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Studies on 5-8 Fused Ring Compounds. I. Halogenation of 4,4-Dimethylbicyclo[6.3.0]undecane-2,6-dione

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Bromination and chlorination of 4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione (**2**) with pyridinium bromide perbromide and sulfuryl chloride gave several α-halo-diones. The substituted positions and the stereochemistry of the halogen atoms have been assigned on the basis of their dehydrohalogenation and spectral data. The chlorination of **2** also gave a tricyclic dione (**8**) containing a cyclopropane ring. The structure of **8** was determined by means of ^{13}C-NMR, as well as other types of spectroscopy. Dehydrochlorination of **7** gave a 5*H*-benzocycloheptene derivative (**18**).

Umehara *et al.* recently reported results concerning the photochemical cycloaddition of the enol acetate of dimedone to cyclopentene, and indicated that the photoadducts, 2-acetoxy-4,4-dimethyltricyclo[6.3.0.0^{2,7}]-undecan-6-one (**1a** and **1b**), undergo retro-aldol cleavage under acidic conditions to give 4,4-dimethylbicyclo-[6.3.0]undecane-2,6-dione (**2**).[1] Halogenation of the dione (**2**) was attempted to prepare intermediates for the synthesis of terpenes containing a medium-size ring, and several α-halo-diones were obtained. In the present paper, the dehydrohalogenation of the α-halo-diones and the substituted positions of the halogen atoms are reported.

It is interesting to study the chemical properties of compounds containing a 5-8 fused ring, since few investigations have been reported concerning them. Furthermore, such compounds constitute the partial skeleton of sesterterpenes (5-8-5 fused ring) and are of interest in this respect.

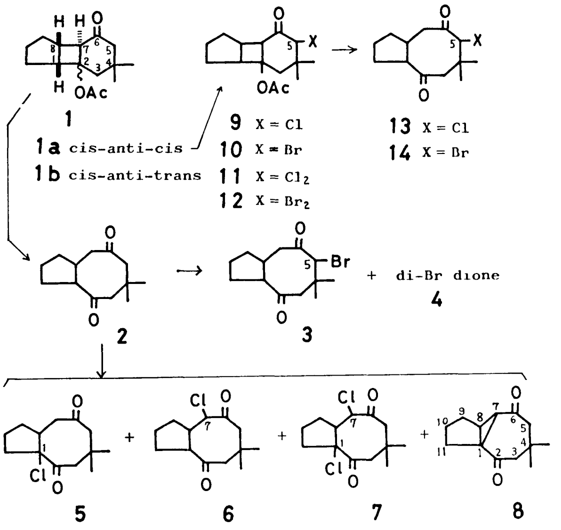
Results and Discussion

Bromination of the dione (**2**) with pyridinium bromide perbromide in ethanol yielded only a monobromo-dione (**3**), but, in acetic acid, **3** and a dibromo-dione (**4**) were obtained.

Chlorination of **2** with sulfuryl chloride in carbon tetrachloride yielded a mixture of two monochloro-dione (**5** and **6**), a dichloro-dione (**7**) and a compound (**8**) presumably formed as the result of the dehydrochlorination.

Other halogenated diones were also synthesized through the halogenation of the photoadduct **1a** (*cis-anti-cis*), followed by retro-aldol cleavage. The halogenation of **1a** with sulfuryl chloride and pyridinium bromide perbromide gave chloro derivatives (**9** and **11**), and bromo derivatives (**10** and **12**), respectively. Then retro-aldol cleavage of **9** and **10** under similar conditions,[1] used for the synthesis of **2** from **1a** and **1b**, gave monohalo-diones (**13** and **14**), respectively.

