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DIACETOXYLATION OF CONJUGATED DIENES WITH THALLIUM(III) ACETATE IN ACETIC ACID

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Abstract The reaction of conjugated dienes such as 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene, 1,3-cyclopentadiene, and 1,3-cyclohexadiene with thallium(III) acetate in acetic acid at 10–65° for 0.5–15 hr affords an isomeric mixture of the corresponding diacetoxyalkenes (1,2- and 1,4-addition products) in 10–92% yields. The 1,2-addition products are predominantly formed in all cases examined except the case of 1,3-cyclopentadiene. The reaction is assumed to proceed through acetoxythallation and dethallation steps, the latter step being accompanied and/or followed by an attack of acetoxyl group. An initial attack of thallium moiety is proposed to occur mainly at C-1 and C-2 carbons in the cases of linear terminal dienes and cyclic dienes, respectively.

Since Criegee reported the isolation of methoxythallation adduct of styrene-thallium(III) acetate and its oxidative decomposition on heating,[1] the oxidation of mono-olefins by various thallium(III) salts has been studied in the last two decades.[2] Oxidation of diolefins with these salts, however, has not yet been studied thoroughly. Recent interesting reports[3] on the oxidation of dienes by thallium(III) perchlorate to cause the C–C bond formation and also the report[4] on the oxidation of some conjugated dienes with thallium(III) trifluoroacetate in dichloromethane prompted us to report our results on diacetoxylation of several conjugated dienes with thallium(III) acetate in acetic acid. The preliminary report on this subject has already appeared in a communication form.[5]

RESULTS AND DISCUSSION

The reaction was carried out by stirring a mixture of a diene and thallium(III) acetate (diene/Tl(III)=2) in acetic acid containing *ca* 5% (by volume) acetic anhydride at 10–65° for 0.5–15 hr. In the cases of 1,3-butadiene and isoprene the reaction was carried out in a glass or stainless autoclave. The products were mainly the isomeric diacetoxyalkenes (namely, 1,2- and 1,4-addition products). Typical results are summarized in the Table. The yields of the products shown in the Table were determined by iodometry on the basis of thallium(III) acetate consumed.

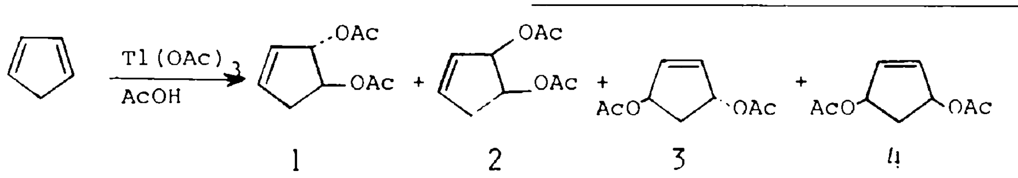
The reaction of 1,3-cyclopentadiene proceeded smoothly at 10–25° to afford four diacetoxyalkenes (**1**–**4**, eqn 1) where 1,4-addition products (**3** and **4**) prevail. The oxidation with lead(IV) acetate had been reported to give the same products, 1,2-additions being mainly obtained both in acetic acid and in benzene.[6–8] Separate experiments revealed that almost no interconversion between these isomers occurred under the reaction conditions employed.

The reaction of 1,3-cyclohexadiene was slower than that of 1,3-cyclopentadiene and was carried out at 60°.

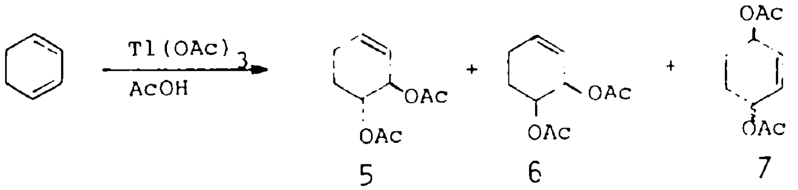
Table 1. Oxidation of conjugated dienes with $Tl(OAc)_3$ in acetic acid[a]

