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SYNTHESIS OF OPTICALLY ACTIVE "DEWAR" BENZENES, III [1]

DERIVATIVES AND CD SPECTRA

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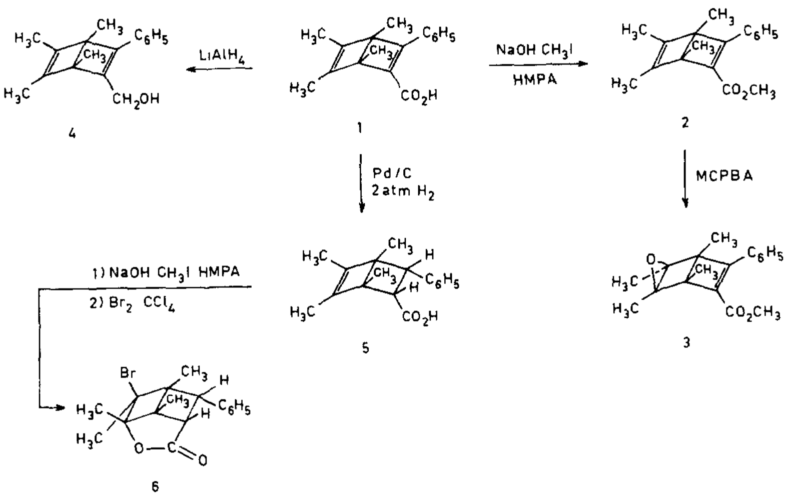
Recently we reported the synthesis of optically active 1 [1] In the CD spectrum of (-) 1[2] (figure 1) four optically active transitions at 345, 282, 250 and 218 nm are recognized In order to assign these transitions, 5 new compounds (all optically active) were prepared (scheme 1)

Synthesis of these compounds

The epoxide 3 (mp 100-102°, $|\alpha|_{578}^{20}$ - 4 0°, c 0 5)[3] is obtained in 82% yield when a solution of 2[1] ($|\alpha|_{578}^{20}$ - 29 0°, c 0 59) in benzene is treated at 0° with m-chloroperbenzoic acid Pure 3 is obtained by low-temperature recrystallization from n-hexane When a solution of 1 ($|\alpha|_{578}^{20}$ - 95 8°, c 0 48) in pentane/ether 10 1 is treated with 5% Pd on carbon at 2 atm hydrogen pressure, the 2-3 double bond in 1 is selectively reduced, furnishing 5 (mp 152 5-153 5°, $|\alpha|_{578}^{20}$ - 48 0°, c 0.37) in 90% yield The exo-position of the introduced hydrogen atoms was demonstrated spectroscopically by the high field position of the 5C-CH_3 absorption in the ^{1}HNMR (table 1) and chemically by the conversion of 5 into the bromolactone 6 (decomp > 110°, IR CO 1755 cm^{-1}) This last compound is obtained by treating a CCl_4/benzene 3 2 solution of 5 with an equimolar quantity of bromine in CCl_4 during 48 hr at -10° The yield is 75% The alcohol 4 (colorless oil, $|\alpha|_{578}^{20}$ - 40 5°, c 0 37) is obtained in 90% yield by treating 1 ($|\alpha|_{578}^{20}$ - 73 8°, c 0 42) with $LiAlH_4$ in ether, followed by a basic work-up of the reaction mixture When a equimolar mixture of the complex 7 and methyl tetrolate is treated at 0-5° with DMSO, the ester 8 is obtained in 90% yield (scheme 2) Hydrolysis furnished the acid 9 (mp 142-143°) in 80% yield Resolution of 9 was achieved via the brucine salt The highest observed specific rotation of resolved 9 was $|\alpha|_{578}^{20}$ - 36 2° (c 0 29), which corresponds with an optical purity[4] of 40 ± 5% The UV and CD spectra of the new compounds are drawn in figure 1, and the ^{1}HNMR data collected in table 1 scheme 1



scheme 2

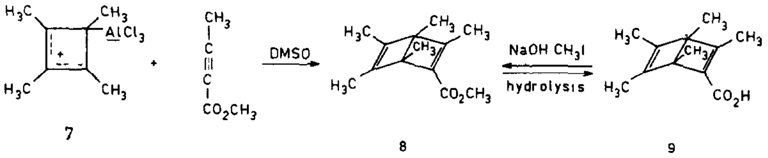


table 1 ^{1}HNMR data, CCl_4 solutions, chemical shifts in δ values

3	3H(s) 1 19, 3H(s) 1 23, 3H(s) 1 39, 3H(s) 1 40, 3H(s) 3 67, 3H(m) 7.32, 2H(m) 7 92
4	3H(s) 1 22, 3H(s) 1 26, 3H(q) 1 61 and 3H(q) 1 69 $J_{1\ 2}$ = 1 cps, 1H (broad s) 2 61, 1H(d) 4 17 and 1H(d) 4 47 $J_{1\ 2}$ = 14 cps, 5H(m) 7 17
5	3H(s) 1 08, 3H(s) 1 15, 3H(q) 0 99 and 3H(q) 1 72 $J_{1\ 2}$ = 1 cps, 1H(d) 3 33 and 1H(d) 3 64 $J_{1\ 2}$ = 11 cps, 5H(m) 7 06
6	3H(s) 1.44, 3H(s) 1 58, 3H(q) 1 27 and 3H(q) 1 72 $J_{1.2}$ = 2 cps, 1H(d) 3 14 and 1H(d), 4 47 $J_{1\ 2}$ = 11 cps, 5H(m) 7 16
8	3H(s) 1 12, 3H(s) 1 18, 3H(q) 1 54 and 3H(q) 1 56 $J_{1\ 2}$ = 1 2 cps, 3H(s) 1.94, 3H(s) 3 62
9	3H(s) 1.15, 3H(s) 1 23, 3H(q) 1 58 and 3H(q) 1 62 $J_{1\ 2}$ 1 cps, 3H(s) 2 01