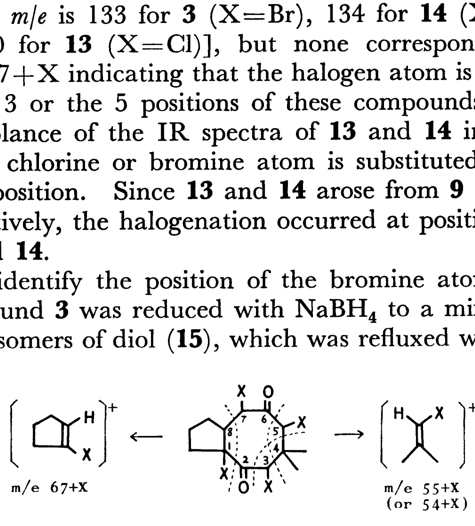
The monohalo-diones (**3**, **5**, **6**, **13**, and **14**) were subjected both to mass spectrometric analysis and to dehydrohalogenation with γ-collidine in order to determine the positions of halogen. The halogen atom can be substituted on the dione (**2**) at positions 1, 3, 5, or 7.



Scheme 1.

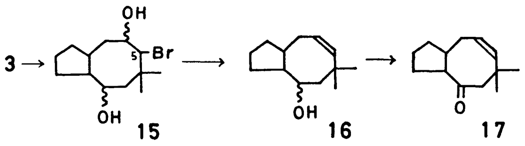
Compounds **3**, **13**, and **14** were found to remain unreacted upon treatment with γ-collidine, suggesting that the halogen atom is present at position 3 or 5 in any of these compounds because of the absence of a hydrogen atom at a neighboring position. The mass spectral data also support this. Scheme 2 shows the possible fragmentation patterns giving the fragment ions, $m/e=55+X$ (or $54+X$) (containing a *gem*-dimethyl group) and $m/e=67+X$ (containing a halogenated five-membered ring). Compounds **3**, **13**, and **14** showed a fragment peak corresponding to $m/e=55+X$ (or $54+X$) [where m/e is 133 for **3** (X=Br), 134 for **14** (X=Br), and 90 for **13** (X=Cl)], but none corresponding to $m/e=67+X$ indicating that the halogen atom is present at the 3 or the 5 positions of these compounds. The resemblance of the IR spectra of **13** and **14** indicates that a chlorine or bromine atom is substituted at the same position. Since **13** and **14** arose from **9** and **10**, respectively, the halogenation occurred at position 5 in **13** and **14**.

To identify the position of the bromine atom in **3**, compound **3** was reduced with NaBH$_4$ to a mixture of stereoisomers of diol (**15**), which was refluxed with zinc



Scheme 2. (X=Cl or Br)

in acetic acid,[2] converted to **16** and then oxidized to enone **17** with chromic acid. The enone **17** was subjected to ^{13}C-NMR spectroscopy by proton noise decoupling and off-resonance decoupling and the multiplicity of the α-carbon atom in the carbonyl group was carefully observed. The ^{13}C-NMR spectroscopy of the enone revealed that the one α-carbon atom of the carbonyl group resonated at 62.6 ppm as a doublet while the other occured at 52.4 ppm as a triplet. This finding suggests that the enone has the same structure as **17** (4,4-dimethylbicyclo[6.3.0]undec-5-en-2-one) and it can be concluded that the bromine atom in **3** is not at position 3 but is at position 5. Therefore, **3** and **14** are epimers.



Scheme 3.

In α-halo ketones, the relationship between the IR[3] or UV[4] spectra and the orientations of the halogen atoms is known. The IR spectra of the dione (**2**) and the α-halo-diones (**3**, **5**, **6**, **13**, and **14**) were measured in carbon tetrachloride and the UV spectra in ethanol (Table 1). From these results, the C–X links in **6**, **13**, and **14** are nearly coplanar with the carbonyl group while the bromine atom in **3** is twisted away from the carbonyl oxygen atom. These results agree with the above-mentioned finding that **3** and **14** are epimers with respect to the bromine atom at position 5.

