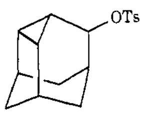
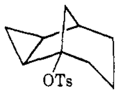
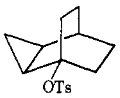
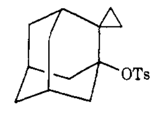
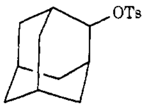
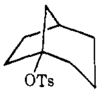
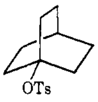
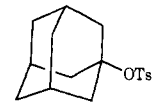
kinetic and product work-up procedures except that rates for the reactive tosylate **7**-OTs were followed with the titrimetric procedure used by Wiberg and Hess.[17] The only acetolysis product isolated (greater than 85%) was unrearranged bridgehead acetate, identified by comparison with an authentic sample. The rate data are listed in Table I.

Table I. Solvolytic Rate Constants

Compd	Solvent	T, °C	$k_1 \times 10^4$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
7-OTs	HOAc	39.85	19.5 ± 0.1	21.70	−1.71
		45.36	36.8 ± 3.2		
		50.03	59.2 ± 0.7		
		56.03	$115. \pm 1.$		
		25.00[a]	3.25		
11-OTs	HOAc	79.57	0.685 ± 0.010	25.27	−6.26
		87.98	1.68 ± 0.01		
		98.06	4.35 ± 0.06		
		25.00[a]	7.96×10^{-4}		
6-ODNB	49.7% EtOH	92.88	0.124 ± 0.004	28.24	−4.28
		102.07	0.357 ± 0.002		
		132.10	5.99 ± 0.19		
		25.00[a]	1.43×10^{-5}		
t-Bu	49.7% EtOH	25.00[a]	4.84×10^{-4}	26.03	−4.70

[a] Extrapolated from the data at higher temperatures.

Table II. Relative Acetolysis Rate Constants at 25°

0°	30°	60°	90°
			
5-OTs	**6**-OTs	**7**-OTs	**8**-OTs
1.47×10^{0}[a]	1.4×10^{-3}[c,d]	3.25×10^{-4}[c]	4.20×10^{-6}[f]
			
9-OTs	**10**-OTs	**11**-OTs	**12**-OTs
5.94×10^{-9}[b]	3.50×10^{-9}[e]	7.96×10^{-8}[c]	8.37×10^{-4}[f]
	Rate Ratio		
2.5×10^{8}	4.0×10^{5}	4.1×10^{3}	5.0×10^{-3}

[a] Reference 7. [b] Reference 12. [c] This work. [d] Calculated using rate ratios from ref 7. [e] R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 3189 (1971). [f] Reference 3.

The bridgehead alcohol **6**-OH was prepared by Simmons–Smith[18] cyclopropanation of bicyclo[3.2.1]-oct-6-en-1-ol isolated from preparative hydrolysis of 1-bicyclo[2.2.1]hept-2-enylcarbinyl tosylate.[19] Cyclopropanation[18] gave only one isomer, assumed to be exo by analogy to cyclopropanation of norbornene, norbornadiene, and 2-bicyclo[3.2.1]octa-3,6-dienol.[20] In addition the cyclopropyl region of the nmr spectrum of **6**-OH was identical with that of *exo*-tricyclo[3.2.1.0^{2,4}]-octane[18] derivatives and very different from that of endo derivatives.

The tosylate of this alcohol, **6**-OTs, proved to be even more reactive than that of **7**. Using the Coates procedure[16] white crystals were obtained which turned black in less than 30 sec and titrated for complete ionization. Thus the dinitrobenzoate **6**-ODNB was prepared in the standard manner and used for solvolysis studies. Product analyses after 10 half-lives for this compound also showed no rearrangement, the product consisting solely of unrearranged alcohol **6**-OH and ethyl ether **6**-OEt.

As the inductive effect of cyclopropane should be constant and independent of angle of orientation, the only variables remaining in these systems are the strain energy, which may be corrected for by the choice of model compounds (see Table II), and the angle of orientation of the cyclopropane to the developing cation, comparable to the conformations of a freely rotating cyclopropylcarbinyl cation. Inspection of relative rate data as a function of angle for the cyclopropylcarbinyl cations studied, Table II, suggests a smooth continuous function of geometry[21] covering a range of reactivity of eleven powers of ten, rather than the discontinuous function implied by the variety of species proposed to explain cyclopropylcarbinyl reactivity in the past. Of particular importance is the observation that the ion with 60° geometry, approximately the geometry of a bicyclobutonium ion, is considerably less stable than the ion with 30 or 0° geometries. It thus appears that the energy of a cyclopropylcarbinyl cation as a function of geometry may be understood as simply as that of an allyl cation.