Diene	React. temp(°C)	React. time(h)	Product and Ratio	Yield[b] (%)	Isomer Ratios of 1,2-/1,4-	Tl^{3+} consumed[c]
1,3-Cyclopentadiene[d]	10	0.5	1+2+3+4(8:21:44:27)	57	29/71	87
1,3-Cyclohexadiene	60	0.5	5+6+7(42:27:31)	57	69/31	97
1,3-Butadiene	60	2	8+9	10	61/39	63
1,3-Butadiene[c]	60	2	8+9	11	65/35	38
1,3-Butadiene	40	5	8+9	10	61/39	45
Isoprene	60	1	10+11+12(61:15:24)	47	61/39	68
2,3-Dimethyl-1,3-butadiene	60	1	13+14	49	80/20	87
2,3-Dimethyl-1,3-butadiene	20	1	13+14	71	83/17	31
2,5-Dimethyl-2,4-hexadiene	65	15	15	92	100/0	95

[a] Diene(20 mmol), $Tl(OAc)_3$(10 mmol), and $AcOH-Ac_2O$(10 ml-0.5 ml) were used unless otherwise stated. The reaction of 1,3-butadiene and isoprene was carried out in a glass autoclave(50 ml). [b] Based on $Tl(OAc)_3$ consumed and determined by glc. [c] Residual Tl(III) was determined by iodometry. [d] Diene(100 mmol), $Tl(OAc)_3$(50 mmol), and $AcOH-Ac_2O$(60 ml-2 ml) were used. [e] NaOAc(10 mmol) was added.


(1)

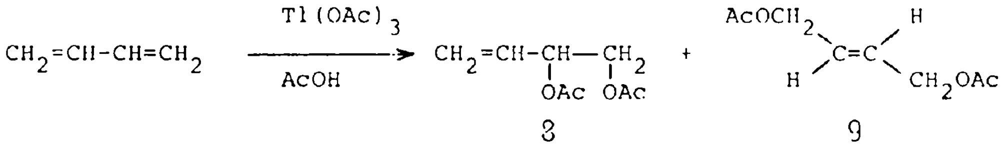
The products were also diacetoxyalkenes as shown in eqn (2) where 1,2-addition products (**5** and **6**) are predominant. Although the isomer ratio of **5** to **6** could be determined by glc, **7**, in which both *trans*- and *cis*-isomers should be present, showed only one peak or unseparable peak on glc under various conditions we employed. Therefore, the isomer ratio in **7** is not known. The oxidation with lead(IV) acetate had been reported to give the same compounds (**5**:**6** = *ca* 3:1 and *trans*-**7**:*cis*-**7** = *ca* 1:1), the ratio of the latter two compounds having been determined after hydrogenation.[9]

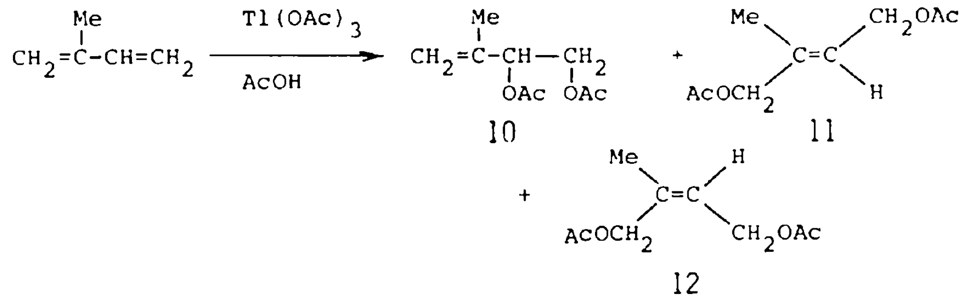

(2)

The reaction of 1,3-cyclooctadiene was slow and many products were obtained. For example, in the reaction at 80° for 3 hr (70% of thallium(III) ion consumed) at least seven compounds were detected as the products in which *trans*- and *cis*-3,8-diacetoxycyclooctene, 3-acetoxycyclooctene and 3-acetoxy-1,4-cyclooctadiene could be assigned by ^{1}H NMR after their isolation by preparative glc.[10] The total yields of these products were at most 30% (based on thallium(III) ion consumed) and a detailed study was abandoned. The addition of sodium acetate to the system slowed down the reaction without a large effect on the product ratio.

Transannular cyclization involving C–C bond formation has been reported by Yamada *et al* in the reaction of 1,5-cyclooctadiene with thallium(III) trifluoroacetate.[3c] The treatment of the same diene with thallium(III) acetate in acetic acid at 60–80° for 3 hr however, resulted in the formation of many products in low yields, without determining their structures. It is clear from this observation that thallium(III) acetate is not a suitable reagent for such cyclization.