TABLE 1. THE SPECTRAL DATA OF MONOHALO-DIONES

Compound	UV (EtOH)			IR (CCl_4)	
	λ_{max}(nm)	ε	$\Delta\lambda$	ν(cm^{-1})	$\Delta\lambda$
2 (dione)	300	53	0	1700	0
3 (5-Br)	317	120	+17	1703	+3
14 (5-Br)	308	76	+8	1700 1720	+20
13 (5-Cl)	305	58	+5	1700 1723	+23
5 (1-Cl)	313	77	+13	1700 1710	+10
6 (7-Cl)	313	74	+13	1700 1720	+20

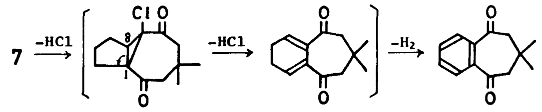
Both **5** and **6**, which were obtained by chlorination of **2**, undergo dehydrochlorination upon treatment with γ-collidine yielding **8**. The mass spectra of **5** and **6** show no fragment peak of $m/e=55+Cl$ (or $54+Cl$). On the other hand, **5** has a fragment peak at $m/e=102$ ($67+Cl$), which was not detected in **6**. Hence, it is inferred that the chlorine atom of **5** is at position 1 and the chlorine atom of **6** is at position 7.

In the mass spectrum of **8**, the parent peak is 206 (M^+). The IR spectrum of **8** shows a weak C–H stretching peak at 3040 cm^{-1}, and carbonyl absorption peaks appear at 1660 and 1675 cm^{-1} in Nujol, which are at frequencies lower than the 1695-cm^{-1} peak observed for **2**. In the UV spectrum of **8**, the end absorption at 210 nm has a higher intensity ($\varepsilon=7100$ in EtOH) compared with the value for **2** ($\varepsilon=131$, EtOH). Furthermore, the ^{1}H-NMR spectrum of **8** has no signal for any magnetic field lower than 3δ, and no signals appear in the ^{13}C-NMR spectrum over the range from 100—160 ppm. These experimental results can be explained more satisfactorily by the presence of a three-membered ring than by the presence of a double bond.

The structure of **8** was determined to be 4,4-dimethyltricyclo[6.3.0.0^{1,7}]undecane-2,6-dione with the aid of the multiplicity results of the ^{13}C-NMR spectra due to proton noise decoupling and off-resonance decoupling. In addition to the signals of two carbonyl carbon atoms (both at 206 ppm), two singlet peaks are present at 49.2 and 34.2 ppm. The peak at 34.2 ppm is assigned to C-4 carrying a *gem*-dimethyl group, and that at 49.2 ppm to C-1, since only C-1 can be converted into a quarternary carbon by dehydrohalogenation. Moreover, two doublet peaks at 40.9 and 37.6 ppm indicate the presence of two tertiary carbon atoms which are assigned to C-7 and C-8, respectively.

The cyclopropane ring of **8** is probably formed by intramolecular nucleophilic substitution involving an intermediate carbanion.[5] Compound **8** appears to be rather strained judging from a molecular model, but conjugation of the cyclopropane ring and two carbonyl groups is likely to stabilize the compound to such an extent as to readily permit its formation.

The dichloro compound (**7**) obtained by the chlorination of **2** yielded 7,7-dimethyl-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-5,9-dione (**18**) containing a benzene ring when treated with γ-collidine. The structure of **18** was determined by ^{1}H-NMR spectroscopy. The signals centered at 7.71 δ, attributable to benzene ring protons, appear as a symmetrical multiplet. The signal for the *gem*-dimethyl protons appears as a singlet (6H) at 1.25 δ and that for the equivalent two methylene protons as a singlet (4H) at 2.75 δ.



Scheme 4.

Experimental

The ^{13}C-NMR and the ^{1}H-NMR spectra were obtained on Hitachi R-26 and R-22 spectrometers in $CDCl_3$ with TMS as the internal standard. The mass spectra were measured with Hitachi RMU-6L and RMU-7M spectrometers. The IR and UV spectra were recorded using JASCO IR-G and Hitachi EPS-3 spectrophotometers, respectively. The VPC analysis was carried out on a 063 Hitachi gas chromatograph.

