to remove undissolved sample. This stock solution was then stored in ice water to retard decomposition. The optical density of the stock solution was checked periodically to determine purity; experiments were never extended beyond about 4 hr. Stock solution was added to a volumetric flask by weight using a top loading analytical balance and diluted to volume with sulfuric acid solution (dilution of stock was generally about 1:100; so final temperature was ambient, 25°). Spectra were taken immediately, and then the pH was measured. The existence of isosbestic points indicated that there was no decomposition. For each of the compounds **1a-e**, the spectrum was determined at 5 or 6 sulfuric acid concentrations. Because of the problem of overlapping bands, the ratio of the acid to the anionic form was determined at about ten different wavelengths for each spectrum, and the average was used in determining pK.

Nqr Spectra. Compounds **2a-e** were repurified either by vacuum distillation or recrystallization before determination of the nqr spectra, which were run at 77°K using a Decca Radar Ltd. nqr spectrometer.

Acknowledgments. This work was partially supported by a grant from the National Science Foundation.

Registry No.—**1a**, 1600-39-1; **1b**, 51212-52-3; **1c**, 51212-53-4; **1d**, 51212-54-5; **1e**, 51212-55-6; **1f**, 51212-56-7; **2a**, 24648-07-5; **2b**, 51212-57-8; **2c**, 3854-79-3; **2d**, 51212-58-9; **2e**, 51212-59-0; **2f**, 51212-60-3; **3**, 20434-13-3; $AlCl_3$, 7446-70-0; C_3Cl_4, 6262-42-6; *p*-dibromobenzene, 106-37-6.

References and Notes

(1) D. G. Farnum and P. E. Thurston, *J. Amer. Chem. Soc.*, **86**, 4206 (1964).
(2) G. L. Closs and W. A. Boll, *J. Amer. Chem. Soc.*, **85**, 3796 (1963).
(3) S. Tobey and R. West, *J. Amer. Chem. Soc.*, **86**, 4215 (1964).
(4) D. G. Farnum, J. S. Chickos, and P. E. Thurston, *J. Amer. Chem. Soc.*, **88**, 3075 (1966).
(5) R. West, D. C. Zecher, and S. W. Tobey, *J. Amer. Chem. Soc.*, **92**, 168 (1970).
(6) R. West, J. Chickos, and E. Osawa, *J. Amer. Chem. Soc.*, **90**, 3885 (1968).
(7) R. H. Bible, "Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1965, Chapter 4.
(8) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., p 222.
(9) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
(10) P. J. Bray and R. G. Barnes, *J. Chem. Phys.*, **27**, 551 (1957).
(11) R. M. Smith and R. West, *Tetrahedron Lett.*, 2141 (1969).
(12) Additional proof of structure of **1a** is given by its conversion to a known four-membered ring compound (unpublished studies by J. Chickos). Reaction of **1a** with diazomethane gives phenylmethoxycyclopropene, which reacts with 2,6-dimethylphenylisonitrile[13] with ring expansion to give (2,6-dimethylphenylimino)phenylmethoxycyclobutenone; the latter upon hydrolysis yields phenylmethoxycyclobutenedione, identified by comparison with an authentic sample.[14]
(13) N. Obata and T. Takizawa, *Tetrahedron Lett.*, 3403 (1969); 2231 (1970).
(14) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 1793 (1960).
(15) Values in parentheses are relative absorbances of band maxima. Low solubility of the compounds made determination of actual absorbances quite difficult.
(16) E. Patton and R. West, *J. Amer. Chem. Soc.*, **95**, 8703 (1973).

A General Synthetic Route to Cycloalkylidenecycloalkanes. Reactions of α Anions of Cycloalkanecarboxylic Acid Salts with Cycloalkanones

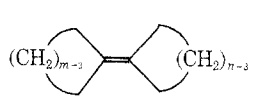
A. Paul Krapcho* and E. G. E. Jahngen, Jr.[1]

