182. The Preparation of Optically Pure 7-Oxabicyclo[2.2.1]hept-2-ene Derivatives. The CD Spectrum of (+)-(1*R*)-7-Oxabicyclo[2.2.1]hept-5-en-2-one

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Dedicated to Prof. *Ch. Tamm* on the occasion of his 60th birthday

(12.4.83)

Summary

(–)-1-Camphanoyloxyacrylonitrile (=(–)-1-cyanovinyl camphanate; **1**) obtained from the commercially available (–)-camphanoyl chloride and 2-oxopropiononitrile added to furan at 20° in the presence of $Cu(BF_4)_2 \cdot 6\,H_2O$ or ZnI_2 and gave a mixture of 2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl camphanates (**2**–**5**) from which isomer **5** could be obtained pure by crystallization. The latter was transformed into (+)-(1*R*)-7-oxabicyclo[2.2.1]hept-5-en-2-one (**6**) in high yield and optical purity. Adducts **2**-**4** were recycled into **1** + furan by heating in toluene, and (–)-camphanic acid was recovered after saponification of **5**. The absolute configuration of **6** was deduced from its CD spectrum which showed two 1200-cm^{-1} *Franck-Condon* series for its $n \rightarrow \pi^*_{CO}$ transition.

Introduction. – Differently substituted 7-oxabicyclo[2.2.1]heptanes have been used as starting materials in the syntheses of anthracyclines [1], nucleosides [2], muscarine derivatives [3], prostaglandines [4], antibiotics [5], and other products of biological interest [6]. This bicyclic framework is available through the *Diels-Alder* addition of furans to strongly activated dienophiles [7], and these often sluggish cycloadditions can be accelerated by applying very high pressure [8] or, more simply, by adding catalytic amounts of Cu(I)-, Cu(II)- [9] or Zn(II)-salts [10]. Optically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives should have a particularly promising future in the synthesis of natural products and compounds of biological interest such as nucleosides [11] and cyclitols [10a], because the stereo- and regioselectivity of electrophilic additions to their C,C double bond can be directed by modifying the nature of the substituents at C(2) [12][1]. We report now

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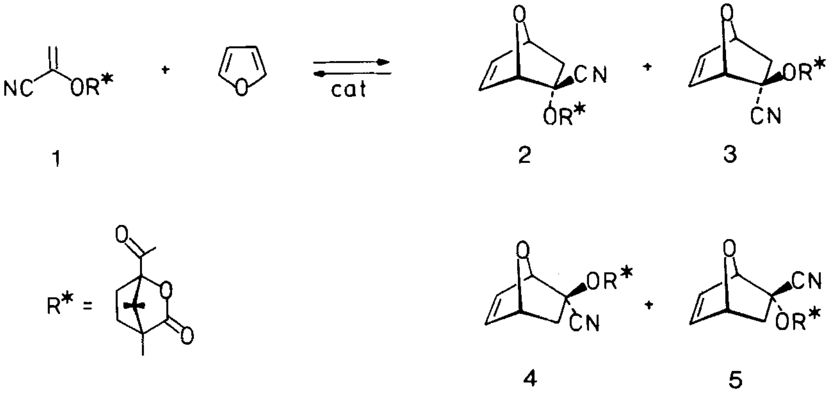
[1] Benzeneselenyl and arenesulfenyl halides add to 2-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl acetate with high stereo- and regioselectivity. In the corresponding adducts, the electrophile substitutes the *exo*-position of C(6) and the halide the *endo*-position of C(5). In contrast, the additions to 7-oxabicyclo[2.2.1]hept-5-en-2-one give adducts where the electrophile substituent is in *exo*-position of C(5) [13].

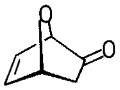
preliminary results concerning the preparation of such optically active bicyclic systems, which might become advantageous synthetic intermediates by providing a possible alternative to carbohydrate derivatives in the asymmetric synthesis of natural products [14].

