ^{1}H NMR methyl signal correlated with both the carbonyl and thiocarbonyl ^{13}C NMR signals and the other with the ^{13}C signal of the thiocarbonyl group only. Isomer **5** had similar NMR spectra but the three-bond couplings showed that one ^{1}H methyl signal was coupled to both the thiocarbonyl and carbonyl carbons and the other to the carbonyl carbon only. These results mean that the connectivities of **4** and **5** are those depicted and that the carbonyl functional group is preferred over the thiocarbonyl group for ring expansion, which is a rather surprising result. Although a diaminocarbene (**8**) reacts with both CS_2 and CO_2 (Scheme 2) to afford stable dipolar adducts (**9**)[11] and **10**,[12] the C=S bond is generally more reactive toward nucleophiles



Scheme 2. R^1 = Me, Et, *i*Pr; R^2 = Me.

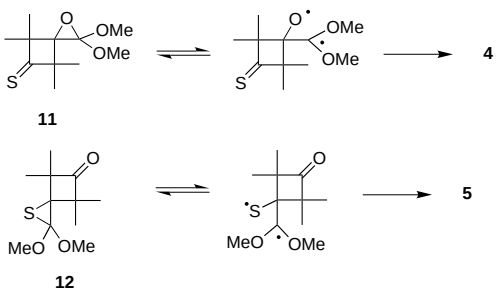
than the C=O bond.[13] One might expect, on the basis of analogy, that DMC too would react readily at a thiocarbonyl group, because it is a nucleophile.[14] It is capable of nucleophilic aromatic substitution,[15] for example, as is a diaminocarbene.[16]

Nucleophiles (presumably including nucleophilic carbenes) attack C=S bonds in two ways, thiophilic attack[17] and carbophilic attack, probably because the electronegativities of sulfur and carbon are not very different.[18] On the other hand electrophilic carbenes, such as dichlorocarbene, react with a thiocarbonyl compound to generate a thiocarbonyl ylide intermediate.[3]

The structures of thiiranes **6** and **7** were established by means of their ^{1}H and ^{13}C NMR spectra, and their mass spectra. Thus, the ^{1}H NMR spectrum of **6** consisted of four methyl singlets and four methoxy singlets, all of equal intensity. The ^{13}C NMR spectrum also showed four distinct methyl carbons and four methoxy carbons, as well as signals for the quaternary carbons C2, C3, C4, C5, and C7. Moreover, a signal at $\delta = 221$ clearly showed the presence of a carbonyl group. Thiirane **6** was thermally stable, having survived heating in benzene at 110 °C for 24 h, and it was not hydrolysed readily, as indicated by its survival upon exposure of the solution of **6** in benzene to the atmosphere. Similarly, the structure of **7** is based on its spectra, which matched the data reported.[10b]

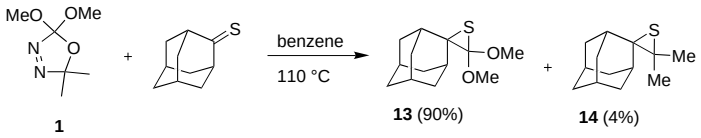
In **3** the carbonyl group is more reactive than the thiocarbonyl group, but in **5** the reverse is true. How can the apparent reversals of the relative reactivities of the carbonyl and thiocarbonyl groups toward DMC be rationalized?

We postulate that the reaction of DMC with **3** in benzene is concerted, but asynchronous in the sense depicted by **11** and **12**. The higher polarity of the carbonyl group, relative to that of the thiocarbonyl group (dipole moment for H_2CO: 2.33 D; for H_2CS: 1.65 D)[4] could be an important factor that determines the preference for attack on the former. Stable betaines are not formed, however, because the ability of the oxygens to support a full positive charge is insufficient. The better donor atoms (N) of **9** and **10** are required for the formation of stable betaines. The observed ring expansion might occur through a transition state with the $(MeO_2)C-C$ bond partly developed or intermediates **11** and **12** might form and subsequently undergo ring expansion by a diradical mechanism (Scheme 3) leading to **4** and **5**. Concerted cycloaddition of the carbene to generate **12** could be slowed because the C=S bond is too long (1.63 Å) for good overlap of the carbene orbitals at both C and S. Stepwise addition, on the other hand, might face a higher barrier because the dipolar intermediate would be poorly solvated in benzene. Precedents for the formation of a dimethoxyoxirane[19] analogous to **11**



Scheme 3.

