The Eschweiler-Clarke methylation of *11* gave the tertiary amine *6* described below.

N,N-Dimethyl-3-phenylbicyclo[2.2.1]hept-2-ene-2-methanamine (*5*, 3 %, $C_{16}H_{21}N$, mol. wt. 227.33), which has been described earlier.[1]

MS [IP 70 eV; *m/e* (% rel. int.)]: 227 (75, M), 212 (23, $[M-CH_3]$), 198 (40), 186 (39), 155 (35), 115 (23), 91 (27), 84 (72), 67 (29), 58 (100).

^{1}H NMR (60 MHz, CCl_4): δ 7.24 (5 H, s, Ph protons), 3.13 (2 H, broad s, bridgehead protons), 2.98 (2 H, s, CH_2N), 2.20 [6 H, s, $N(CH_3)_2$], 2.11 – 1.00 (6 H, complex signal).

N,N-Dimethyl-1-phenyltricyclo[2.2.1.0^{2,6}]-heptane-7-methanamine (*6*, 3 %, $C_{16}H_{21}N$, mol. wt. 227.33), whose structure was confirmed earlier.[1]

MS [IP 70 eV; *m/e* (% rel. int.)]: 227 (8, M), 115 (3), 91 (2), 84 (1), 77 (1), 58 (100, $[(CH_3)_2NCH_2]$).

N,N-Dimethyl-*endo*-3-phenylbicyclo[2.2.1]-heptane-*exo*-2-methanamine (*7*, 2 %), whose ^{1}H NMR spectrum is identical with that reported in the literature.[10]

endo-3-Phenylbicyclo[2.2.1]heptane-*exo*-3-methanamine (*12*, 1 %), whose mass spectrum has the same peaks as that of an authentic sample.[1]

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Preparation of *gem*-Dibromocyclopropyl Aldehydes and Acids from Conjugated Dienes

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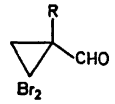
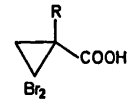
The *gem*-dibromocyclopropyl unit is an allene synthon,[1] and we were interested in compounds where it is connected to a carbonyl function, particularly an aldehyde group. No useful method for the preparation of aldehydes of the general structure *1* has been described. The addition of dihalocarbenes to α,β-unsaturated aldehydes is not a feasible reaction, but addition to the corresponding acetals takes place albeit in poor yields.[2] Subsequent hydrolysis of the acetals afforded the aldehydes and the parent compound, 2,2-dibromocyclo-



1

a R = H
b R = Me
c R = Ph



2

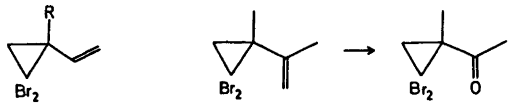
a R = H
b R = Me
c R = Ph

propylcarbaldehyde (1a), was first prepared in this way,[3] but no yields were reported. In the present work we describe convenient synthetic routes to the aldehydes *1* and the corresponding acids *2* starting from conjugated dienes.

Conjugated dienes react with dibromocarbene, generated by various methods, to give the monoadducts *3* in good yields.[4] Addition to the second double bond will also take place to a certain extent depending on the structure of the diene, but provided an excess of diene is used the amount of bis-adducts becomes insignificant in most cases. Furthermore, separation of the adducts usually creates no problem. In the present work dibromocarbene was generated from bromoform and 50 % aqueous sodium hydroxide by the phase transfer method [5] or from bromoform and potassium *t*-butoxide. These monoadducts are conveniently oxidixed to the aldehydes *1* in good yields by either ruthenium dioxide – sodium *meta*-periodate (method A) or by ozone (method B).

By method A the oxidation was carried out in dilute water – carbon tetrachloride mixture using catalytic amounts of ruthenium dioxide.[6] In the aqueous phase the latter was oxidized to the tetroxide by sodium *meta*-periodate which was used in excess. The rate of oxidation

depends on the acidity of the solution which should be kept between pH 3 and 5. This occasionally required addition of sodium bicarbonate. The tetroxide is soluble in the organic phase where oxidation to *1* takes place. The rate of oxidation was strongly dependent on the substituent on C-1; the phenyl groups retarded the rate to the extent that 3 days were required for completion and it is of interest to note that the aromatic ring was not oxidized to



3 *4* *5*

a R = H
b R = Me
c R = Ph

any detectable amount. To some degree, however, oxidation proceeded further to the acids *2* which were easily removed from the aldehydes by simple extraction with base. Oxidation of 1-isopropenyl-1-methyl-2,2-dibromocyclopropane (*4*) by this method was very slow affording the ketone *5* in 40 % yield together with much polymeric material; however, ketones like *5* are more conveniently prepared by reaction of the appropriate alkenone with bromoform and base under phase transfer conditions.[7]

Oxidation of *3a* according to method B was carried out by passing ozone-enriched oxygen into a solution of the substrate in methanol-methylene chloride at −78 °C. The peroxide formed was not isolated but reduced with methyl sulfide to the aldehyde *1a*. This method also worked very well for the oxidation of *4* to the ketone *5*. It should also be mentioned that the peroxide precursor of *1a* was reduced with sodium borohydride to the alcohol *6* in 78 % yield, while oxidation of the same peroxide with chromic trioxide in aqueous sulfuric acid–acetone (Jones reagent) gave the acid *2a* in 69 % yield. All yields from the ozonolysis reactions are based on the monoadducts.