Department of Chemistry, University of Vermont, Burlington, Vermont 05401

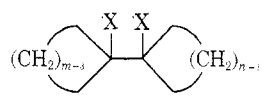
Received December 11, 1973

A versatile synthetic route leading to symmetrical and unsymmetrical cycloalkylidenecycloalkanes of general formula **1** has been developed. Treatment of α-lithiated cycloalkanecarboxylic acid salts **5** with cycloalkanones **6** leads to the β-hydroxy acids **7**. These acids are then converted into the corresponding β-lactones **8**. Thermolyses of **8** produce excellent yields of **1**. Symmetrical olefins **1** ($m = n$ = 4, 5, 6, 7, and 8) and unsymmetrical olefins **1** (m = 4, n = 5 or 6; m = 5, n = 6) have been prepared by application of this procedure. Other substituted cyclic ketones such as adamantanone have also been successfully utilized in this reaction scheme. The α-lithiated salt of 4-cycloheptene-1-carboxylic acid undergoes a facile reaction with **6** (n = 6) to yield the β-hydroxy acid, which can then readily be converted into the corresponding diene without any problem of double-bond isomerizations. Attempts to utilize cyclopropanecarboxylic acid were unsuccessful.

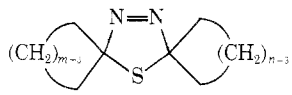
During the course of another research project being performed in our laboratories we had need of a number of cycloalkylidenecycloalkanes of general formula **1**. Although several useful synthetic routes to tetrasubstituted olefins of type **1** have been reported previously, an examination of each method indicates some limitation to general applicability.



1



2



3

In only a few cases is the Wittig[2] procedure applicable to the synthesis of **1**. Cyclopropylidenetriphenylphosphorane, on treatment with cyclopentanone or cyclohexanone, leads to **1** (m = 3, n = 5) and **1** (m = 3, n = 6), respectively.[3] Other cycloalkylidenetriphenylphosphoranes have been prepared with four-, five-, six-, and seven-membered rings.[4] Cyclohexylidenetriphenylphosphorane, on treatment with cyclohexanone, leads to enolate formation.[4a]

Vicinal dinitro compounds such as **2** (X = NO_2) have been converted to **1** ($m = n$ = 5 or 6, and m = 6, n = 7).[5] The major limitation is the accessibility of the requisite nitrocycloalkane precursors for the preparation of **2** (X = NO_2, $m = n$) and the accessibility of 1,1-dinitrocycloalkanes required to prepare **2** (X = NO_2, $m \neq n$).

The zinc debromination of vicinal dibromides **2** (X = Br, $m = n$) leads to **1** ($m = n$ = 5, 6, or 7).[6] Unsymmetrical olefins **1** ($m \neq n$) would be difficult to prepare by this procedure because of the inaccessibility of pinacols of type **2** (X = OH, $m \neq n$).[7]

The preparation of several 2,5-dispiro-Δ^3-1,3,4-thiadiazolines **3** ($m = n$) have recently been reported.[8] Thermolysis of **3** ($m = n$ = 6) led to loss of nitrogen to form the episulfide, which afforded **1** ($m = n$ = 6) on treatment with *n*-butyllithium.[8a] However, thermolysis of **3** ($m = n$ = 7) did not yield the episulfide or **1** ($m = n$ = 7). Cyclobutylidenecyclobutane **1** ($m = n$ = 4) was prepared from **3** ($m = n$ = 4) when heated with triphenylphosphine.[8c] This

procedure would only appear to be applicable to the preparation of symmetrical olefins of type 1 because of the difficulty involved in the preparation of 3 with $m \neq n$.

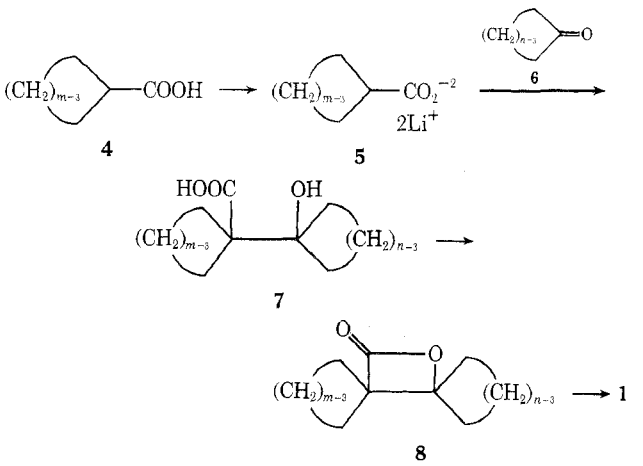
Desulfurization–decarboxylation of the 1,2-thionocarbonate derivative of cyclohexanone pinacol (X = OH, $m = n = 6$) led to 1 ($m = n = 6$).[9] This method again would only be applicable to the preparation of symmetrical systems 1 ($m = n$).[7]