Results and Discussion. – Furan adds to α-acetoxyacrylonitrile (= 1-cyanovinyl acetate) at 20° in the presence of catalytical amounts of $Cu(BF_4)_2 \cdot 2\,H_2O$ [9]. The cycloaddition can also be catalyzed with $ZnCl_2$, $ZnBr_2$ or ZnI_2 [13]; the latter catalyst gives the smallest amount of side-products and does not require the presence of a protic acid scavenger such as propene oxide [9]. Under the same conditions, furan added to the new dienophile **1**, prepared by *O*-acylation of oxopropiononitrile with (–)-camphanoyl chloride following *Oku*'s technique [15] (benzene/pyridine, 20°, 24 h), and gave a mixture of adducts **2-5** (92% yield; 20°, 4 days, 1 equiv. of **1**, 4 equiv. of furan and 0.5 equiv. of ZnI_2).



The ratio between the pairs of *exo*- and *endo*-cyano isomers (**2**+**5** *vs.* **3**+**4**) was *ca.* 80:20 when the catalyzed *Diels-Alder* reaction was carried out between 0° and 30 °C. When a 1:10:0.1 mixture of **1**, furan, and ZnI_2 was heated at 60 °C for one day in a sealed pyrex tube, an equilibrium mixture of starting materials and cycloadducts was obtained which contained a 58–60% yield of cycloadducts **2**–**5**, and the ratio of **2**+**5** to **3**+**4** was approximately 65:35. When the same mixture of starting materials was heated to 80 °C, equilibrium was reached after a few hours (adducts **2**–**5** produced in *ca.* 50% yield), and the ratio of **2**+**5** to **3**+**4** was about 55:45 (by ^{1}H-NMR spectroscopy).

Three successive recrystallizations from AcOEt/hexane of the adduct mixture obtained at 20 °C furnished isomer **5** (the more polar one by HPLC), 98% pure (by 360-^{1}H-NMR analysis of the CH_3-signals and by HPLC), in 29% yield (based on dienophile **1**). The other isomers **2**–**4** were decomposed almost quantitatively into furan and **1** (which can be recycled to generate more **5**) by heating at reflux in toluene. Saponification of **5** followed by treatment with formalin (40% H_2CO in water) afforded optically active (+)-(1*R*)-7-oxabicyclo[2.2.1]hept-5-en-2-one (**6**, 96%) and (–)-camphanic acid (76%) which can be recycled into **1**.



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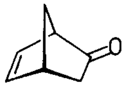

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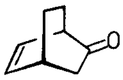

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The distinction between *exo*- and *endo*-cyano derivatives **2**+**5** and **3**+**4**, respectively, was based on the 360-MHz-^{1}H-NMR spectra, and by comparison of these spectra with those of analogous 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives [9]. It must be considered as tentative. The absolute configuration of **6** was based on its circular dichroism (CD) spectrum (*cf. Fig. 1b*) and by comparison with those of (+)-(1*R*)-bicyclo[2.2.1]hept-5-en-2-one (**7**) [16] and (+)-(1*R*)-bicyclo-[2.2.2]oct-5-en-2-one (**8**) [17]. As expected for β,γ-enones [18-20], a relatively strong, positive *Cotton* effect is measured for the carbonyl $n \rightarrow \pi^*_{CO}$ transition at 312 nm ($\Delta\varepsilon$ + 13.2, isooctane). As for the analogs **7** ($\Delta\varepsilon_{214}$) and **8** ($\Delta\varepsilon_{213}$) [16] [17], another positive *Cotton* effect is also observed at 205 nm ($\Delta\varepsilon$ + 20.8, isooctane) for a transition assigned to a 'charge-transfer' band between the homoconjugated

