109. Note on the Synthesis of 1, 1-Dichloro-2, 3-divinylcyclopropane and Other Functionalized Dichlorocyclopropanes

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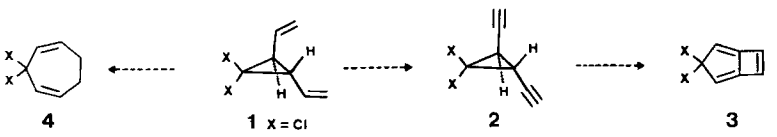
Summary

The title compound **1** was synthesized *via* addition of dichlorocarbene to dimethyl *trans*-3-hexenedioate (**5**), using *o*-nitrophenylselenic acid-elimination to form the double bonds. Reaction of dichlorocyclopropane **8** with ozone on silica gel furnished the monoketone **10**; no diketone **11** could be isolated upon further exposure of **10** to O_3/SiO_2. When the bis(*p*-toluenesulfonate) **13b** was treated with *t*-BuOK, **16** was obtained in low yield as the only isolable product. It is believed to arise from *Cope*-rearrangement of an intermediate *cis*-divinylcyclopropane **14** to cycloheptadiene **15**, which undergoes a subsequent allylic rearrangement to **16**.

Dihalogenodivinylcyclopropanes (*e.g.* **1**) are of interest as potential intermediates for the synthesis of dihalogenobicyclo[3.2.0]hepta-1,4,6-trienes **3** *via* diethynylcyclopropanes **2** [1], and for mechanistic reasons in relation with the *Cope*-rearrangements to 1,3-cycloheptadienes **4** [2] *(Scheme 1)*. This communication reports the synthesis of *trans*-1,1-dichloro-2,3-divinylcyclopropane (**1**) as well as that of some other functionalized dichlorocyclopropanes which were synthesized during exploratory studies of access to **2** and **3**.

Scheme 1



Synthesis of *trans*-1,1-dichloro-2,3-divinylcyclopropane (1). – Addition of dichlorocarbene to *trans*-3-hexenedioate **5** using the *Dehmlow* procedure [3] gave **6** in 27% yield *(Scheme 2)*. The latter was reduced with $LiAlH_4$ to diol **7a**. Considerable efforts was spent in order to convert **7a** to **1** *via* base-induced elimination of the corresponding bis(*p*-toluenesulfonate) **7b**; however, all base/solvent systems failed. Either unreacted starting compound was recovered, or the reaction led to

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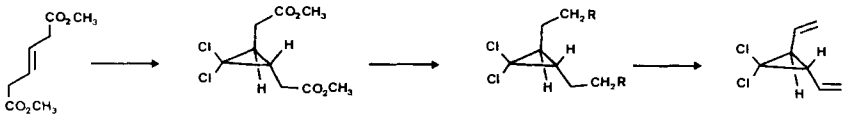
Scheme 2



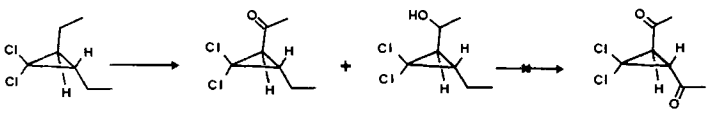
5 **6** **7a** R = OH; **7b** R = OTs; **7c** R = $SeC_6H_4NO_2$ **1**

complex and untractable mixtures of decomposition products. A modified approach was therefore applied using the well-documented *syn*-elimination of *o*-nitrophenylselenic acid [4] which has the advantage to allow particularly mild reaction conditions. Diol **7a** was converted to the *o*-nitrophenylseleno compound **7c** by treatment with *o*-nitrophenyl selenocyanate and tributylphosphine [5] [6] (41% yield). Oxidation with H_2O_2 or HIO_4 [4] [7] afforded **1** in 10–20% yield. The spectra of **1** are consistent with its structure.

The ^{1}H-NMR. shows multiplets at 6.43 (6 H), typical for vinylic protons and at 2.22 ppm (2 H) for the protons at the cyclopropane ring. In the ^{13}C-NMR. the C-atoms of the cyclopropane ring resonate at 40.4 (*d*, ^1J(C,H) = 159 Hz, C(2) and C(3)) and 65.1 ppm (*s*, C(1)), while those of the double bond appear at 118.6 (*t*, ^1J(C,H) = 159.6, C(β)) and 132.9 ppm (*d*, ^1J(C,H) = 162 Hz, C(α)).