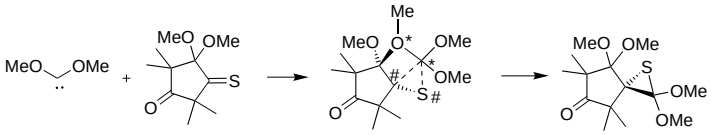
and a dimethoxythiirane analogous to **12** have been reported (Scheme 4).[20] The dimethoxythiirane (**13**) was accompanied by the known thiirane **14**.[21]



1 **13** (90%) **14** (4%)

Scheme 4.

To explain the higher reactivity of the C=S bond in **5**, where the competition is also between the C=O and C=S groups, we suggest that a methoxy group of **5** plays a role in stabilizing the transition state for reaction of DMC at the thiocarbonyl group (Scheme 5). Thiocarbonyl groups are attacked at sulfur by soft nucleophiles[3] and attack at sulfur of **3**–**5** should be favoured in any case because the steric hindrance is less as a result of the length of the C=S bond: 1.67 Å (C=S) versus 1.20 Å (CO).[4] However, attack at S without concurrent bonding to C causes charge separation, and the positive charge can best be dispersed by neighbouring methoxy groups if attack occurs at the C=S group of **5**. The thiocarbonyl carbon would adopt some negative charge, and that would be stabilized inductively by the carbonyl group across the ring as depicted in Scheme 5. In a dipolar transition state, with partial

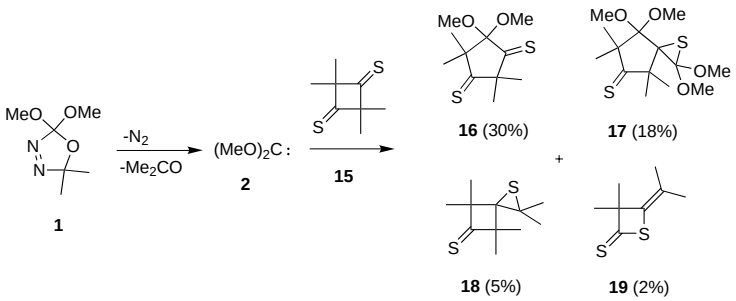


5 **I** **6**

Scheme 5. Transition state **I**, * = site of partial positive charge; # = site of partial negative charge.

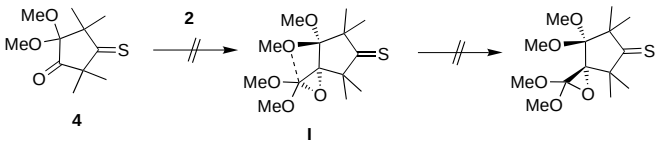
positive charge in the erstwhile carbene portion, the methoxy group situated on the same side as the attacking carbene could share some of the charge. A methoxy group of **4** would be less effective in stabilizing the transition state for relatively synchronous carbonyl addition than analogous cycloaddition to the C=S group, leaving less to be gained from stabilization of a dipolar transition structure (Scheme 6).

Support for the explanation came from treatment of 2,2,4,4-tetramethylcyclobutan-1,3-dithione (**15**) with DMC from thermolysis of **1**, see Scheme 7. The major product was 2,2-



1 **2** **15** **16** (30%) **17** (18%) **18** (5%) **19** (2%)

Scheme 7.



4 **I**

Scheme 6. Oxirane-like transition state **I** with little charge separation.

dimethoxy-3,3,5,5-tetramethylcyclopentan-1,3-dithione (**16**) and, again, furthur reaction of **16** with DMC gave **17**, the product from attack of the carbene at the C=S group nearest to the methoxy substituents. A likely explanation for that preference is stabilization of a dipolar transition state by a methoxy group, as in Scheme 4, although the inductive effects of the alkoxy groups would also increase the electrophilicity of the closer thiocarbonyl group. Attack at the other C=S group could not profit as much from nucleophilic participation by an alkoxyl group, because the positive site to be stabilized would be farther away.

The discovery of **6** and **17** opens the way for the preparation of other 2,2-dialkoxythiiranes and it suggests that a methoxy substituent, or another substituent with an unshared electron pair, tethered alpha to a carbonyl or thiocarbonyl group might enhance reactivity toward a dialkoxycarbene. We will test this hypothesis with 2-alkoxy- and 2,2-dialkoxycycloalkanones.