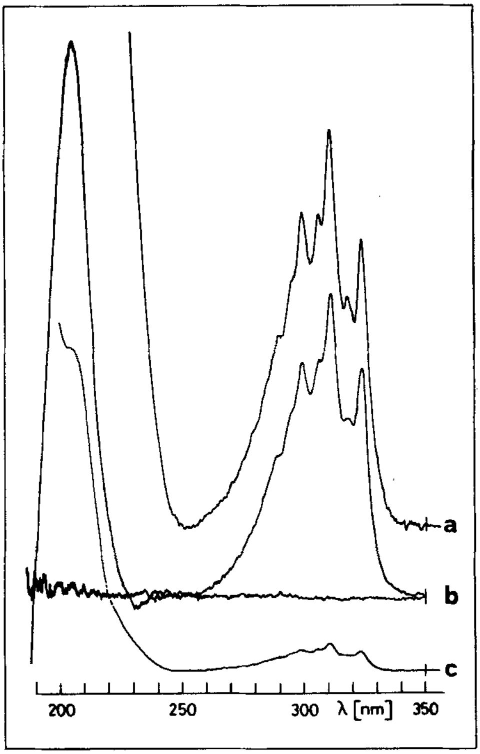

Figure. a and c: *Gas Phase UV Absorption Spectra of* **6**; b: *Gas Phase CD Spectrum of (+)-***6** *with Experimental Base-line* carbonyl and ethylene chromophores [17a] [19]2). The latter transition is already apparent in the UV absorption spectrum of **6** *(Fig. 1c)*.

Between 250 and 350 nm, the CD and UV spectra of **6** differ slightly from those of **7** [16] and **8** [17]: the *Franck-Condon* contour of the $n \rightarrow \pi^*_{CO}$ band of **6** reveals two 1200-cm^{-1} series. The first consists of conspicuous peaks, the second of 'bumps' and shoulders which are perceptible inbetween *(Fig. 1)*. This observation can be ascribed to the double minima potential of the $^1n,\pi^*_{CO}$ state. This is due to the C=O-bond stretching and bending, *i.e.*, the nuclear configuration around the C-atom of the carbonyl group is no longer planar, but rather pyramidal [22]. Because of the non-symmetrical environment of the β,γ-enone **6**, the double-minima energy well of the excited state is no longer degenerate3) [16]. Some other vibration may also be involved and made responsible of the double vibronic series observed4).

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Experimental Part

General Remarks. See [23]. UV absorption spectra were recorded on a *Perkin-Elmer-Hitachi 340* spectrometer, the CD spectra on a *JASCO J500-C* dichrograph (λ_{max} ($\Delta\varepsilon$) in nm), and the specific rotations on a *Perkin-Elmer 241* polarimeter. None of the procedures given below has been optimized.

(–)-1-Cyanovinyl Camphanate (**1**). (–)-Camphanoyl chloride (21.7 g, 0.1 mol, *Fluka*) and 2-oxopropiononitrile (8.53 ml, 0.12 mol) were mixed in anh. benzene (50 ml). After cooling to 0°, 4M anh. pyridine in benzene (36 ml) was added dropwise under stirring and under N_2. After stirring at 20° for 24 h, the mixture was filtered through silica gel (40 g, washing with $CHCl_3$) and washed with sat. aq. $CuSO_4$ (100 ml, 3 times) and then with H_2O (100 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated *i.v.* yielding 20.7 g (83%) of **1**, white solid, m.p. 99–101°; $[\alpha]^{25}_{589} = -14.1$, $[\alpha]^{25}_{578} = -14.8$, $[\alpha]^{25}_{546} = -17.0$, $[\alpha]^{25}_{436} = -30.6$, $[\alpha]^{25}_{365} = -52.2$ ($c = 17.1$ mg/ml, CH_2Cl_2). UV (dioxane): final absorption $\varepsilon_{212} = 5440$. IR (KBr): 3150, 3060, 3010, 2980, 2245, 1800, 1775, 1645, 1100, 1055. ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.91, 5.77 (2 *d*, $J_{gem} = 4$, 2 H); 2.8–1.5 (*m*, 4 H); 1.17, 1.12, 1.06 (3 *s*, 9 H). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 176.9, 164.5 (2 *s*); 126.8 (*s*); 120.0 (*t*, $^1J_{C,H} = 171$); 112.4 (*s*); 89.9 (*s*); 54.9, 54.7 (2 *s*); 30.6, 28.6 (2 *t*, $^1J_{C,H} = 139$); 16.4, 16.4, 9.4 (3 *q*, $^1J_{C,H} = 130$). MS (70 eV): 249 (0.6, M^+), 248 (2.2), 221 (23), 181 (32), 153 (4.4), 83 (100).