The photodidecarbonylation of dispiro[5.1.5.1]tetradecane-7,14-dione leads to 1 ($m = n = 6$).[10] Attempts to prepare 1 ($m = n = 4$) from the corresponding dione were unsuccessful.[11]

Results and Discussion

We wish to report a synthetic route of considerable versatility which leads to cycloalkylidenecycloalkanes of general formula 1. Both symmetrical ($m = n$) and unsymmetrical ($m \neq n$) olefins of type 1 can be readily obtained in excellent yields. The steps involved in the synthetic route are outlined in Scheme I.

Scheme I



Treatment of cycloalkanecarboxylic acids 4 with a solution of lithium diisopropylamide in THF leads to the formation of the α-lithiated cycloalkanecarboxylic acid salts 5. Addition of cycloalkanones 6 to these α anions yields the β-hydroxy acids 7.[12] These β-hydroxy acids 7 can then be cyclized to the β-lactones 8, which on thermolysis readily lose CO_2 to yield olefins of type 1 with introduction of the double bond at a specific site.[13]

The cycloalkylidenecycloalkanes 1 and several other substituted analogs prepared by the route in Scheme I are summarized in Table I.

From the data tabulated in Table I it can be seen that unsymmetrical olefins of type 1 can be prepared by interchanging the ring size of the cycloalkanecarboxylic acid and the cycloalkanone 6. Adamantanone and dispiro[2.1.2.3]decan-4-one have been successfully treated with the α anion of cyclohexanecarboxylic acid and the resulting β-hydroxy acids have been converted into the substituted cycloalkylidenecycloalkanes. The α anion of 4-cycloheptene-1-carboxylic acid readily reacts with 6 ($n = 6$) to yield the corresponding β-hydroxy acid, which is then readily converted into the desired diene without any double-bond isomerization.

It was found that the α-lithiated cyclohexanecarboxylic acid salt was formed in a yield of greater than 80% by quenching the reaction mixture with D_2O and determining the amount of α deuteration *via* nmr. The yields of the β-hydroxy acids 7 were generally in the 70–80% range.

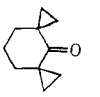
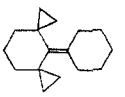
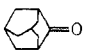
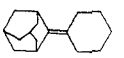
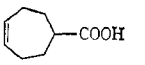
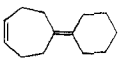
Treatment of dispiro[5.1.5.2]pentadecan-7-one with the α anion from cyclohexanecarboxylic acid gave only about a 20% yield of the β-hydroxy acid. When 2,6-dimethylcyclohexanone (mixture of cis and trans isomers) was treated with the α anion of cyclohexanecarboxylic acid, a quantitative recovery of the starting materials was obtained. The success of the initial alkylation appears to be dependent on the steric hindrance around the carbonyl group and the availability of the α hydrogens of the ketone. Thus the two bulky spiro cyclohexyl groups flanking the carbonyl group effectively block the attack of the α anion and a poor yield of the β-hydroxy acid results. In the case of 2,6-dimethylcyclohexanone, the α anion of the acid attacks the α hydrogen of the ketone to form the enolate salt. Enolate formation may also be seen when the α anion of cyclopentanecarboxylic acid is treated with cyclopentanone. The β-hydroxy acid 7 ($m = n = 5$) is formed in 74% yield; however, the remaining 26% is a mixture of cyclopentanone and cyclopentylidenecyclopentanone.

The β-hydroxy acids 7 can be converted to the β-lactones 8 by treatment with benzenesulfonyl chloride in pyridine.[12a] The β-lactones can be isolated in 80–95% yields in most cases and are stable at room temperature.