Oxidation of the vinylcyclopropanes *3* with potassium permanganate in benzene using the phase transfer technique (method C)[8] afforded the acids *2* in good yields; the ketone *5* was also formed from 4 under these conditions but only in about 40 % yield and not easily separated from other products. Isolation of the organic material can be quite tedious due to the manganese dioxide present in the reaction mixture. We found that this problem was conveniently solved by adjusting the pH of the reaction mixture to < 2 and adding sufficient hydrazine sulfate until a clear aqueous phase resulted.

The alcohol *6* was also easily obtained from the aldehyde *1a* and the acid *2a* by reduction with sodium borohydride and diborane, respectively. This alcohol is not obtainable from allyl alcohol and dibromocarbene, although alcohols structurally related to *6* have been prepared in this way with good results.[9]

Experimental General. The spectral and gas chromatographic equipment used has been described previously.[10] The NMR data are given in δ values. Elemental analyses were carried out by Ilse Beetz Microanalytical Laboratory, 8640 Kronach, West-Germany.

General procedure for the oxidation of monoadducts 3 with ruthenium tetroxide. (Method A). Sodium *meta*-periodate (5.35 g, 25 mmol) was dissolved in 50 ml of water and the pH of the solution adjusted to 3–4 with the addition of $NaHCO_3$. A solution of *3* (6 mmol) in 50 ml of CCl_4 was added followed by ruthenium dioxide (10 mg, 0.75 mmol). The reaction mixture was stirred vigorously at 0 °C until all of *3* had reacted (GLC). The reaction was terminated with the addition of 1 ml 2-propanol, pH adjusted to 8–9, and the precipitated salt filtered. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phase was worked up in the usual way to give the aldehyde.

The aqueous layer was acidified with dilute H_2SO_4, and the carboxylic acids were isolated with ether in the usual way.

General procedure for the ozonolysis of the monoadducts 3 (Method B). Ozone enriched oxygen, obtained from a Welbach T 23 generator, was passed into an alcoholic solution of *3* kept at −78 °C until a faint blue colour persisted. Nitrogen was then swept into the solution until no ozone could be detected (KI test).

2,2-Dibromocyclopropylcarbaldehyde (1a). Method A. Oxidation of the monoadduct *3a*[11] required 6 h reaction time to give the aldehyde *1a* in 79 % yield, b.p. 56–57 °C/2 mmHg. IR (film): 2840 (w), 1720 (s), 1100 (m), 960 (m), 710 (m), 680 (m) cm^{-1}. ^1H NMR (CCl_4): 1.9–2.8 (3 H, m), 9.20 (1 H, d, *J* 4.5 Hz).

The 2,4-Dinitrophenylhydrazone (2,4-DNP) was formed in the usual way, m.p. 160 °C (ethanol-benzene). Anal. $C_{10}H_8Br_2N_4O_4$: C, H. From the aqueous solution the acid *2a* was isolated in 12 % yield. The reaction was performed on a 0.1 mol scale with the same result.

Method B. To the ozonolysis product from *3a* (33.9 g, 0.15 mol) in 50 ml of methanol and 150 ml CH_2Cl_2 was added dropwise methyl sulfide (18 ml, 0.25 mol) in 25 ml of CH_2Cl_2. The solution was allowed to slowly attain room temperature. Distillation of the residue gave 24.6 (72 %) of the aldehyde *1a*.

2,2-Dibromo-1-methylcyclopropylcarbaldehyde (1b). Oxidation of *3b*[4,12] according to method A required 14 h reaction time. The aldehyde *1b* was obtained in 86 % yield, b.p. 75–76 °C/6 mmHg. IR (film): 2980 (m), 1720 (s), 960 (m), 900 (m), 700 (m). ^1H NMR (CCl_4): 1.55 (3 H, s), 1.84 (1 H, d, J 8.0 Hz), 2.44 (1 H, d, J 8.0 Hz) 9.26 (1 H, s).

The 2,4-DNP was prepared in the usual way, m.p. 175 °C (ethanol-benzene): Anal. $C_{11}H_{10}Br_2N_4O_4$: C, H.

From the aqueous phase the acid *2b* was obtained in 3 % yield.