Bromination of Dione (2). A mixture of **2** (0.2 g) and pyridinium bromide perbromide (0.3 g) in ethanol (10 ml) was stirred at 40—50 °C. The reaction mixture was poured into water (150 ml) and the precipitated bromodione (**3**) (0.21 g) was collected. The product showed one spot on a TLC (silica gel). Recrystallization from ethanol gave pure **3** (0.15 g); mp 111—113 °C. IR and UV (see Table 1). Found: C, 54.67; H, 6.58%. Calcd for $C_{13}H_{19}O_2Br$; C, 54.37; H, 6.62%. MS: *m/e* 288 (M+2, 4%), 286 (M$^+$, 5), 273 (5), 271 (6), 232 (7), 230 (7), 220 (5), 218 (5), 207 (72), 191 (5), 189 (6), 179 (47), 163 (5), 161 (6), 151 (35), 135 (5), 133 (5), 123 (30), 109 (48), 95 (27), 83 (base, 100), 81 (62), 67 (27), 55 (62), and 41(62).

A similar reaction of **2** in acetic acid (10 ml) yielded a crude product (0.25 g) which was subjected to column chromatography on silica gel. Elution with ether–hexane (1 : 1) gave **4**. Crystallization (EtOH) gave pure **4**; mp 164—165 °C. IR (CCl_4) 1710 cm^{-1}. UV (EtOH) λ_{max} 324 nm (ε, 180). Found: C, 42.53; H, 4.86%. Calcd for $C_{13}H_{18}O_2Br_2$: C, 42.65; H, 4.92%. Further elution with ether–hexane (1 : 1) gave **3**. Mp 110—112 °C (EtOH), which was identified by IR spectroscopy.

*Chlorination of Dione (**2**).* Into a solution of **2** (0.4 g) in CCl_4 (15 ml), a solution of sulfuryl chloride (0.26 g) in CCl_4 (10 ml) was added dropwise with stirring. The mixture was allowed to stand at room temperature overnight. The resulting solution was washed successively with water and aqueous sodium hydrogencarbonate. After the organic solution had been dried over sodium sulfate, it was concentrated under reduced pressure. The residual oil was chromatographed on a silica gel column with ether–hexane (1 : 2). The amounts of the products isolated in the order of their elution were: 51 mg of dichloro-dione (**7**), 42 mg of monochloro-dione (**6**), 20 mg of monochloro-dione (**5**), 58 mg of dione (**2**), and 167 mg of 4,4-dimethyltricyclo[6.3.0.0^{1,7}]undecane-2,6-dione (**8**). Recrystallization of chlorodiones **5**, **6**, and **7** from ethanol and of **8** from hexane–ether (5 : 1) gave pure products.

5: mp 108—110 °C. IR and UV (see Table 1). Found: C, 64.47; H, 7.68%. Calcd for $C_{13}H_{19}O_2Cl$: C, 64.33; H, 7.84%. MS: *m/e* 242 (M$^+$, 3%), 207 (3), 151 (3), 141 (80), 123 (5), 112 (36), 109 (2), 104 (2), 102 (6), 95 (7), 83 (base, 100), 81 (10), 67 (17), 55 (13), and 41 (18).

6: mp 126—127 °C. IR and UV (see Table 1). Found: C, 64.39; H, 7.52%. MS: *m/e* 242 (M$^+$, 2%), 207 (37), 179 (7), 151 (2), 123 (3), 122 (3), 111 (12), 109 (6), 95 (13), 83 (base, 100), 81 (17), 67 (12), 55 (16), and 41 (14).