Thermal decomposition of the β-lactones 8 at 140° leads to the cycloalkylidenecycloalkanes in yields of greater than 90%.[12a,14]

Attempts to utilize cyclopropanecarboxylic acid in this reaction sequence were unsuccessful. When the reaction of cyclopropanecarboxylic acid and 2 equiv of lithium diisopropylamide was quenched with D_2O, starting acid was recovered in about a 25% yield and showed no incorporation of deuterium. The remainder of the isolated material appears to be dimeric with the starting acid and the structure has not been determined as yet.

Table I
Cycloalkylidenecycloalkanes Prepared *via* Scheme I

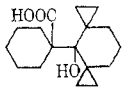
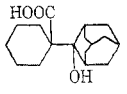
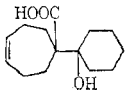
Carboxylic acid 4 ring size m, or acid	Cycloalkanone 6 ring size n, or ketone	Cycloalkylidene cycloalkane 1 m, n, or structure
4	4	4, 4
4	5	4, 5
4	6	4, 6
5	4	4, 5
5	5	5, 5
5	6	5, 6
6	4	4, 6
6	5	5, 6
6	6	6, 6
7	7	7, 7
8	8	8, 8
6		
6		
	6	

Experimental Section

All melting points are uncorrected. The nmr spectra were obtained using a JEOL MH-100 spectrophotometer with TMS as an internal standard in $CDCl_3$ as the solvent. Microanalyses were performed by Robertson Laboratories, Florham Park, N. J. 07932.

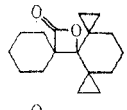
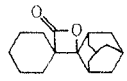
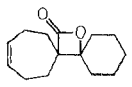
General Procedure for the Formation of β-Hydroxy Acids 7. Lithium diisopropylamide was prepared by dissolving 2.02 g (20 mmol) of diisopropylamine in 50 ml of anhydrous THF under N_2, and adding 10.5 ml (20 mmol) of 1.9 M n-butylithium in hexane at −40°. The mixture was stirred for 20 min below 0° and recooled to −40° and 10 mmol of the cycloalkanecarboxylic acid was added. The reaction was heated to 50° for 2 hr and again cooled to −40° and 10 mmol of the ketone was added. The reaction mixture was stirred for an additional 2 hr, poured over 100 g of ice,

Table II
β-Hydroxy Acids

β-Hydroxy acid 7[a,b] m – n or structure	Mp, °C	Yield, %	Registry no.
4 – 4	102–104	86	51175-05-4
4 – 5	84–86	76	51175-06-5
4 – 6	115–117	72	51175-07-6
5 – 4	54–56	82	51175-08-7
5 – 5	84–86	74	51175-09-8
5 – 6	121–122	79	51175-10-1
6 – 4	97–101	70	51175-11-2
6 – 5	153–154	73	51175-12-3
6 – 6	178–179	77	51175-13-4
7 – 7	112–114	77	51175-14-5
8 – 8	113–115	70	51175-15-6
	135–136	61	51175-16-7
		*c*	51175-17-8
	165–166	74	51175-18-9

[a] All compounds exhibited OH absorptions in the region 3400–3300 and 3200–3100 cm^{-1}. The nmr in most cases showed a coalesced broad peak at δ 7–9 for the OH protons of the acid and the hydroxyl group. [b] Satisfactory analytical data were reported for all new compounds. [c] Upon recrystallization from methyl alcohol the β-lactone formed.

Table III
β-Lactones

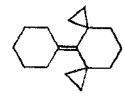
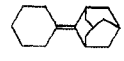
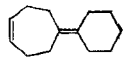
β-Lactones 8[a,b] m – n or structure	Mp, °C	Yield, %	Registry no.
4 – 4	*c*	92	51175-19-0
4 – 5		*d*	51175-20-3
4 – 6	88–90	90	51175-21-4
5 – 4	30–31	65	51175-22-5
5 – 5	98–100	86	51175-23-6
5 – 6	83–84	80	51175-24-7
6 – 4	98–99	88	51175-25-8
6 – 5	98–100	88	51175-26-9
6 – 6	140 dec	94	51175-27-0
7 – 7	86–88	88	51175-28-1
8 – 8	*c*	88	51175-29-2
		*d*	51202-15-4
	107–109	82	51175-30-5
	85–87	77	51175-31-6

[a] All compounds showed carbonyl absorption between 1820 and 1800 cm^{-1}. [b] Satisfactory analytical data were reported for all new compounds. [c] The β-lactones were used as crude oils without further purification. [d] Only the olefins were found in the reaction mixture.

and extracted with 4 × 25 ml of ether. The aqueous phase was acidified with 3 *N* HCl, extracted with 4 × 25 ml of ether, and dried over $MgSO_4$, and the solvent was removed at reduced pressure. The resulting β-hydroxy acids were recrystallized from hexane–chloroform. The compounds are summarized in Table II.