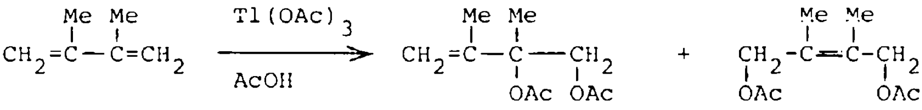
The oxidation of low-boiling linear dienes such as 1,3-butadiene and isoprene was carried out in a glass or stainless autoclave at 40–60° for 1–5 hr. The products were both 1,2- and 1,4-diacetoxyalkenes (eqns 3 and 4), 1,2-isomer being predominant in both cases. The yields of **8** and **9** were quite low and yet the high-boiling products such as tri- and tetra-acetoxyalkanes were scarcely formed, in spite of the high consumption of thallium(III) ion. This may be partly due to a formation of low-boiling ketones, esters, aldehydes and/or epoxides, the identification and determination of these, however, being not carried out. Although it has been reported in the preliminary communication[5] that the addition of sodium or potassium acetate in the system of 1,3-butadiene


(3)


(4)

resulted in a predominant formation of **9**, more thorough investigation has revealed that this was wrong. The addition of sodium acetate only slowed down the reaction and did not give significant effects on the isomer ratios of **8** to **9** and also of **10** to **11** + **12**. From isoprene 3,4-diacetoxy-3-methyl-1-butene may be formed as the other 1,2-addition product. Although a small peak due to unidentified product was observed in a diacetoxyalkene region on glc, this could not be identified. The predominant formation of **10** as 1,2-addition product is interesting, since the usual electrophilic 1,2-addition on isoprene (HCl, ClOAc, ClOH *etc*) has been known to occur at the double bond bearing the Me group.[11] A similar unusual attack has been observed in the oxyselenation of isoprene with PhSeCN/CuCl$_2$/MeOH system[12] in which 2-methyl-3-methoxy-4-phenylseleno-1-butene was the sole product (82%, yield, at 20° for 24 hr). A steric interaction between the Me group and a large attacking species such as Tl(OAc)$_2^+$ or PhSe$^+$ may be one of the reasons for these unusual attacks, though the details are not yet known.

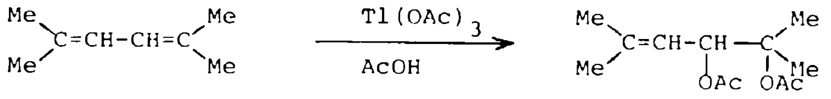
2,3-Dimethyl-1,3-butadiene reacted more readily than the former two dienes to give **13** and **14** (eqn 5), the ratio of the 1,2-addition product became larger. The isomer ratio was almost independent of the reaction temperature. Separate experiments showed that thallium(III) and/or (I) acetate has no effects on the isomerization between **8** and **9** and also between **13** and **14** under these reaction conditions (in acetic acid at 60° for 1 hr).



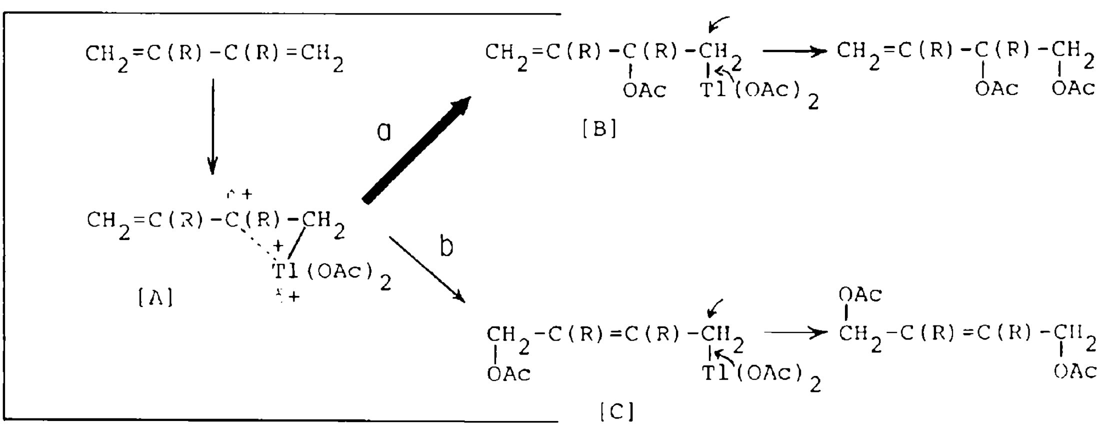
$$\mathrm{CH_2{=}\overset{Me}{\overset{|}{C}}-\overset{Me}{\overset{|}{C}}{=}CH_2 \xrightarrow[AcOH]{Tl(OAc)_3} CH_2{=}\overset{Me}{\overset{|}{C}}-\underset{\underset{OAc}{|}}{\overset{Me}{\overset{|}{C}}}-\underset{\underset{OAc}{|}}{CH_2} + \underset{\underset{OAc}{|}}{CH_2}-\overset{Me}{\overset{|}{C}}{=}\overset{Me}{\overset{|}{C}}-\underset{\underset{OAc}{|}}{CH_2}} \qquad (5)$$