7: mp 168—170 °C. IR and UV (see Table 1). Found: C, 56.47; H, 6.24%. Calcd for $C_{13}H_{18}O_2Cl_2$: C, 56.32; H, 6.50%. MS: *m/e* 276 (M$^+$, 0.5%), 261 (1.5), 243 (5), 242 (14), 227 (2), 213 (3), 207 (3), 205 (3), 178 (2), 176 (8), 174 (25), 163 (2), 161 (7), 159 (3), 157 (4), 153 (2), 150 (2), 149 (2), 143 (4), 141 (5), 123 (4), 115 (6), 111 (17), 108 (3), 107 (3), 102 (3), 95 (3), 83 (base, 100), 79 (13), 77 (12), 67 (12), 55 (19), and 41 (19). The mass spectrum of **7** shows a fragment peak at *m/e*=102 (67+Cl) and it is likely that one chlorine atom is present at the ring junction and the other at position 7.

8: mp 106—107 °C. IR: (CCl_4) 3040, 2950, and 2805 cm^{-1} (C–H), 1685 cm^{-1} (C=O); (Nujol) 1660 and 1675 cm^{-1} (C=O). UV (EtOH) λ_{max} 288 nm (ε, 69), ε at 210 nm (7100). ^{1}H-NMR ($CDCl_3$) 0.91 δ (s, 3H, CH_3) and 1.10 δ (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$) 206 ppm (s, C-2, C-6), 56.2 and 54.6 ppm (t, C-3, C-5), 49.2 ppm (s, C-1), 40.9 ppm (d, C-7), 37.6 ppm (d, C-8), 34.2 (s, C-4), 32.9 and 24.7 ppm (q, diCH_3), 29.0 and 27.7 ppm (t, C-9, C-11), and 19.5 ppm (t, C-10). Found: C, 75.45; H, 9.06%. Calcd for $C_{13}H_{18}O_2$: C, 75.73, H, 8.74%. MS: *m/e* 206 (M$^+$, $C_{13}H_{18}O_2$, 63%), 191 ($C_{12}H_{15}O_2$, 8), 188 ($C_{13}H_{16}O$, 5), 178 ($C_{12}H_{18}O$, 9), 163 ($C_{11}H_{15}O$, 11), 150 ($C_9H_{10}O_2$, 41), 135 ($C_8H_7O_2$, 11), 122 ($C_8H_{10}O$, 48), 108 (C_7H_8O, 80), 94 (C_6H_6O, C_7H_{10}, 14), 83 (C_5H_7O, 100), 79 (C_6H_7, 36), and 67 (C_5H_7, 8).

*Chlorination of **1a**.* To a solution of **1a** (0.3 g) in CCl_4 (10 ml), sulfuryl chloride (0.1 ml) in CCl_4 (5 ml) was added dropwise with stirring at 60 °C. The resulting solution was stirred for 1 h and then washed with water, aqueous sodium hydrogencarbonate and aqueous sodium chloride. After the organic solution had been dried over (sodium sulfate) and concentrated under reduced pressure, a crude crystalline compound (0.35 g) was obtained. Recrystallization (EtOH) afforded pure **9** (0.22 g); mp 130—132 °C. IR (Nujol) 1703 cm^{-1} (C=O) and 1730 cm^{-1} ($OCOCH_3$). Found: C, 63.41; H, 7.10%. Calcd for $C_{15}H_{21}O_3Cl$: C, 63.27; H, 7.38%.

From the parent solution, **11** (25 mg) was obtained; mp 163—165 °C. IR (Nujol) 1708 cm^{-1} (C=O) and 1733 cm^{-1} ($OCOCH_3$). Found: C, 56.32; H, 6.03%. Calcd for $C_{15}H_{20}O_3Cl_2$: C, 56.43; H, 6.27%.

*Bromination of **1a**.* A mixture of **1a** (0.3 g) and pyridinium bromide perbromide (0.5 g) in acetic acid (10 ml) was stirred at room temperature until the reagent was dissolved and the mixture had reacted. The reaction mixture was poured into ice water (150 ml) and the precipitate (0.42 g) was collected. Recrystallization (EtOH) gave **10** (0.25 g); mp 142—144 °C. IR (Nujol) 1690 cm^{-1} (C=O) and 1740 cm^{-1} ($OCOCH_3$). Found: C, 54.88; H, 6.61%. Calcd for $C_{15}H_{21}O_3Br$: C, 54.73; H, 6.38%.