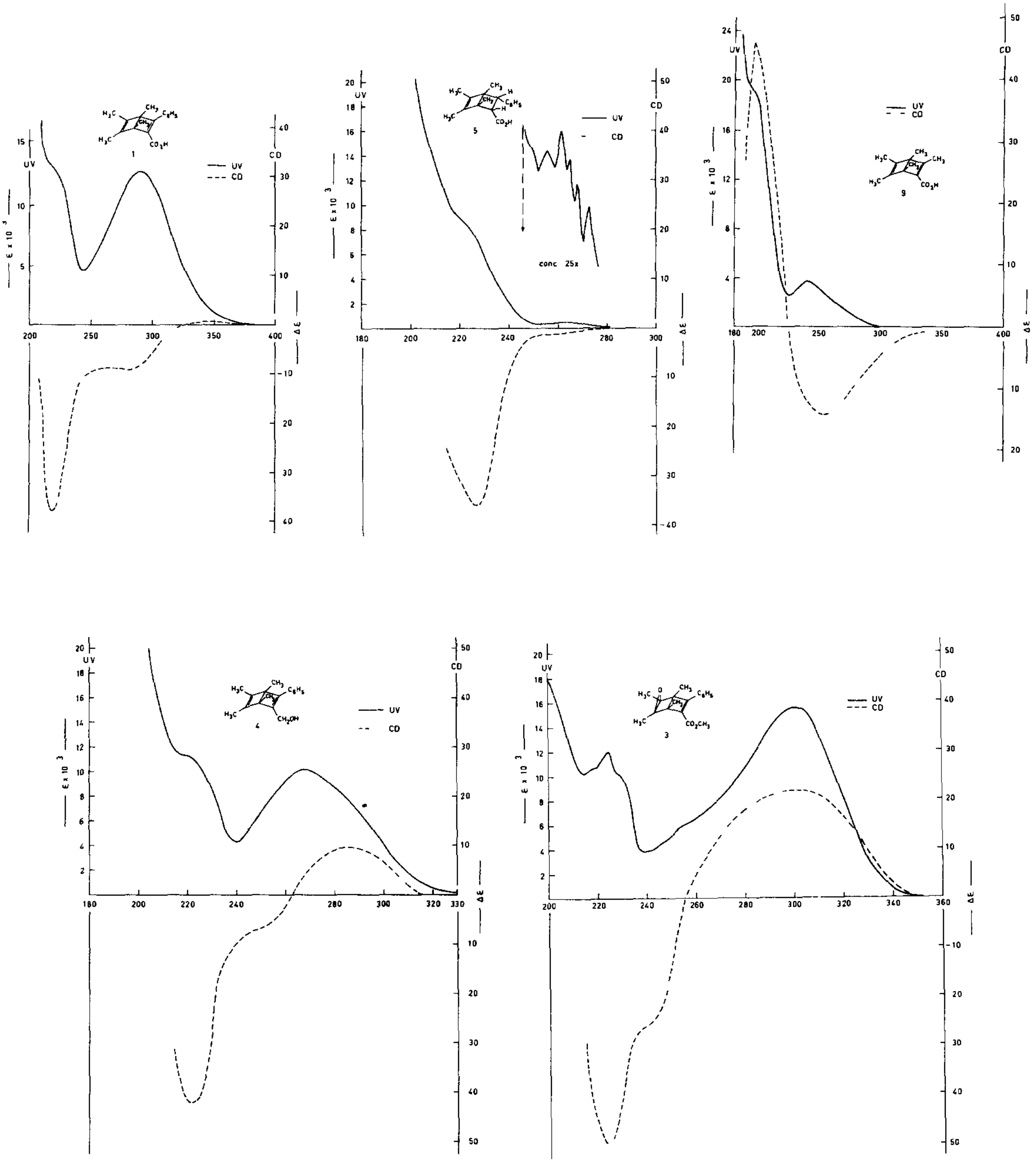


Figure 1 UV and CD spectra. The values of Δε have been extrapolated to 100% optical purity

The CD spectra

Having the CD spectra of the compounds 3-6 and 9 in hand, the transitions in the CD spectrum of (-) 1 can be assigned with reasonable certainty We ascribe the weak positive dichroism at 345 nm to the $n-\pi^*$ transitions of the conjugated carbonyl group[5] (compare 1 and 4) The negative dichroism at 282 nm is attributed to a $\pi-\pi^*$ transition of the cinnamic acid chromophore (1 and 3, 5) The shoulder at 250 nm and the very intensive band at 218 nm are assigned to transitions of the phenyl ring (1 and 3-5, 9)

In agreement with the photoelectron work[6] on hexamethyl "Dewar" benzene, we can find no firm evidence for $\pi-\pi$ overlap between the two cylcobutene moieties of 1, our earlier speculations notwithstanding

References.

1 Part I J H Dopper, B Greijdanus and H Wynberg, J Amer Chem Soc , 97, 216 (1975) Part II J.H Dopper, B Greijdanus , D Oudman and H Wynberg, Chem Commun , submitted for publication

2. Our CD spectrum of (-) 1 as published before[1] was incomplete because it was taken of a sample of low optical purity

3 All rotations were measured in absolute ethanol A correct elemental analysis has been obtained for all new compounds

4 Optical purity of 9 was determined by treating 8 with optically active NMR Europium shift reagent [1]

5. U. Weiss and H Ziffer, J Org. Chem , 28, 1248 (1963)

6 G Bieri, E Heilbronnen, M J Goldstein, R S Leight and M S Lipton, Tetrahedron Lett , 581 (1975)