Preparation of other functionalized dihalogenocyclopropanes. – Functionalization in α-position to cyclopropane rings with ozone on silica gel leads to alcohols and ketones [8]. α,α'-Diketones are obtained from cyclopropanes carrying two alkyl substituents [9]. The same procedure applied to *trans*-1,1-dichloro-2,3-diethylcyclopropane (**8**; *Scheme 3*) led to alcohol **9** (2%) and monoketone **10** (62%). Upon repeated exposure of **8** to ozone (up to 10 cycles), both **9** and **10** disappeared from the reaction mixture, which ultimately contained a series of unidentified carboxylic acids, but no diketone **11**. Thus it appears that the dichloro substituents desactivate the cyclopropane ring sufficiently to limit introduction of O-atoms into the α-position of one side chain.

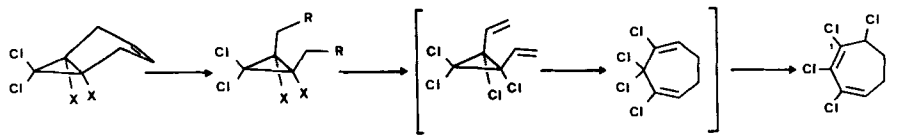
Scheme 3



8 **10** **9** **11**

The *cis*-1,1-dichloro-2,3-disubstituted cyclopropanes are readily accessible *via* liquid-phase ozonolysis of 7,7-dichlorobicyclo[4.1.0]hept-3-enes (**12a**; *Scheme 4*). The latter compounds are obtained by addition of dichlorocarbene to 1,4-cyclohexadiene [10] or by *Diels-Alder* reaction of butadiene and tetrachlorocyclopropene [11]. Ozonolysis of **12a** followed by reduction with dimethyl sulfide in methanol and trimethyl orthoformate gave the acetal **13a** in 60% yield. However, the correspond-

Scheme 4



12a X = H **13a** X = H, R = $CH(OCH_3)_2$ **14** **15** **16**
12b X = Cl **13b** X = Cl, R = CH_2OH
13c X = Cl, R = CH_2OTs

ing dialdehyde could not be obtained *via* hydrolysis of **13a**. Similarly, the tetrachloro derivative **12b** was treated with O_3. Reduction of the intermediate ozonide with $NaBH_4$ furnished diol **13b** which was transformed to the bis(*p*-toluenesulfonate) **13c** by conventional methods. Elimination with *t*-BuOK afforded a complex product mixture from which one compound could be isolated by preparative GC. The structure **16** was assigned on the grounds of spectral data.

The ^{13}C-NMR. shows seven different C-atoms, four of which sp^2-hybridized and three sp^3-hybridized. In the ^1H-NMR. there is one olefinic proton at 6.56 ppm (H–C(4)) which couples with two protons of the methylene group at C(5). The proton at C(7) appears as a $d \times d$ ($^3J(H,H) = 6$ and 8 Hz) at 4.92 ppm owing to coupling with the protons at C(6). The protons at C(5) and C(6) are complex multiplets at 2.6 and 2.3 ppm, respectively. Both UV. and IR. spectra indicate the presence of a conjugated diene, while the MS. is in agreement with the proposed structural formula showing the parent ion and successive loss of Cl-atoms.

The formation of diene **16** is most likely due to the following sequence: Two-fold elimination from **13c** will lead to the *cis*-divinylcyclopropane **14** which may undergo spontaneous *Cope*-rearrangement to cycloheptadiene **15**. Allylic rearrangement of **15** will give rise to the conjugated diene **16**.

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Experimental Part

General remarks. S. [12].