13 14

The reaction of 2,5-dimethyl-2,4-hexadiene with thallium(III) acetate was fairly slow, but the yield of the product was highest in the dienes examined. The product was solely the 1,2-addition isomer **15** (eqn 6) which was readily hydrolyzed to its half-ester by standing it at room temperature after its isolation.

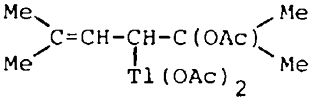


15 (6)



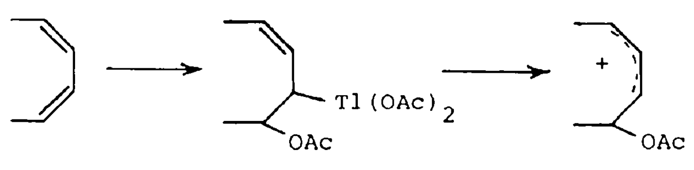
(7)

In view of the reported oxidation mechanism of mono-olefins with mercury(II) and thallium(III) acetate,[13] it is probable that both diacetoxyalkenes are formed through oxythallation and dethallation steps, the former step involving an electrophilic attack of thallium moiety to dienes. As shown in eqn (7), in the cases of linear terminal dienes thallium moiety predominantly attacks on the terminal carbon, as expected from the polarization effect of the double bond induced by an electrophile[14] (thallium moiety in this case), to give such an intermediate as **A**. **A** can be attacked by acetic acid to afford the labile organothallium compounds, **B** and **C**, via path **a** and **b**, respectively. Both **B** and **C** are unstable under the reaction conditions and give 1,2- and 1,4-diacetoxyalkenes, respectively by an S$_N$2 attack of acetic acid and/or an intramolecular attack of ligand acetate on the carbon bearing Tl(OAc)$_2$. A favorable formation of 1,2-isomer may be ascribed to a preferred formation of **B** because of a weak interaction of thallium with the neighboring carbon. In oxymercuration of dienes, on the other hand, it has been reported that no 1,4-addition product was ever detected.[15] This may be due to the presence of mercurinium ion intermediate where mercury interacts more strongly with the neighboring carbon than in the thallium case. In the case of 2,5-dimethyl-2,4-hexadiene an experimental result showed a selective formation of 1,2-isomer, **15**. Since an electron density at C-3 is much higher than that at C-2 as expected from the effect of two Me groups, an electrophilic thallium species attacks C-3 selectively, followed by the attack of acetic acid, to give **D**. If the species attacks C-2, 1,4-isomer should also be formed according to eqn (7).



[D]

In the cases of cyclic dienes an electrophilic thallium species may attack C-2 preferably as a first step to give **E** because of a larger steric hindrance of neighboring methylene protons than methine proton and/or slightly higher electron density of this carbon than that of C-1. Here, an S_N2 type reaction giving 1,2-isomer seems to be slow because of its cyclic structure and therefore **E** may decompose to give the allylic cation intermediate which gives both 1,2- and 1,4-isomers. Intramolecular acetoxyl attack in **E** and an S_N2' attack of acetic acid on **E** may also afford 1,2- and 1,4-isomer, respectively.