Conclusion

Dimethoxycarbene attacks at both the carbonyl and thiocarbonyl groups of 2,2,4,4-tetramethyl-3-thioxocyclobutanone, leading to isomeric five-membered rings that are the products of insertion of the carbene into the sp^2–sp^3 bonds. In the initial reaction, the carbonyl group is more reactive than the thiocarbonyl group but the product from insertion into the C–C(=S) bond reacts with a second carbene to afford a dimethoxythiirane. The product from insertion of the carbene into the C–C(=O) bond does not react further with dimethoxycarbene. Thus, the relative reactivities of the carbonyl and thiocarbonyl groups are reversed in the starting material and in the initial products.

Experimental Section

Thermolysis of 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (**1**) in the presence of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**3**). The following thermolysis procedure is typical. A solution of **3** (0.075 g, 0.48 mmol) and **1** (0.080 g, 0.50 mmol) in dry benzene (5 mL) in a thermolysis tube was degassed by means of three freeze–pump–thaw cycles before the tube was sealed under vacuum. It was then placed into an oil bath (110 °C) for a 24 h period.

In the case of **3**, evaporation of the solvent and the volatile components left a residue that was purified by chromatography on silica (Chromatotron, 1 mm plate, 50 mL 100% hexane → 50 mL 10% EtOAc in hexane → 50 mL 20% EtOAc in

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hexane → 50 mL 40% EtOAc in hexane) to afford 3,3,5,5-tetramethyl-2,2-dimethoxy-4-thioxocyclopentanone (**4**, 48%), 2,2,5,5-tetramethyl-4,4-dimethoxy-3-thioxocyclopentanone (**5**, 5%), 2,2,4,4-tetramethoxy-5,5,7,7-tetramethyl-6-oxo-1-thiaspiro[2.4]heptane (**6**, 3%), 2,2,4,4,6,6-hexamethyl-5-oxo-1-thiaspiro[2.3[hexane (**7**, 2%) and unreacted **3** (20%).

Compound **4** (red crystals): m.p. 42 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta = 3.06$ (s, 6H, OMe), 1.36 (s, 6H, Me), 1.30 (s, 6H, Me); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 271.1$, 209.6, 104.2, 62.8, 58.7, 50.4, 28.3, 23.5; MS (70 eV, EI): *m*/*z* (%): 230 $[M]^+$ (3), 202 (30), 96 (100), 81 (86), 71 (51), 59 (50); MS (HR): *m*/*z*: calcd for $C_{11}H_{18}O_3S$: 230.0976; found 230.0970; IR (KBr pellet): $\tilde{\nu} = 2977$, 2946, 1769 (C=O), 1559, 1468, 1258, 1107, 1076, 1062 cm^{-1}.

Compound **5** (magenta liquid): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.31$ (s, 6H, OMe), 1.33 (s, 6H, Me), 1.26 (s, 6H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 275.6$, 218.3, 106.6, 60.8, 55.5, 50.5, 28.1, 19.5; MS (70 eV, EI): *m*/*z* (%): 230 $[M]^+$ (5), 202 (30), 96 (100), 81 (86), 71 (51), 59 (50); MS (HR): *m*/*z*: calcd for $C_{11}H_{18}O_3S$: 230.0976; found 230.0977; IR (neat): $\tilde{\nu} = 2977$, 2946, 1769, 1550, 1468, 1258 (m), 1107, 1076, 1062 cm^{-1}.

Compound **6** (colorless crystals): m.p. 53 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 3.67$ (s, 3H, OMe), 3.52 (s, 3H, OMe), 3.35 (s, 3H, OMe), 3.34 (s, 3H, OMe), 1.37 (s, 3H, Me), 1.32 (s, 3H, Me), 1.21 (s, 3H, Me), 1.07 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 221.2$, 145.3, 132.0, 60.2, 55.6, 52.2, 50.6, 27.1, 23.5, 22.6, 20.0; MS (70 eV, EI): *m*/*z* (%): 304 $[M]^+$ (9), 273 (6), 188 (23), 160 (100), 116 (58), 85 (42), 73 (29); IR (KBr pellet): $\tilde{\nu} = 2980$, 2944, 2839, 1743, 1461, 1228, 1195, 1150, 1064, 879 cm^{-1}.

Compound **7** (colorless crystals): m.p. and ^{1}H NMR spectrum in agreement with published data;[10b] ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 220.7$, 72.2, 62.4, 52.2, 29.2, 24.7, 23.2.