General Procedure for the Formation of β-Lactones 8. The β-hydroxy acid 7 (*ca.* 4 mmol) was dissolved in 40 ml of anhydrous pyridine and cooled to −5°. To the stirred mixture, 12 mmol of benzenesulfonyl chloride was added, and the mixture was held at 0° for 18 hr, then poured over 100 g of ice. The resulting aqueous suspension was either filtered or extracted with 5 × 25 ml of ether. If extraction was used, the organic phase was washed with 2 × 50 ml of saturated $NaHCO_3$ and dried over $MgSO_4$, and the solvent was stripped at reduced pressure (0.5 mm) to remove pyridine. The resulting β-lactones were recrystallized from hydrocarbon solvents and their properties are recorded in Table III.

Table IV
Cycloalkylidenecycloalkanes

1, m, n or[a,b] structure	Bp (mm) or mp,[c] °C	Nmr, δ[d]	Registry no.
4, 4	85 (100)[e]	2.0 (4 H), 2.6 (t, 8 H)	6708-14-1
4, 5	155 (760)	1.7 (4 H), 2.1 (6 H), 2.6 (4 H)	51175-32-7
4, 6	65 (30)	1.5 (6 H), 2.0 (6 H), 2.6 (4 H)	51175-33-8
5, 5	70 (20)[f]	1.6 (8 H), 2.0 (8 H)	16189-35-8
5, 6	80 (20)[g]	1.5 (10 H), 2.0 (8 H)	16189-54-1
6, 6	52–54[f]	1.5 (12 H), 2.2 (8 H)	4233-18-5
7, 7	95 (20)[f]	1.6 (16 H), 2.3 (8 H)	51175-34-9
8, 8	39–41	1.5 (20 H), 2.2 (8 H)	51175-35-0
	24–26	1.5 (12 H), 1.8 (4 H) 0.6 (t, 4 H), 1.2 (t, 4 H)	51175-36-1
	110 (30)	1.5 (6 H), 1.7 (10 H) 2.9 (2 H), 2.1 (4 H)	51175-37-2
	50 (0.1)	1.6 (6 H), 2.1 (12 H) 5.4 (2 H)	51175-38-3

[a] All yields were greater than 90%. [b] Satisfactory analytical data were reported for all new compounds. [c] All boiling points are the pot temperatures. [d] All nmr patterns are multiplets except where noted. [e] Reference 8c. [f] Reference 6. [g] H. Christol, C. Arnal, R. Vanel, and J. M. Bessiere, *Bull. Soc. Chim. Fr.*, 2485 (1967).

General Procedure for the Formation of Cycloalkylidenecycloalkanes 1. The β-lactones 8 (*ca.* 2–5 mmol) were heated at 140° for 3–4 hr until the evolution of gas ceased. The resulting olefins were distilled directly using a Kontes microdistillation apparatus usually at reduced pressure. Physical and spectral properties were consistent with known literature values. These compounds are tabulated in Table IV.