From the parent solution, **12** (48 mg) was obtained; mp 164—166 °C. IR (Nujol) 1705 cm^{-1} (C=O) and 1730 cm^{-1} ($OCOCH_3$). Found: C, 43.96; H, 5.14%. Calcd for $C_{15}H_{20}O_3Br_2$: C, 44.14; H, 4.90%.

*Chloro-dione (**13**) and Bromo-dione (**14**).* A solution of 0.35 g of **9** (or **10**) in methanol (40 ml) containing sulfuric acid (2 ml) was left to stand at room temperature for two weeks. The reaction mixture was concentrated at reduced pressure and extracted with ether. The ethereal extract was neutralized with aqueous sodium hydrogencarbonate, washed with water, and then dried over sodium sulfate. After the removal of the ether, a crystalline residue was obtained. Recrystallization from methanol gave **13** (0.10 g) (or **14** (0.12 g)).

13: mp 90—92 °C. IR and UV (see Table 1). Found: C, 64.17; H, 7.96%. Calcd for $C_{13}H_{19}O_2Cl$: C, 64.33; H, 7.84%. MS: *m/e* 242 (M$^+$, 1%), 207 (1.5), 188 (2), 186 (4), 175 (11), 173 (18), 152 (17), 124 (56), 109 (10), 95 (73), 92 (5), 90 (12), 83 (base, 100), 81 (25), 67 (73), 55 (38), and 41 (58).

14: mp 115—116 °C. IR and UV (see Table 1). Found: C, 54.52; H, 6.40%. Calcd for $C_{13}H_{19}O_2Br$: C, 54.37; H, 6.62%. MS: *m/e* 288 (M+2, 2%), 286 (M$^+$, 2), 232 (4), 230 (4), 221 (11), 219 (14), 207 (64), 179 (4), 152 (42), 136 (7), 134 (7), 124 (72), 111 (10), 109 (10), 97 (23), 95 (70), 83 (base, 100), 81 (28), 67 (56), 55 (37), and 41 (50).

*Dehydrochlorination of **5**, **6**, and **7**.* A mixture of **5** (20 mg) and γ-collidine (0.5 ml) was refluxed for 10 min in a nitrogen atmosphere. Rapidly, a precipitate of γ-collidine hydrochloride was produced. The resulting mixture was diluted with petroleum ether, filtered to separate of γ-collidine hydrochloride and then washed successively with 4% aqueous hydrochloric acid, aqueous sodium hydrogencarbonate, and water. The solvent was removed and the residue was crystallized from hexane, mp 100—103 °C (92% yield). The product was identical to **8** on the basis of a comparison of their IR spectra.

A similar reaction of **6** (20 mg) with refluxing for 2 h also gave **8** (85% yield).

Similarly, **7** (0.2 g) was refluxed with γ-collidine (1.5 ml) for 2 h and treated in the manner described above. The product was crystallized from hexane, mp 90—92 °C (58 mg). Recrystallization (hexane) afforded pure **18**; mp 97—99 °C. IR (Nujol) 1690 cm^{-1} (C=O) and 1590 cm^{-1} (C=C). UV

(EtOH) λ_{max} 221.5 nm (ε, 22700), 258 (7080), and 296 (2070). ^{1}H-NMR ($CDCl_3$) 1.25 δ (s, 6H, $diCH_3$), 2.75 δ (s, 4H, $2CH_2$), and 7.56—7.87 δ (m, 4H, ArH). Found: C, 77.18; H, 7.06 %. Calcd for $C_{13}H_{14}O_2$: C, 77.23; H, 6.93%. MS: *m/e* 202 (M^+, 14%), 174 (3), 159 (3), 146 (base, 100), 129 (4), 104 (26), 90 (9), 76 (22), 50 (9), and 41 (9), The formation of **18** from **7** probably proceeds *via* an intermediate containing a cyclopropane ring similar to **8**, followed by the opening of the cyclopropane ring at C_1–C_8 and further dehydrogenation (Scheme 4).