2,2-Dibromo-1-phenylcyclopropylcarbaldehyde (1c). Oxidation of *3c*[13] according to method A required 36 h reaction time. Crude aldehyde *1c* was obtained in 85 % yield. It was purified by chromatography. IR (film): 2840 (m), 1725 (s), 1460 (s), 1240 (s) 710 (s) cm^{-1}. ^1H NMR (CCl_4): 2.28 (1H, d, *J* 8.0 Hz), 2.74 (1H, d, *J* 8.0 Hz), 7.36 (5H, broad s), 9.54 (1H, s).

The 2,4-DNP was prepared in the usual way, m.p. 181 °C (ethanol-benzene). Anal. $C_{16}H_{12}Br_2N_4O_4$: C, H.

From the aqueous phase the acid *2c* was obtained in 8 % yield.

General procedure for the oxidation of mono-adducts 3 with potassium permanganate. (Method C). A mixture of *3* (6 mmol) in 30 ml of benzene and 3.95 g (25 mmol) of $KMnO_4$ in 60 ml of water was stirred vigorously with 0.2 g tetra-alkylammonium chloride at room temperature until all of the organic substrate had reacted (GLC). The reaction was terminated by the addition of 3 ml of a saturated aqueous solution of $NaHSO_3$. The pH was adjusted to 1 with dilute H_2SO_4, and hydrazine sulfate (2 g) was added in small portions until the reaction mixture was clear. Extraction with ether and isolation of acidic material in the usual way afforded almost pure acids.

2,2-Dibromocyclopropanecarboxylic acid (*2a*) was prepared in 75 % yield from *3a* according to method C with benzyl-triethylammonium chloride (TEBA) as catalyst and 1 h reaction time; m.p. 94–95 °C (hexane) (lit.[11] 94–95 °C).

The acid was also prepared in 69 % yield by oxidation of the ozonolysis product with CrO_3 (Jones reagent).[14]

2,2-Dibromo-1-methyl-1-carboxylic acid (2b) was prepared in 79 % yield from *3b* according to method C using TEBA as catalyst and 5 h reaction time; m.p. 110–112 °C (subl.) (lit.[5] 110–112.5 °C).

2,2-Dibromo-1-phenylcyclopropane-1-carboxylic acid (2c) was prepared in 70 % yield from *3c* according to method C using tetrabutylammonium bromide as catalyst and 3 days reaction time; m.p. 118–120 °C (subl.). Anal. $C_{10}H_8Br_2O_2$: C, H. IR (KBr): 3200 (m), 1720 (s), 1690 (m), 1240 (m), 1200 (s), 700 (m) cm^{-1}; ^1H NMR (CCl_4): 2.20 (1 H, d, *J* 7.5 Hz), 2.76 (1 H, d, *J* 7.5 Hz), 7.39 (5 H, m), 11.77 (1 H, s).

2,2-Dibromo-1-acetyl-1-methylcyclopropane (5). Method A. Oxidation of *4*[4] for 4 days gave a liquid in 46 % yield, b.p. 44–46 °C/0.6 mmHg, consisting mainly (85 %) of the desired ketone *5* contaminated with two lower-boiling impurities.

Method B. Ozonolysis of *4* followed by treatment with methyl sulfide as described for *1a* gave the ketone *5* in 88 % yield; b.p. 80–82 °C/6 mmHg (lit.[7] b.p. 75 °C/2 mmHg).

Method C. Oxidation of *4* for 50 h with tetrabutylammonium bromide as catalyst gave a neutral liquid in 44 % yield, b.p. 46–47 °C/0.6 mmHg, consisting mainly (85 %) of the ketone *5*. From the acidic fraction crude *2b* was obtained in 20 % yield.

2,2-Dibromocyclopropylmethanol (6). A. A solution of *3a* (6.78 g, 30 mmol) in 60 ml of ethanol was ozonized according to method B. The reaction mixture was transferred to a beaker which was cooled in ice. A solution of 2.50 g (66 mmol) of $NaBH_4$ in 5 ml of water containing a drop of 50 % NaOH was added dropwise with stirring. The stirring was continued overnight at 0 °C and 5 ml of acetone was added. Work-up in the usual manner gave 5.41 g (78 %) of the alcohol *6*, b.p. 58 °C/0.5 mmHg. Anal. $C_4H_6Br_2O$: C, H, IR (film): 3340 (s), 1110 (s), 1040 (s), 680 (s) cm^{-1}. ^1H NMR (CCl_4): 1.2–2.5 (3H, m), 3.78 (2H, m), 4.10 (1H, broad s).

B. Reduction of a solution of the acid *2a* in THF with diborane, prepared *in situ* from $NaBH_4$ and BF_3 gave 72 % of the alcohol *6*. Reduction of the aldehyde *1a* with $NaBH_4$ at 0 °C in the usual way gave the alcohol *b* in 57 % yield.

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