References and Notes

(1) National Defense Education Act Fellow, 1972–1974.
(2) (a) U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959); (b) S. Trippett, *Pure Appl. Chem.*, **9**, 255 (1964); (c) A. Maercker, *Org. React.*, **14**, 270 (1965); (d) M. Schlosser, *Top. Stereochem.*, **5**, 1 (1970).
(3) E. E. Schweizer, C. J. Berninger, and J. G. Thompson, *J. Org. Chem.*, **33**, 336 (1968).
(4) (a) U. Schöllkopf, Doctoral Dissertation, Universität Tübingen, 1956, as quoted in ref 2c, p 349; (b) K. V. Scherer, Jr., and R. S. Lunt, III, *J. Org. Chem.*, **30**, 3215 (1965); (c) H. J. Bestmann and E. Kranz, *Chem. Ber.*, **102**, 1802 (1969).
(5) N. Kornblum, S. D. Boyd, H. W. Pinnick, and R. G. Smith, *J. Amer. Chem. Soc.*, **93**, 4316 (1971).
(6) R. Criegee, E. Vogel, and H. Hoger, *Chem. Ber.*, **85**, 144 (1952).
(7) (a) R. D. Sands, *Tetrahedron*, **21**, 887 (1965). (b) H. Christol, A. P. Krapcho, and F. Pietrasanta, *Bull. Soc. Chim. Fr.*, 4059 (1969).
(8) (a) J. Buter, S. Wassenaar, and R. M. Kellogg, *J. Org. Chem.*, **37**, 4045 (1972); (b) D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Perkin Trans. 1*, 305 (1972); (c) J. W. Everett and P. J. Garratt, *J. Chem. Soc., Chem. Commun.*, 642 (1972); (d) A. P. Schapp and G. R. Faler, *J. Org. Chem.*, **38**, 3061 (1973). Adamantylideneadamantane was obtained by heating the appropriate Δ^3-1,3,4-thiadiazoline **3** with triphenylphosphine.

(9) (a) E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, **85**, 2677 (1963); (b) E. J. Corey, F. A. Carey, and R. A. E. Winter, *ibid.*, **87**, 934 (1965).
(10) N. J. Turro, P. A. Leermakers, and G. F. Vesley, *Org. Syn.*, **5**, 297 (1973).
(11) Unpublished observations. Photolysis of the appropriate diones leads to 30–40% yields of **1** ($m = n = 5$) and **1** ($m = n = 7$).
(12) (a) W. Adam, J. Baeza, and J. C. Liu, *J. Amer. Chem. Soc.*, **94**, 2000 (1972); (b) G. W. Moersch and A. R. Burkett, *J. Org. Chem.*, **36**, 1149 (1971).
(13) This route to olefins has been reported in ref 12a. Its application to compounds of type **1** was not investigated, although cycloalkanecarboxylic acids and cycloalkanones were used in several of the reactions reported in ref 12.
(14) (a) M. U. S. Sultanbawa, *Tetrahedron Lett.*, 4569 (1963); (b) T. Rull and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1581 (1958).

Synthesis of (1*R*) -[1-D]-α-Fenchocamphoronequinone[1,2]

W. C. M. C. Kokke* and Frans A. Varkevisser

Department of Theoretical Organic Chemistry, University of Leiden, P. O. Box 75, Leiden, The Netherlands

Received June 12, 1973

The title compound (**6b**) was prepared from (1*R*)-[1-D]-α-fenchocamphorone (**5b**), which was obtained from (+)-camphor (**1**) *via* ketopinic acid (**2**). Introduction of deuterium was achieved by $LiAlD_4$ reduction of 1-bromo-α-fenchocamphorone (**3**), a degradation product of ketopinic acid (**2**). (1*R*)-[1-D]-α-Fenchocamphoronequinone, a diketone whose chirality is due only to deuterium substitution, showed a small but measurable effect in CD of both low-intensity absorption bands in the region of 250–520 nm.

In the recent literature several authors have published results[3] of calculations on the optical activity of the twisted α-dicarbonyl chromophore. Glyoxal was used as a model compound for these calculations. It was found that when in *cis*-glyoxal the formyl groups are slightly rotated with respect to each other around the C–C bond, the Cotton effects associated with the two low-intensity absorption bands at longest wavelength should have an opposite sign. As it is known that the Cotton effects in camphorquinone at about 300 and 480 nm have an opposite sign, these authors[3] felt that the CD of camphorquinone corroborated their predictions and they assumed twist to be present in its -dicarbonyl chromophore.

In view of the successful synthesis of (1*R*)-[2-^{18}O]-α-fenchocamphoronequinone[4] and of the measurement of its CD[4,5] it seemed worthwhile to synthesize a similar compound with chirality due only to deuterium substitution in the hope that this compound would also show a measurable effect in CD. Such a CD curve might contribute to the knowledge of the electronic and geometrical structure of the α-dicarbonyl group in norcamphorquinones.