*Reactions of **3**, **13**, and **14** with γ-Collidine.* In the manner described above, **3**, **13**, and **14** (20 mg) were refluxed with γ-collidine for 2 h. In each case, no precipitation of γ-collidine hydrochloride occured and the starting material was recovered in a 80—87% yield, and identified by IR spectroscopy.

*4,4-Dimethylbicyclo[6.3.0]undec-5-en-2-one (**17**).* In a solution of **3** (0.3 g) in ethanol (20 ml), $NaBH_4$ (0.15 g) in ethanol (20 ml) was added at 20 °C. The solution was left to stand at room temperature for 48 h, diluted with water and extracted with ether. The ethereal solution was dried and evaporated *in vacuo*. The glassy residue (**15**) was dissolved in acetic acid (30 ml) and refluxed with zinc dust (2 g) for 1.5 h. The reaction mixture was filtered and extracted with ether. The extract was processed by the usual method and gave an oily residue (**16**); Tetranitromethane test positive. To a solution of crude **16** in acetic acid (10 ml), chromic trioxide (0.3 g) in acetic acid (12 ml) was added dropwise with stirring at 25 °C and the solution was allowed to stand at room temperature overnight, diluted with water and extracted with ether. After the usual procedure, the extract gave an oily residue. Column chromatography (on silica gel) of the product using hexane elution gave **17** (62 mg) and a by-product (54 mg) which is probably acetate of **16** (ν 1730 cm^{-1}). Product **17** was further purified by column chromatography and preparative TLC (Silica Gel G) and obtained as a colorless oil which solidified in a refrigerator and showed one peak on a VPC; Beilsteine test negative and tetranitromethane test positive. Mp 26 °C. IR (neat) 3000, 2940, and 2850 cm^{-1} (C–H), 1695 cm^{-1} (C=O), 1640 cm^{-1} sh (C=C). ^{1}H-NMR ($CDCl_3$) 0.93 δ (s, 3H, CH_3), 1.12 δ (s, 3H, CH_3) and 5.56—5.80 δ (m, 2H, olefinic). ^{13}C-NMR ($CDCl_3$) 211.6 ppm (s, C-2), 134.8 and 128.8 ppm (d, C-5, C-6), 62.6 ppm (d, C-1), 52.4 ppm (t, C-3), 43.2 ppm (d, C-8), 39.6 and 34.2 ppm (t, C-7, C-11), 33.0 ppm (s, C-4), 29.0 and 29.4 ppm (q, $diCH_3$), 25.8 and 23.0 ppm (t, C-9, C-10). Found: C, 81.07; H, 10.51%. Calcd for $C_{13}H_{20}O$: C, 81.25; H, 10.42%. MS: *m/e* 192 (M^+, 6%), 177 (16), 159 (2), 149 (5), 136 (28), 121 (11), 108 (base, 100), 93 (47), 81 (17), 80 (18), 79 (15), 68 (15), and 67 (14). 2,4-DNP: mp 148—149 °C.

References

1) M. Umehara, T. Oda, Y. Ikebe, and S. Hishida, *Bull. Chem. Soc. Jpn.*, **49**, 1075 (1976).

2) L. F. Fieser and R. Ettorre, *J. Am. Chem. Soc.*, **75**, 1700 (1953); L. F. Fieser and X. A. Dominguez, *ibid.*, **75**, 1704 (1953).

3) R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952); R. N. Jones, *ibid.*, **75**, 4839 (1953); E. J. Corey, *ibid.*, **75**, 2301 (1953); N. J. Leonard and F. H. Owens, *ibid.*, **80**, 6039 (1958).

4) R. C. Cookson, *J. Chem. Soc.*, **1954**, 282.

5) A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc.*, *B*, **1968**, 67; R. Bird and C. J. M. Stirling, *ibid.*, **1968**, 111.