Short Communication

A Novel Alkoxycyclopropene Ring-Opening Reaction

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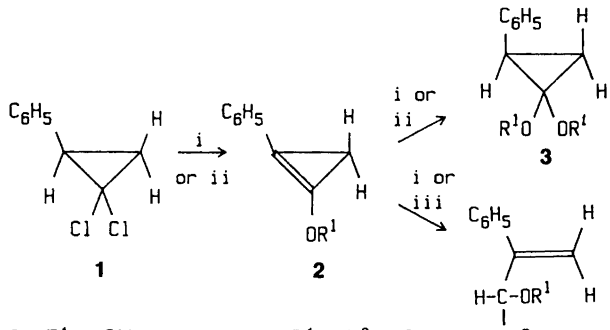
In an attempt to elucidate the reaction sequences involved in the synthesis of atropaldehyde diethylacetal[1] (see Fig. 1), the 1-alkoxy-2-phenylcyclopropenes **2a–2c** were prepared and a novel ring-opening reaction of these labile[2] compounds studied. 1,1-Dichloro-2-phenylcyclopropane (**1**) and sodium alkoxide in *N,N*-dimethylformamide (DMF) (conditions ii in Fig. 1) gave via elimination–addition–elimination reactions[3] the cyclopropenes **2**. Purification was not accomplished: both fractional distillation and chromatography resulted in decomposition, and attempts to induce crystallization failed. Reaction of **2** with alkanols gave the corresponding acetals **4**. This novel ring opening reaction is not catalyzed by alkoxide (see Experimental), but apparently the two reactions (**2**→**3** and **2**→**4**) compete when both alcohol and alkoxide are present, as in the synthesis of atropaldehyde diethylacetal (conditions i in Fig. 1). This observation probably also accounts for the by-product observed[4] in the standard preparation of **3a**.[3a] Formation of **4** was not observed when the reaction was performed in DMF (conditions ii) and neither was any of the ketal **3** formed in the absence of alkoxide (conditions iii).

Reactions in methanol deserve a special comment: a small (ca. 1 mole %) amount of sodium methoxide must be added to ensure reproducible results in the reaction of **2**→**4a** or **4d**, and also to avoid the conversion of the acetal **4d** into the corresponding dimethylacetal **4a**. The methoxide concentration is too low to give any measurable ketal formation (reaction **2**→**3**) and has, as already mentioned, no catalytic effect on the reaction **2**→**4**. The reactions in ethanol and in



2a: $R^1 = CH_3$
2b: $R^1 = C_2H_5$
2c: $R^1 = i\text{-}C_3H_7$

3a, 4a: $R^1 = R^2 = CH_3$
3b, 4b: $R^1 = R^2 = C_2H_5$
3c, 4c: $R^1 = R^2 = i\text{-}C_3H_7$
4d: $R^1 = CH_3$, $R^2 = C_2H_5$

Fig. 1. Reactions **1** to **2a**, **2b** or **2c** involve eliminations, additions and eliminations. Conditions: i: NaOH + R^1OH; ii: $NaOR^1$ in DMF; iii: R^2OH.

2-propanol could be run without encountering the problems mentioned for methanol. No evidence (kinetic data) as to the mechanisms involved in the ring opening of **2** is available. In the case of heavily substituted 1-alkylthiocyclopropenes, a vinylcarbene is suggested to be an intermediate in similar ring opening reactions.[5]

Experimental

Mass spectra were recorded on a VG Micromass 7070 F instrument (IP 70 eV) and NMR spectra on Bruker WH-90, HXE-90, and AM 500 instruments (solvent: $CDCl_3$). A "Mimer" program was used for NMR simulations. ^1H NMR spectra were recorded at 90 MHz unless otherwise stated.

1-Alkoxy-2-phenylcyclopropenes (**2**), *general.* To a solution of the appropriate sodium alkoxide (0.4 mol) in the smallest possible volume of alkanol was added DMF (60 ml) and the mixture was distilled (water bath) until the vapour temperature reached ca. 35 °C/15 mmHg. More DMF (30 ml) and finally **1**[1] (18.6 g, 0.1 mol) were added. The suspension was flushed with N_2 (for reaction times and temperatures, see below). Ice and water were added, and the aqueous phase was extracted with light petroleum and the combined extracts were washed with water, dried with potassium carbonate and concentrated *in vacuo*. The crude products were identified on the basis of their ^1H NMR spectra.