Thermolysis of 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (1) in the presence of adamantanethione: The standard procedure gave, from adamantanethione (0.089 g, 0.54 mmol) and **1** (0.093 g, 0.58 mmol), a residue that was purified by chromatography on silica (Chromatotron plate, 1 mm, 5% EtOAc in hexane) to afford 3,3-dimethoxyspiro[thiirane-2,2′-tricyclo[3.3.1.13,7]decane (**13**, 90%), the known[21] 3,3-dimethylspiro[thiirane-2,2′-tricyclo[3.3.1.13,7]decane (**14**, 4%), and unreacted thioketone (3%).

Comound **13** (colorless crystals): m.p. 44 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 3.62$ (s, 6H), 2.02, 1.98, 1.90, 1.85, 1.79 (5 × br m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 115.5$, 66.6, 57.7, 37.2, 37.0, 36.1, 35.9, 27.6, 26.8; MS (70 eV, EI): *m*/*z* (%): 240 $[M]^+$ (19), 225 (10), 207 (8) 165 (15), 86 (36), 84 (54), 49 (100); MS (HR) *m*/*z*: calcd for $C_{13}H_{26}O_2S$: 240.1184; found 240.1169.

Thermolysis of 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (1) in the presence of 2,2,4,4-tetramethylcyclobutan-1,3-dithione (15): From 2,2,4,4-tetramethylcyclobutan-1,3-dithione (0.91 g, 0.53 mmol) and **1** (0.082 g, 0.51 mmol), the standard procedure gave a residue that was purified by chromatography on silica (Chromatotron plate, 1 mm, 10% EtOAc in hexane) to afford 2,2-dimethoxy-3,3,5,5-tetramethylcyclopentane-1,3-dithione (**16**, 30%), 2,2,4,4-tetramethoxy-5,5,7,7-tetramethyl-6-thioxo-1-thiaspiro[2.4]heptane (**17**, 18%), 2,2,3,3,5,5-hexamethyl-4-thioxo-1-thiaspiro[2.3]pentane (**18**, 5%), the known **19** (2%) and unreacted **15** (19%).

Compound **16** (magenta liquid): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 3.33$ (s, 6H, OMe), 1.49 (s, 6H, Me), 1.37 (s, 6H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 272.0$, 259.1, 198.6, 70.3, 64.5, 50.6, 33.6, 24.1; MS (70 eV, EI): *m*/*z* (%): 246 $[M]^+$ (12), 231 (30), 216 (5), 172 (11), 85 (32), 71 (100); MS (HR) *m*/*z*: calcd for $C_{11}H_{18}O_2S_2$: 246.0748; found: 246.0749; IR (neat): $\tilde{\nu} = 2977$, 2939, 1466, 1454, 1229, 1132, 1096, 1055, 1017, 966 cm^{-1}.

Compound **17** (pink oil): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 3.69$ (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.35 (s, 3H, OMe), 1.54 (s, 3H, Me), 1.48 (s, 3H, Me), 1.26 (s, 6H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 278.5$, 109.4, 108.4, 66.4, 60.2, 55.6, 52.5, 50.6, 32.4, 29.1, 27.9, 24.8; MS (70 eV, EI): *m*/*z* (%): 320 $[M]^+$ (100), 305 (48), 289 (29), 257 (17), 246 (67), 231 (12); IR (neat): $\tilde{\nu} = 2981$, 2942, 2837, 1457, 1311, 1222, 1114, 1067, 1028, 876 cm^{-1}.

Compound **18** (orange oil): ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.74$ (s, 6H, Me), 1.54 (s, 6H, Me), 1.23 (s, 6H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 27.3$, 28.7, 29.0, 52.7, 65.5, 72.5, 276.2; MS (70eV, EI): *m*/*z* (%): 214 $[M]^+$ (56), 199 (21), 113 (27), 84 (54), 85 (58), 71 (100); IR (neat): $\tilde{\nu} =$ 2971, 2923, 1457, 1361, 1294, 1087, 1053 cm^{-1}.

Compound **19** (yellow oil):[22–24] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.84$ (s, 3H, Me), 1.71 (s, 3H, Me), 1.45 (s, 6H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 244.0$, 123.0, 111.9, 73.9, 25.7, 22.4, 20.5; MS (70 eV, EI): *m*/*z* (%): 172 $[M]^+$ (41), 96 (42), 84 (28), 81 (100), 71 (32); IR (neat): $\tilde{\nu} = 2970$, 2927, 2862, 1455, 1242, 1075, 862, 837 cm^{-1}.

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