Synthesis of dimethyl trans-*3,3-dichloro-1,2-cyclopropanedicarboxylate* (**6**). A solution of **5** (10.3 g, 60 mmol), sodium trichloroacetate (22.2 g, 120 mmol) and (hexadecyl)trimethylammonium bromide (450 mg, 1.2 mmol) in 60 ml of $CHCl_3$ was heated to 70° with vigorous stirring. After 24 h, another portion of sodium trichloroacetate was added, and heating was continued for 24 h. The emulsion was then poured into a large volume of water. Extraction with CH_2Cl_2 followed by distillation afforded unreacted **5** (62%) and **6** (4.2 g, 27%). B.p. of **6** 79°/0.1 Torr. – IR. (film): 3000*m*, 2960*m*, 2850*w*, 1730*s*, 1440*s*, 1420*s*, 1370*s*, 1310*s*, 1270*s*, 1210*s*, 1180*s*, 1080*m*, 1030*m*, 900*m*, 860*m*, 820*s*. – ^1H-NMR. (CCl_4, 60 MHz): 3.66 (*s*, 6 H); 2.60 (*m*, 4 H); 1.60 (*m*, 2 H). – MS.: 258, 256, 254 (11, M^+); 227, 225, 223 (15); 221, 219 (3); 199, 197, 195 (4); 198, 196, 194 (24); 185, 183, 181 (70); 161, 159 (19); 59 (100).

Synthesis of trans-*3,3-dichloro-1,2-cyclopropanediethanol* (**7a**). To a solution of **6** (14 g, 55 mmol) in 100 ml of anh. ether was added at −10° under N_2 a suspension of $LiAlH_4$ (2.9 g, 76.5 mmol) in ether (120 ml). After stirring at 0° during 15 h, the mixture was treated with 2N HCl. Extraction with ether followed by distillation gave **7a** (8.4 g, 77%) as a yellow and hygroscopic oil, b.p. 120°/0.1 Torr. – IR.

($CHCl_3$): 3600*w*, 3400–3250*s* br., 3000*m*, 2960*s*, 2920*s*, 2880*s*, 1450*m*, 1130*w*, 1070*s*, 1010*m*, 980*m*, 900*m*. – ^{1}H-NMR. ($CDCl_3$, 60 MHz): 4.70 (*s*, 2 H, exchangeable with D_2O); 3.75 (*t*, ^3J(H,H) = 6, 4 H); 2.33–1.33 (*m*, 6 H).

Synthesis of trans-*3,3-dichloro-1,2-cyclopropanediethyl bis(*p*-toluenesulfonate)* (**7b**). To a solution of **7a** (2.6 g, 13 mmol) in freshly distilled pyridine (35 ml) was added at $-10°$ *p*-toluenesulfonyl chloride (7.5 g, 39 mmol). The mixture was stirred for 15 h between -5 and $-10°$, poured on ice and extracted with CH_2Cl_2. After several washings with 2N HCl and water, the extract was filtered through a column of 10 g of SiO_2 and evaporated. The product **7b** (5.34 g, 81%) crystallized on standing, m.p. 84–86°. – IR. (film): 3040*w*, 2980*m*, 2920*m*, 2880*m*, 1600*s*, 1500*m*, 1460*m*, 1440*m*, 1370*s*, 1180*s*, 1110*s*, 980*s*, 920*s*, 820*s*, 760*s*, 670*s*. – ^{1}H-NMR. ($CDCl_3$, 60 MHz): 7.56 (4*m*, 8 H); 4.10 (*t*, ^3J(H,H) = 6, 4 H); 2.43 (*s*, 6 H); 1.83 (*m*, 4 H); 1.25 (*m*, 2 H). – MS.: 510, 508, 506 (1, M^+); 355, 353, 351 (1); 338, 336, 334 (4); 172 (21); 166, 164, 162 (19); 155 (70); 129, 127 (16); 91 (100).

When the reaction was carried out at RT., the mixture contained 15% of *trans*-2,2-dichloro-3-(2-chloroethyl)-1-cyclopropaneethyl *p*-toluenesulfonate and *ca.* 1% of *trans*-1,1-dichloro-2,3-bis(2-chloroethyl)cyclopropane. Both compounds were identified by their ^{1}H-NMR. and MS.