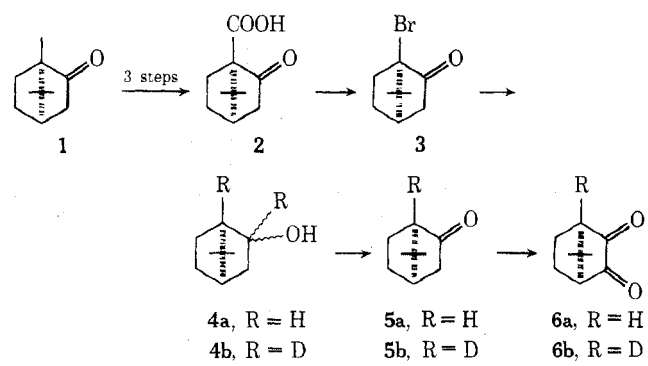
We were successful in synthesizing (1*R*)-[1-D]-α-fenchocamphoronequinone (**6b**), which showed a CD spectrum (Figure 1[6])) differing in many respects from the CD spectrum of (1*R*)-[2-^{18}O]-α-fenchocamphoronequinone.[2,4,5] This result suggests that in general optical activity due to isotopic substitution may provide new information about the structure of chromophores.

Details of the Synthesis. The route we followed to (1*R*)-[1-D]-α-fenchocamphoronequinone (**6b**, Scheme I) is obvious once one knows that the bridgehead methyl group in camphor (**1**) can be converted into a carboxyl group in three steps.

For the replacement of the bridgehead halogen in **3** by hydrogen we chose $LiAlH_4$. The halogen was rather unreactive toward this reducing agent: when *N*-methylmorpholine[12] (bp 115–116°) was used as a solvent a large excess of $LiAlH_4$ and a reaction time of several days were necessary to achieve complete reduction.

After it was verified that α-fenchocamphorone (**5a**) did not contain annoying impurities [it could be oxidized to give α-fenchocamphoronequinone (**6a**) which was inactive in CD], the desired deuterium-containing diketone (**6b**) was synthesized following the same route.

Scheme I[a]



[a] Absolute configurations of the compounds are depicted.[11]

Experimental Section

Melting points are not corrected; angles of rotation were measured with a Perkin-Elmer polarimeter (Model 131) at room temperature; concentrations (*c*) are given in grams of solute per 100 ml of solution; labels were calculated from peak intensities of mass spectra obtained with a MS-9 mass spectrometer; nmr spectra were recorded at room temperature using a Jeol 100-MHz nmr spectrometer; nmr shifts (both ^{1}H, ^{2}H and ^{18}C shifts) are with respect to TMS; new compounds gave satisfactory elemental analyses.

Ketopinic acid (2) can be prepared in three steps from camphor[13] *via* camphor-10-sulfonic acid and camphor-10-sulfonyl chloride. Some labor can be saved if one starts with (+)-(1*S*)-camphor-10-sulfonic acid, which is commercially available. Oxidation[13] of (1*S*)-camphor-10-sulfonyl chloride and recrystallization of the crude product from water gave (1*S*)-**2** in 20.9–24.5% yield, mp 226–228°, $[\alpha]_D$ +25.8° (*c* 0.65, MeOH). This low yield is in disagreement with the yield claimed in the procedure followed (38–42%). We obtained a by-product in this reaction: a white compound sublimed on the flat flange lid of the reaction vessel. It was identified as (1*S*)-10-chlorocamphor by comparison of its spectra with those of an authentic sample of this compound, yield 2.7–2.9% after resublimation, mp 130–131°, $[\alpha]_D$ +39.75° (*c* 0.79, $CHCl_3$), $[\alpha]_D$ +41.7° (*c* 0.85, absolute EtOH). This chlorocamphor was formed not only when crude sulfonyl chloride was used for the preparation of **2**, but also when pure recrystallized (from benzene–hexane) sulfonyl chloride was used in this reaction. Thus the assumption that the isolation of 10-chlorocamphor is a consequence of overheating during the preparation of the sulfonyl chloride is not justified.

(1*S*)-10-Chlorocamphor has been reported by Forster,[14] but in Beilstein[15] an alternative structure (6-chlorocamphor) is proposed