[E]

EXPERIMENTAL

All organic materials except 1,3-cyclopentadiene were commercial products and used without further purification. 1,3-Cyclopentadiene was prepared from dicyclopentadiene by the reported method.[16] Thallium(III) acetate was prepared from thallium(III) oxide and AcOH.[17] IR spectra (liquid film) were recorded with JASCO IR-S and Hitachi EPI-S2 spectrometers. ^{1}H NMR spectra were taken with Varian A-60 and Varian EM-360 instruments for soln in CCl_4 with TMS as an internal standard. Glc analyses were carried out with Shimadzu 5APTF and 4BMPF apparatus using *p*-methylacetophenone, benzyl acetate, and ethyl cinnamate as the internal standard [Apiezon-L (30%)-Celite(3m), PEG 6000 (25%)-Chromosorb W(3m), and EGSS-X (30%)-Chromosorb W(1 and 3m) columns; N_2 as carrier gas]. Authentic samples for **1** and **2** were prepared by oxidation of 1,3-cyclopentadiene with lead(IV) acetate in AcOH and in benzene.[6–8] Those for **3** and **4** were prepared by acetylation (Ac_2O/pyridine) of the corresponding diols obtained by the reported method:[18] b.p. 71–72/1 mmHg. Both **8** and **9** were synthesized by the known method.[19] Some typical procedures are as follows.

Reaction of 1,3-cyclopentadiene. To a suspension of $Tl(OAc)_3$ (19.2 g, 50 mmol) in AcOH–Ac_2O (60 ml–2 ml) was added the freshly distilled 1,3-cyclopentadiene (6.61 g, 100 mmol) and the resulting mixture was stirred for 0.5 hr at 10. The mixture was poured into H_2O (*ca* 200 ml) and extracted with Et_2O. The iodometry of the water layer showed that 87% of thallium(III) was converted to thallium(I). Glc analysis of the ether extract revealed the presence of **1**, **2**, **3**, and **4** (8:21:44:27) in 57% yield (based on Tl(III) consumed). Distillation gave a mixture of **1**–**4**: 3.0 g, b.p. 87–89/2.6 mmHg (Found: C, 58.87; H, 6.70. $C_9H_{12}O_4$ requires: C, 58.69; H, 6.52%).

The products mixture (0.20 g; **1**:**2**:**3**:**4** = 36:18:35:11) obtained by the reaction of 1,3-cyclopentadiene (10 mmol) and lead(IV) acetate (5 mmol)[6,7] in AcOH–Ac_2O (10 ml–0.5 ml) at 20 for 10 min was dissolved into AcOH–Ac_2O (10 ml–0.5 ml) containing $Tl(OAc)_3$ (1 mmol) and the resulted soln was stirred at 20 for 1 hr. The mixture was then treated as above and glc analysis of the benzene extract revealed the presence of **1**–**4** of almost the same amount and isomer ratio to the starting one.

Reaction of isoprene. The soln of isoprene (6.81 g, 100 mmol) and $Tl(OAc)_3$ (19.2 g, 50 mmol) in AcOH–Ac_2O (60 ml–2 ml) was stirred at 60° for 1.5 hr in a stainless autoclave (100 ml). After the mixture was cooled to room temp, it was treated as above. The conversion of thallium(III) to thallium(I) was 97% (by iodometry). Distillation of the concentrated ether extract which was revealed to consist of **10**, **11** and **12** (65:17:18, 30% yield) by glc afforded a mixture of three products; 2.5 g, b.p. 114–119/17 mmHg. Each of **10**, **11** and **12** was isolated in a pure form by preparative glc. **10** NMR δ 1.79 (s, 3 H), 2.06 (s, 3 H), 2.11 (s, 3 H), 4.53 (m, 2 H), 5.05 (s, 2 H), 5.40 (t, J = 6 Hz, 1 H). IR 2850 (w), 1710 (s), 1420 (m), 1350 (s), 1210 (s), 1037 (s), 1020 (s), 963 (w), 935 (w), 897 (m), 859 (w), 598 (w) cm^{-1}. **11** NMR δ 1.84 (s, 3 H), 2.06 (s, 3 H), 2.09 (s, 3 H), 4.66 (s, 2 H), 4.67 (d, J = 7 Hz, 2 H), 5.58 (t, J = 7 Hz, 1 H). IR 2870 (w), 1715 (s), 1430 (m), 1368 (s), 1215 (s), 1015 (s), 955 (m), 905 (w), 828 (w), 600 (w) cm^{-1}. (Found: C, 57.81; H, 7.67. $C_9H_{14}O_4$ requires: C, 58.05; H, 7.58%). **12** NMR δ 1.75 (s, 3 H), 2.06 (s, 3 H), 2.10 (s, 3 H), 4.52 (s, 2 H), 4.66 (d, J = 7 Hz, 2 H), 5.64 (t, J = 7 Hz, 1 H). IR spectrum was almost identical to that of **11**. (Found: C, 58.57; H, 7.71%). Assignment for **11** and **12** is tentative (**11** has a shorter retention time than **12** in glc on all three different columns used) and might be reversed.