Synthesis of trans-*1,1-dichloro-2,3-bis(2-(*o*-nitrophenylseleno)ethyl)cyclopropane* (**7c**). To a solution of **7a** (3.98 g, 20 mmol) and *o*-nitrophenyl selenocyanate [5] (10.98 g, 48 mmol) in THF (200 ml) was added at RT. and under N_2 tributylphosphine (12 ml, 48 mmol) in 40 min. After 30 min the solution was evaporated to dryness. The solid residue was washed with pentane and purified by column chromatography on SiO_2 using CH_2Cl_2/hexane 2:1 to afford **7c** (4.67 g, 41%), m.p. 137–138° (from $CHCl_3$). – IR.: 3030*w*, 3000*w*, 2940*w*, 2850*w*, 1595*m*, 1580*m*, 1450*w*, 1335*s*, 1305*m*, 1250*w*, 1170*w*, 1150*w*, 1110*w*, 1040*m*, 850*m*, 810*w*. – ^{1}H-NMR. ($CDCl_3$, 360 MHz): 8.28 (*d*, 2 H); 7.55 (*m*, 4 H); 7.35 (*m*, 2 H); 3.11 (*AB*-system × *m*, $^2J_{AB}$ = 11.5, H_A at 3.07, H_B at 3.16, 4 H, 2 CH_2CH_2Se); 2.09 (*AB*-system × *m*, $^2J_{AB}$ = 15, H_A at 2.04, H_B at 2.15, 4 H, 2 CH_2CH_2Se); 1.45 (*m*, 2 H). – MS.: 576–560 (5, M^+); 541–525 (21); 530–514 (5); 454–438 (6); 372–362 (23); 248–238 (13); 204–198 (78); 188–182 (100); 139, 137, 135 (94).

Synthesis of trans-*1,1-dichloro-2,3-divinylcyclopropane* (**1**). To a solution of **7c** (1.13 g, 2 mmol) in THF (40 ml) was added triethylamine (0.85 ml, 6 mmol) and 30% H_2O_2-solution (1.4 ml, 16 mmol) at RT. After 19 h, the mixture was poured into water and extracted with pentane. The organic phase was dried and concentrated at 40° to 5–10 ml. After addition of CCl_4, distillation was continued at 40°/200 Torr to eliminate remaining THF. The remaining solution (3–5 ml) was distilled rapidly (50°/3 Torr) and collected in a trap at $-100°$. Pure **1** was obtained in 10–20% yield in CCl_4 solution. Analytical samples were further purified by prep. GC. – IR.: 3085*w*, 2950*m*, 2890*w*, 1640*m*, 1250*m*, 1040*m*, 980*m*, 860*s*. – ^{1}H-NMR. ($CDCl_3$, 100 MHz): 6.43 (*m*, 6 H); 2.22 (*m*, 2 H). – ^{13}C-NMR. ($CDCl_3$, 25.2 MHz): 132.87 (*d*, $^1J_{CH}$ = 162); 118.60 (*t*, $^1J_{CH}$ = 159.6); 65.07 (*s*); 40.36 (*d*, $^1J_{CH}$ = 159). – MS.: 166, 164, 164 (2, M^+); 129, 127 (13); 115, 113 (6); 91 (100); 77 (6); 65 (17).

Synthesis of trans-*1,1-dichloro-2,3-diethylcyclopropane* (**8**). A mixture containing *trans*-3-hexene (5.05 g, 60 mmol), $CHCl_3$ (21.6 g, 180 mmol), (hexadecyl)trimethylammonium bromide (220 mg) and 50% aq. NaOH-solution (38.4 g) was stirred vigorously at 50° during 6 h. The emulsion was poured into sat. NaCl-solution and extracted with CH_2Cl_2. After usual workup, the organic phase was distilled to afford **8** (7.2 g, 73%), b.p. 50°/15 Torr. – IR. (film): 2960*s*, 2920*s*, 2860*s*, 1460*m*, 1150*m*, 820*s*. – ^{1}H-NMR. (CCl_4, 60 MHz): 1.5 (*m*, 4 H); 1.0 (*m*, 2 H); 1.03 (*t*, ^3J(H,H) = 6, 6 H). – MS.: 170, 168, 166 (2, M^+); 155, 153, 151 (< 1); 141, 139, 137 (21); 133, 131 (7); 128, 126, 124 (60); 113, 111, 109 (31); 103, 101 (10); 91, 89 (100); 70 (48).