$C_{13}H_{15}NO_4$ (249.27) Calc. C 62.64 H 6.07% Found C 62.36 H 6.01%

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2) This contrasts with 5,6-dimethylidene-2-bicyclo[2.2.1]heptanone [21], 5,6-dimethylidene-2-bicyclo-[2.2.2]octanone [17a] and many other β,γ-enones [19] for which the rotational strengths of the $n \rightarrow \pi^*_{CO}$ and charge-transfer bands were found to have opposite signs. The similarity of the CD spectra of **6–8** suggest that the ethereal bridge O(7) in **6** plays no significant role on the chiroptical properties of this β,γ-unsaturated ketone. If there should be a charge-transfer transition involving the oxygen bridge and the carbonyl or/and the olefinic functions, it is not visible.

3) The well-defined *Franck-Condon* contour of the two vibronic series observed between 250 and 350 nm as well as the similarity of the UV and CD spectra measured in the gas-phase and in isooctane make it difficult to attribute one of these series to a charge-transfer $n(O(7)) \rightarrow \pi^*_{CO}$ or $n(O(7)) \rightarrow \pi^*_{CC}$ transition.

4) We thank the referee for the latter suggestion.

2-Cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl Camphanates (**2**–**5**). To a solution of **1** (498 mg, 2 mmol) in furan (0.58 ml, 8 mmol), ZnI_2 (319 mg, 1 mmol) was added, and the mixture was stirred at 20° for 4 days. The mixture was filtered through silica gel (10 g, $CHCl_3$) and washed with H_2O (30 ml, 3 times). After drying ($MgSO_4$), the solvent was evaporated *i.v.* yielding a mixture of **1**–**5** containing a 92-93% yield of the adducts **2**-**5** (*ca.* 45:5:5:45) which were separated by HPLC (*Dupont, Zorbax-sil,* length 25 cm, diameter 21.2 mm, AcOEt/hexane 1:3 (*v/v*), 13-14 ml/min). Characteristics of **2**: m.p. 135.5-136°. $[\alpha]^{25}_{589} = -97.5$, $[\alpha]^{25}_{578} = -102.1$, $[\alpha]^{25}_{546} = -117.4$, $[\alpha]^{25}_{436} = -212.8$, $[\alpha]^{25}_{365} = -364.8$ ($c = 16.7$ mg/mol, CH_2Cl_2). IR ($CHCl_3$): 3040, 2980, 2940, 2250, 1800, 1750, 1100, 1060. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.71, 6.24 (2 *dd*, $J = 6.0$, 2.0, 2 H); 5.66 (*d*, $J = 2$, 1 H, H–C(1)); 5.18 (*dd*, $J = 5.0$, 2.0, 1 H, H–C(4)); 2.81 (*dd*, $J_{gem} = 13$, $J = 5.0$, 1 H, H_{exo}–C(3)); 2.49-2.36 (*m*, 1 H); 2.08-1.90 (*m*, 1 H); 1.84 (*d*, $J_{gem} = 13$, 1 H, H_{endo}–C(3)); 1.76-1.65 (*m*, 1 H); 1.12, 1.06, 0.96 (3 *s*, 9 H). MS (CI, CH_4): 318 (1.5, $M^+ + 1$), 290 (2.3), 278 (10), 271 (2), 250 (20), 205 (21), 181 (20), 153 (100), 68 (65).