A similar treatment of 1,3-butadiene afforded 22% yield of **8** and **9** (**8**:**9** = 66:34), 98% of thallium(III) being consumed. Blank experiment showed that only 4% of thallium(III) was converted to thallium(I) under similar conditions without the addition of isoprene or 1,3-butadiene.

Structural determination of other products, which were isolated by simple distillation or by preparative glc, was carried out by ^{1}H NMR and IR spectra and an elemental analysis as follows. **5** NMR δ 1.77–2.20 (m, 4 H), 2.06 (s, 6 H), 5.82 (s, 2 H), 4.9–5.6 (m, 2 H). IR 1736 (s), 1372 (m), 1244 (s), 1043 (m) cm^{-1} (Found: C, 60.35; H, 7.59. $C_{10}H_{14}O_4$ requires: C, 60.59; H, 7.12%). **6** NMR δ 2.06 (s, 6 H), 2.08 (m, 4 H), 5.06 (q, 1 H), 5.36 (m, 1 H), 5.64 (m, 1 H), 5.86 (t, 1 H). IR spectrum was almost identical to that of **5**. **7** NMR δ 1.88 (m, 4 H), 2.04 (s, 3 H), 2.06 (s, 3 H), 5.26 (m, 2 H), 5.91 (m, 2 H). IR 1740 (s), 1373 (m), 1236 (m), 949 (m), 913 (m) cm^{-1}. (Found: C, 60.53; H, 7.31%). Retention times of **5**–**7** in glc were consistent with those of the products obtained from the reaction of 1,3-cyclohexadiene with lead(IV) acetate.[9] **13** NMR δ 4.22 (s, 2 H), 4.8–5.1 (m, 2 H). **14** NMR δ 1.77 (s, 6 H), 2.06 (s, 6 H), 4.63 (s, 4 H). This spectrum was almost identical to that reported as *trans*-isomer.[20] A mixture of **13** and **14** (80:20) was isolated by distillation; b.p. 59/2 mmHg (Found: C, 60.13; H, 8.47. $C_{10}H_{16}O_4$ requires: C, 59.98; H, 8.05%). **15** NMR δ 1.17 (s, 6 H), 1.77 (s, 6 H), 2.05 (s, 6 H), 5.12 (d, J = 9 Hz, 1 H), 5.35 (d, J = 9 Hz, 1 H), b.p. 100/8 mmHg. Good combustion analytical data was not obtained because of hydrolysis.

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[10] ^{1}H NMR (δ, $CDCl_3$) and IR data are as follows. *trans-3,8-Diacetoxycyclooctene:* 1.50-1.95 (m, 8 H), 2.10 (s, 6 H), 5.50–5.85 (m, 4 H); 1739 (s), 1370 (m), 1250 (s), 1030 (m) cm^{-1}. *cis*-3,8-Diacetoxycyclooctene: 1.40–1.85 (m, 8 H), 2.05 (s, 6 H), 5.40 5.80 (m, 2 H), 5.56 (s, 2 H). IR spectrum was almost identical to that of *trans*-isomer. 3-Acetoxycyclooctene: 1.20 2.10 (m, 6 H), 2.04 (s, 3 H), 2.10-2.60 (m, 4 H), 5.15 6.20 (m, 3 H) 3-Acetoxy-1,4-cyclooctadiene: 1.45 1.88 (m, 2 H), 2.07 (s, 3 H), 2.10 2.55 (m, 4 H), 5.35–6.15 (m, 5 H).

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