Reaction of ***8*** *with* O_3. The dichlorocyclopropane **8** (3.0 g, 18 mmol) was stirred for 2 h with 150 g of dried (150°/0.1 Torr) silica gel in a RV. The mixture was then introduced into a U-tube and cooled to $-78°$. A stream of O_3 was passed through the tube until saturation of the silica gel (blue color). The temp. was allowed to rise to RT. in 2 h; during this time the color faded. This cycle was repeated 3 times. The silica gel was then repeatedly extracted with ether and furnished 2.1 g of a mixture containing trans-*2,2-dichloro-3-ethylcyclopropyl methyl ketone* (**10**; 62%), *1-(*trans-*2,2-dichloro-3-ethylcyclopropyl)-ethanol* (**9**; 2%), unreacted **8** (4%), and several other unidentified products. Analytical samples were separated by prep. GC. (*FFAP* 5% on *Chromosorb W*, 150°).

Data of **10**. – IR. (film): 2980*s*, 2950*s*, 2880*s*, 1720*vs*, 1360*m*, 1170*s*, 820*s*. – ^{1}H-NMR. ($CDCl_3$, 100 MHz): 2.40 (*s*, 3 H); 2.40 (*d*, ^3J(H,H) = 8, 1 H); 2.24 (*t* × *d*, ^3J(H,H) = 7, 1 H); 1.65 (*m*, 2 H); 1.09 (*t*, ^3J(H,H) = 7, 3 H). – MS.: 184, 182, 180 (1, M^+); 169, 167, 165 (< 1); 155, 153, 151 (5); 147, 145 (8); 143, 141, 139 (3); 127, 125, 123 (4); 111, 109 (3); 65 (5); 43 (100).

Data of **9**. – ^{1}H-NMR. ($CDCl_3$, 100 MHz): 3.65 (*m*, 1 H); 2.08 (*m*, 1 H); 1.9–1.2 (*m*, 4 H); 1.34 (*d*, ^3J(H,H) = 6, 3 H); 1.06 (*t*, ^3J(H,H) = 7, 3 H). – MS.: 186, 184, 182 (< 1); 168, 166, 164 (< 1); 143, 141, 139 (< 1); 131, 129 (2); 45 (100).

Synthesis of cis-*1,1-dichloro-2,3-(2,2-dimethoxyethyl)cyclopropane* (**13a**). Ozone was passed through a solution of 7,7-dichlorobicyclo[4.1.0]hept-3-ene [10] (**12a**; 3.20 g, 20 mmol) in methanol (100 ml) at −40° until saturation (blue color). Excess O_3 was removed with a stream of N_2 passing through the solution. To the cold solution was added dimethyl sulfide (2.0 g, 32.2 mmol), $HC(OMe)_3$ (23.2 g, 218 mmol) and a 3% solution of HCl in MeOH (46 ml). The mixture was warmed to RT. and allowed to react for 15 h. It was concentrated, neutralized with sat. $NaHCO_3$-solution and extracted with ether. Workup of the organic phase afforded a yellow oil (4.6 g), which was purified by column chromatography (silica gel and CH_2Cl_2/ethyl acetate 6:1) to afford 3.4 g (60%) of **13a**, b.p. 130°/1 Torr. – IR. (CCl_4): 2980*s*, 2940*s*, 2900*s*, 2840*s*, 1450*s*, 1390*s*, 1370*s*, 1200*s*, 1130*s*, 1090*s*, 1030*s*, 980*s*, 840*m*. – ^{1}H-NMR. ($CDCl_3$, 100.1 MHz): 4.46 (*m*, 2 H); 3.38 (*s*, 6 H); 3.36 (*s*, 6 H); 1.7 (*m*, 6 H). – ^{13}C-NMR.: 103.63 (*d*), 64.79 (*s*), 53.68 (*qa*), 53.23 (*qa*), 28.92 (*d*), 28.33 (*t*). – MS.: M^+ absent; 289, 287, 285 (< 1); 259, 257, 255 (1); 258, 256, 254 (1); 227, 225, 223 (3); 193 (2); 187 (2); 161 (7); 155 (2); 111 (2); 79 (6); 75 (100).