$C_{17}H_{19}NO_5$ (317.34) Calc. C 64.34 H 6.03% Found C 64.66 H 6.21%

Characteristics of **3**: m.p. 150.5-151°. $[\alpha]^{25}_{589} = -38.7$, $[\alpha]^{25}_{578} = -40.5$, $[\alpha]^{25}_{546} = -46.5$, $[\alpha]^{25}_{436} = -83.9$, $[\alpha]^{25}_{365} = -142.8$ ($c = 7.3$ mg/ml, CH_2Cl_2). IR ($CHCl_3$): 3040, 2980, 2940, 2245, 1800, 1750, 1100, 1058. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.76, 6.53 (2 *dd*, $J = 6.0$, 2.0, 2 H); 5.36 (*d*, $J = 2.0$, 1 H, H–C(1)); 5.20 (*dd*, $J = 5.0$, 2.0, 1 H, H–C(4)); 2.53-2.41 (*m*, 1 H); 2.36 (*d*, $J = 13$, 1 H, H_{endo}–C(3)); 2.29 (*dd*, $J = 13.0$, 5.0, 1 H, H_{exo}–C(3)); 2.16-2.04 (*m*, 1 H); 2.01-1.91 (*m*, 1 H); 1.79-1.67 (*m*, 1 H); 1.13, 1.08, 1.00 (3 *s*, 9 H). MS (CI, CH_4): 318 (2.3, $M^+ + 1$), 290 (8), 278 (44), 250 (43), 205 (39), 181 (31), 153 (100), 68 (36).

$C_{17}H_{19}NO_5$ (317.34) Calc. C 64.34 H 6.03% Found C 64.44 H 5.85%

Characteristics of **4**: m.p. 153.5-154°. $[\alpha]^{25}_{589} = +12.9$, $[\alpha]^{25}_{578} = +13.6$, $[\alpha]^{25}_{546} = +15.9$, $[\alpha]^{25}_{436} = +29.1$, $[\alpha]^{25}_{365} = +50.6$ ($c = 9.3$ mg/ml, CH_2Cl_2). IR ($CHCl_3$): 3040, 2980, 2940, 2245, 1800, 1750, 1100, 1058. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.76, 6.53 (2 *dd*, $J = 6.0$, 2.0, 2 H); 5.37 (*d*, $J = 2.0$, 1 H, H–C(1)); 5.20 (*dd*, $J = 5.0$, 2.0, 1 H, H–C(4)); 2.53-2.41 (*m*, 1 H); 2.36 (*d*, $J_{gem} = 13.0$, 1 H, H_{endo}–C(3)); 2.28 (*dd*, $J = 13.0$, 5.0, 1 H, H_{exo}–C(3)); 2.16-2.04 (*m*, 1 H); 2.01-1.91 (*m*, 1 H); 1.79-1.67 (*m*, 1 H); 1.13, 1.09, 1.00 (3 *s*, 9 H). MS (CI, CH_4): 318 (1.5, $M^+ + 1$), 290 (2), 278 (9), 271 (3), 250 (15), 205 (19), 181 (20), 153 (100), 68 (48).