1-Methoxy-2-phenylcyclopropene (**2a**). Reaction of **1** for 50 min at −(25–20) °C gave 13 % conversion. Less than 1 % of **3a** was observed. ^1H NMR: δ 1.90 (2H, s), 4.03 (3H, s). Reaction for a further 3 h at −15 °C gave approximately equimolar amounts of **2a**, **3a** and **1**. Reaction for 22 h at −15 °C gave **3a**.[3a] ^1H NMR: δ 1.33, 1.44, 2.38 (3H, ABX, J_{AB} −6.2 Hz, $J_{AX} = J_{trans}$ 7.5 Hz, $J_{BX} = J_{cis}$ 10.5 Hz), 3.17 (3H, s), 3.40 (3H, s), 7.20 (5H, s).[3a,3d] No **4a** was observed. Reaction of **2a** (200 mg of crude product, see above) with MeOH (5 ml; ca. 10 μmol of sodium methoxide was added, see below) in an evacuated ampoule for 1 h at 58–62 °C gave ca. 16 % of acetal **4a**, identified by the slightly split resonances at δ 5.10, 5.50 and 5.56, and ca. 13 % of unreacted cyclopropene **2a**. For comparison, crude **4a** was prepared by heating **4b** (47 g) in MeOH (290 ml) under reflux for 1 h. Removal of solvents *in vacuo* gave 42 g of an oil, the ^1H NMR spectrum of which revealed the three resonances mentioned above.

1-Ethoxy-2-phenylcyclopropene (**2b**). Treatment of **1** for 30 min at −20 °C gave 14.8 g of crude product consisting of 64 % **2b**, 10 % **3b**, 8 % starting material and 20 % of an assumed polymer (^1H NMR; the latter was estimated by integration of aromatic proton signals relative to those for alkoxy and cyclopropyl protons). No atropaldehyde diethyl acetal (**4b**)[1] was observed. ^1H NMR: δ 1.42 (t, *J* 7 Hz), 1.88 (2H, s). 4.32 (2H, q, *J* 7 Hz), 7.12–7.36 (m). ^{13}C NMR: δ 15.2 (C3 and CH_3), 69.9 (OCH_2), 76.5 (C2), 125.7 (phenyl, *p*), 127.3, 128.3 (phenyl, *o/m*), 129.2, 131.5 (C1/phenyl, *t*). The cyclopropene is labile. Attempted fractionation by distillation, or keeping the crude product at 20 °C overnight, gave unidentified compounds or polymers. Reaction of **2b** with sodium ethoxide in DMF (as in the preparation of **2b**, above) for 1 h at 20 °C gave the crude diethoxy ketal **3b**.[1] ^1H NMR: δ 1.32, 1.42, 2.38 (3H, ABX, J_{AB} −6.2 Hz, $J_{trans} = J_{AX}$ 7.5 Hz, $J_{cis} = J_{BX}$ 10.5 Hz), 1.00 (3H, t, *J* 7.0 Hz), 1.23 (3H, t, *J* 7.0 Hz), 3.07–3.42 (1H, m), 3.42–3.84 (3H, m), 7.16 (5H, s). The same compound was prepared (crude) by removing the solvent from the filtrates after crystallization of atropaldehyde, as described in Ref. 1; b.p. 80–85 °C/0.5 mmHg. Reactions of **2b** (200 mg) with MeOH (5 ml; ca. 10 μmol of sodium methoxide was added) or with EtOH (5 ml) were carried out in evacuated ampoules at 58–62 °C for 1 h. Removal of the solvent *in vacuo* gave the crude acetals **4d** and **4b**,[1] respectively. The reaction with methanol was erratic if no sodium methoxide was added, and any atropaldehyde diethyl acetal formed was converted to the dimethyl acetal in neutral methanol, as described above. Addition of ca. 100 μmol of sodium methoxide gave the same reaction rate. Sodium ethoxide did not catalyze the reaction of **2b** with ethanol. Acetal **4d** was identified by its conversion to atropaldehyde[1] and by ^1H NMR: δ 1.21 (3H, t, *J* 7.0 Hz), 3.30 (3H, s), 3.42–3.74 (2H, m), 5.17 (1H, broad s), 5.50–5.58 (2H, m), 7.12–7.58 (5H, m). Integrations were approximate, owing to the presence of impurities.