Synthesis of cis-*1,2,3,3-tetrachloro-1,2-cyclopropanediethanol* (**13b**). Into a methanolic solution (180 ml) of 1,6,7,7-tetrachlorobicyclo[4.1.0]hept-3-ene [11] (**12b**; 6.9 g, 30 mmol) at −30° was passed a stream of O_3 until saturation. The temp. was risen to −10° and $NaBH_4$ (2.25 g, 60 mmol) in EtOH/H_2O 1:1 (60 ml) was added dropwise. After 15 h, CH_2Cl_2 and water was added in order to obtain separation of the phases. The organic layer was extracted with CH_2Cl_2. Workup of the extract afforded **13b** (5.8 g, 73%), m.p. 108–110° (from $CHCl_3$; [13] 107–108°). – IR. (nujol): 3400–3200*s* br., 1040*s*, 900*m*, 880*m*, 830*m*. – ^{1}H-NMR. ($CDCl_3/D_6$-acetone, 60 MHz): 3.96 (*t*, ^3J(H,H) = 6, 4 H); 3.5 (*s*, exchangeable with D_2O, 2 H); 2.32 (*t*, ^3J(H,H) = 6, 4 H). – MS.: 274, 272, 270, 268, 266 (< 1, M^+); 257, 255, 253, 251, 429 (< 1); 219, 217, 215, 213 (< 1); 199, 197, 195 (100); 169, 167, 165 (41); 151, 149, 147 (19).

Synthesis of cis-*1,2,3,3-tetrachloro-1,2-cyclopropanediethyl bis*(p-*toluenesulfonate)* (**13c**). At −10° **13b** (1.34 g, 5 mmol) was reacted in freshly distilled pyridine with TsCl (2.86 g, 15 mmol) for 24 h. The mixture was poured on ice and extracted with CH_2Cl_2 and ether. After workup of the organic phase, **13c** (2.56 g, 85%) was recrystallized from ether, m.p. 103–105°. – IR. ($CHCl_3$): 3020*m*, 2950*m*, 2920*m*, 2860*m*, 1600*s*, 1500*m*, 1460*m*, 1370*s*, 1180*s*, 1100*s*, 980*s*, 910*s*. – ^{1}H-NMR. ($CDCl_3$, 60 MHz): 7.56 (*m*, 8 H); 4.3 (*t*, ^3J(H,H) = 6.5, 4 H); 2.44 (*s*, 6 H); 2.42 (*t*, ^3J(H,H) = 6.5, 4 H). – MS.: 582, 580, 578, 576, 574 (2, M^+); 373, 371, 369, 367 (3); 353, 351, 349 (16); 239, 237, 235, 233, 231 (8); 219, 217, 215, 213 (37); 181, 179, 177 (93); 172 (75); 155 (100); 91 (96); 79 (32).

Synthesis of 1,2,3,7-tetrachloro-1,3-heptadiene (**16**). To a solution of **13c** (1.15 g, 2 mmol) in THF (10 ml) was added, dropwise at −50° under N_2, *t*-BuOK (960 mg, 8.5 mmol) in THF (15 ml). After 1 h at −50°, the solution was allowed to warm up to RT. in 2 h. It was evaporated *in vacuo* at 25°. The solid residue was extracted with chloroform and ether. The solvent was evaporated and the crude product purified by column chromatography ($SiO_2/CHCl_3$) followed by prep. TLC. ($SiO_2/CHCl_3$). The diene **16** was isolated in 10% yield. – UV. ($CDCl_3$): 257. – IR. (film): 3040*w*, 2940*m*, 2850*m*, 1590*m*, 1570*m*, 1440*m*, 1340*w*, 1315*m*, 1180*w*, 1140*w*, 1120*m*, 840*s*, 750*s*, 710*s*. – ^{1}H-NMR.: 6.56 (*t*, ^3J(H,H) = 7, 1 H); 4.92 (*d* × *d*, ^3J(H,H) = 6, ^3J(H,H) = 8, 1 H); 2.6 (*m*, 2 H); 2.3 (*m*, 2 H). – ^{13}C-NMR. ($CDCl_3$, 25.2 MHz): 136.3 (*s*, C(1)); 134.1 (*d*, C(4)); 128.5 (*s*, C(3) or C(2)); 127.6 (*s*, C(2) or C(3)); 59.1 (*d*, C(7)); 43.8 (*t*, C(5)); 24.7 (*t*, C(6)). – MS.: 238, 236, 234, 232, 230 (13, M^+); 201, 199, 197, 195 (21); 164, 162, 160 (23); 163, 161, 159 (100); 127, 125 (20); 89 (15).

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