$C_{17}H_{19}NO_5$ (317.34) Calc. C 64.34 H 6.03% Found C 64.30 H 5.90%

Characteristics of **5**: m.p. 155-156°. $[\alpha]^{25}_{589} = +78.1$, $[\alpha]^{25}_{578} = +81.7$, $[\alpha]^{25}_{546} = +93.9$, $[\alpha]^{25}_{436} = +169.5$, $[\alpha]^{25}_{365} = +288.9$ ($c = 16.3$ mg/ml, CH_2Cl_2). UV (dioxane): final absorption, $\varepsilon_{212} = 1250$. IR ($CHCl_3$): 3040, 2980, 2940, 2250, 1800, 1750, 1100, 1062. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.69, 6.25 (2 *dd*, $J = 6.0$, 2.0, 2 H); 5.57 (*d*, $J = 2.0$, 1 H, H–C(1)); 5.18 (*dd*, $J = 5.0$, 2.0, 1 H, H–C(4)); 2.82 (*dd*, $J = 13.0$, 5.0, 1 H, H_{exo}–C(3)); 2.43-2.33 (*m*, 1 H); 2.10-1.89 (*m*, 2 H); 1.82 (*d*, $J = 13.0$, 1 H, H_{endo}–C(3)); 1.76-1.64 (*m*, 1 H); 1.12, 1.07, 0.98 (3 *s*, 9 H). MS (CI, CH_4): 318 (1.7, $M^+ + 1$), 290 (2.5), 278 (8), 271 (3), 250 (12), 205 (17), 181 (20), 153 (100), 68 (50).

$C_{17}H_{19}NO_5$ (317.34) Calc. C 64.34 H 6.03% Found C 64.58 H 6.06%

*(+)-(1*R*)-7-Oxabicyclo[2.2.1]hept-5-en-2-one* (**6**). The mixture of camphanates **1**–**5** obtained above (1 g) was dissolved in AcOEt (15 ml). Hexane (35 ml) was added at 20°, and the mixture was allowed to stand at 20° for 1 h. Hexane (10 ml) was added and the mixture allowed to stand at 20° for ½ h. After 3 more additions of hexane (10 ml), 0.442 g of crystalline solid of which 80% was **5**, was isolated by filtration and washed with ether/pentane 1:1. The above recrystallization procedure was repeated with this product using 45% of the above amounts of solvents. This yielded 0.39 g of **5** (*ca.* 90% diastereoisomerically pure). A third recrystallization afforded 0.314 g (29% based on **1**) of **5**, (98% diastereoisomerically pure, as determined by 360-MHz-^{1}H-NMR). In a 100-ml flask, **5** (1.19 g, 3.75 mmol; $[\alpha]_D = +77.1$, 98% optical purity) was dissolved in THF/H_2O 1:1 (18 ml), and 1N KOH in H_2O (8 ml) was added. The mixture was stirred at 20° for 30 min and then formaline (40% H_2CO in H_2O, 25 ml) was added. After stirring at 20° for 10 min, the mixture was extracted with CH_2Cl_2 (80 ml, 4 times). The org. extract was washed with H_2O (35 ml, 2 times). After drying ($MgSO_4$), the solvent was eliminated by distillation (*Vigreux* column). The residue was distilled at 80°/10 Torr in a *Hickmann* apparatus yielding 396 mg (96%) of **6**. $[\alpha]^{25}_{589} = +859.9$, $[\alpha]^{25}_{578} = +909.0$,

$[\alpha]_{546}^{25} = +1080.8$, $[\alpha]_{436}^{25} = +2436.2$, $[\alpha]_{365}^{25} = +6564.6$ ($c = 23.8$ mg/ml, CH_2Cl_2)[5]). CD (isooctane): 312 (+13.2), 205 (+20.8). CD (95% EtOH): 310 (+12.1), 205 (+13.7); s. *Figure 1B* for the gas-phase CD spectrum[5]). The other spectral data are identical to those reported for the racemic ketone [9].

$C_6H_6O_2$ (110.11) Calc. C 65.45 H 5.49% Found C 65.32 H 5.38%

Saponification of **2** and **4** (isolated by HPLC) gave (–)-**6** and (+)-**6**, respectively.

Recovering of (–)-Camphanic Acid. The aq. phase obtained above was acidified with conc. HCl and then extracted with CH_2Cl_2 (25 ml, 2 times). The org. phase was washed with sat. aq. NaCl (50 ml, 4 times), dried ($MgSO_4$), and evaporated *i.v.* The solid residue was recrystallized from AcOEt/hexane and yielded 565 mg (76%) of (–)-camphanic acid, m.p. 198–199°.

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