1-Isopropoxy-2-phenylcyclopropene (**2c**). Reac-

tion of **1** for 15 min at −(23–20) °C gave light brown, crude **2c** (6.30 g), containing 30 % impurities (polymers?) as estimated by integration of the isopropyl proton signals relative to those for the phenyl protons. MS [*m/z* (% rel. int.)]: 174 (15, *M*), 132 (7), 131 (15), 103 (100), 77 (20). ^{1}H NMR: δ 1.50 (6H, d, *J* 6.3 Hz), 1.86 (2H, s), 4.59 (1H, septet, *J* 6.3 Hz), 7.12–7.44 (phenyl, *m*). Neither **1** nor **3c** was observed (^{1}H NMR). ^{13}C NMR: δ 14.8 (CH_2). 22.5 (CH_3), 75.6 (C2), 77.4 (CH), 125.6 (phenyl, *p*), 127.4, 128.4 (phenyl, *o/m*), 129.6, 130.8 (phenyl, *t*/C1). IR (neat): 1590 (m), 1850–1875 (vs), 2860, 2940, 2980 (s), 3020, 3040, 3060 (m) cm^{-1}. When a sample was allowed to polymerize (20 °C, 20 h) the absorption at 1850–1875 cm^{-1} disappeared. The reaction of **2c** with sodium isopropoxide to give **3c** was carried out by changing the conditions used in the preparation of **2c** (above) to 24 h and 3–5 °C. Yield 2.93 g (62 %) from 3.74 g of **1**; b.p. 75–85 °C/0.3 mmHg. Found: C 76.13; H 9.19. Calc. for $C_{15}H_{22}O_2$: C 76.9; H 9.4. MS [*m/z* (% rel. int.)]: 234 (0.5, *M*), 192 (13, $M - C_3H_6$), 150 (61, $M - 2\ C_3H_6$), 132 (27), 104 (79), 91 (60), 43 (100). ^{1}H NMR: δ 1.01, 1.14, 1.21, 1.22 (12H, 4d, *J* 6.3 Hz), 1.34, 1.46, 2.36 (3H, ABX, J_{AB} −6.0 Hz, $J_{trans} = J_{AX}$ 7.0 Hz, $J_{cis} = J_{BX}$ 10.6 Hz), 3.84, 4.18 (2H, 2 septets, *J* 6.3 Hz), 7.00–7.38 (5H, m). ^{13}C NMR: 19.1 (C3), 23.0–23.3 (4 CH_3), 30.9 (C2), 68.7, 70.6 (2 OCH), 90.5 (C1), 125.6 (phenyl, *p*), 127.6, 127.7 (phenyl, *o/m*), 137.8 (phenyl, *t*).

Atropaldehyde diisopropyl acetal (**4c**). Cyclopropene **2c** (210 mg) and 2-propanol were heated in an evacuated ampoule. A reaction time of 1 h (5h) at 60–62 °C gave 40 % (7 %) unreacted **2c**. 30 % (39 %) acetal and 30 % (54 %) polymer, estimated by ^{1}H NMR (see data below). The ketal **3c** was not observed. The acetal was also prepared in analogy with a published procedure,[1] in yields of 25–30 %, and by heating **1** (28.0 g) in a solution of sodium isopropoxide in 2-propanol (9.2 g of sodium in 150 ml of propanol-2) under reflux for 9 h. Yield 14.0 g (42 %), b.p. 70–75 °C/0.3 mmHg. Anal. $C_{15}H_{22}O_2$: C, H. ^{1}H NMR: δ 1.12 (6H, d, *J* 6.1 Hz), 1.19 (6H, d, *J* 6.1 Hz), 3.89 (2H, septet, *J* 6.1 Hz), 5.27 (1H, s), 5.50 (2H, s), 7.12–7.36 (3H, m), 7.44 (2H, m). ^{13}C NMR: 22.2, 22.7 (CH_3), 67.8 (2 OCH), 99.5 (unsubst. vinyl), 115.0 (CH $(OR)_2$), 126.8, 127.2, 128.8, 138.3 (aromatic), 146.2 (disubst. vinyl).

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