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for an institutional grant to New York University for support of this work.

(17) K. B. Wiberg and B. A. Hess, *J. Amer. Chem. Soc.*, **89**, 3015 (1967).

(18) (a) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 1256 (1959); (b) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

(19) J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968).

(20) A. F. Diaz, D. L. Harris, M. Sakai, and S. Winstein, *Tetrahedron Lett.*, 303 (1971).

(21) Preliminary analysis of the data suggests a similarity to a cosine function. Detailed analysis and comparison of rates is deferred to the full paper.

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Optical Activity due to Isotopic Substitution. Circular Dichroism of (1*R*)-[2-^{18}O]-α-Fenchocamphoronequinone

Sir:

During the last 25 years many substances have been synthesized which derive optical activity from deuterium substitution.[1] Only one example of optical activity due to other isotopic substitution has been reported: benzyl *p*-tolyl [^{16}O,^{18}O]sulfone.[2] No Cotton effect has

(1) For reviews on hydrogen–deuterium asymmetry see: D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969); L. Verbit, *Progr. Phys. Org. Chem.*, 7, 51 (1969).

(2) C. J. M. Stirling, *J. Chem. Soc.*, 5741 (1963).

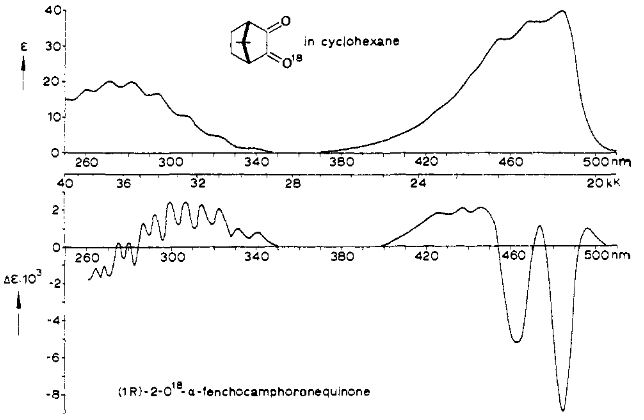

Figure 1.

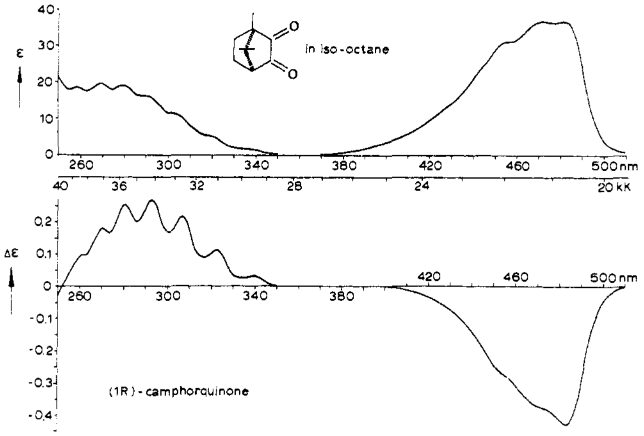

Figure 2.

been measured in any of these compounds, neither in CD nor in ORD. Two ORD curves only show the first half of a Cotton effect.[3]

We have started the synthesis of a number of diketones which derive optical activity from substitution of one ^{16}O by ^{18}O. The first compound which is reported here is an α-diketone: (1*R*)-[2-^{18}O]-α-fenchocamphoronequinone (I). The CD curve between 250 and 520 nm has been measured with a very sensitive instrument built by Mr. Dekkers in this department. Corrected to optical purity it is displayed in Figure 1 together with the absorption curve. Both bands in CD around 280 and 480 nm show exceptionally pronounced structure. For comparison, the CD and absorption spectra of camphorquinone (II) (Figure 2) and of isofenchonequinone (III) (Figure 3) are added.[4]

Recently several papers have been published on the interpretation of electronic spectra and the optical activity of α-diketones.[5,7] The assignment of electronic transitions by some authors[5] differs from the assignment given by others.[7] Nevertheless, they agree

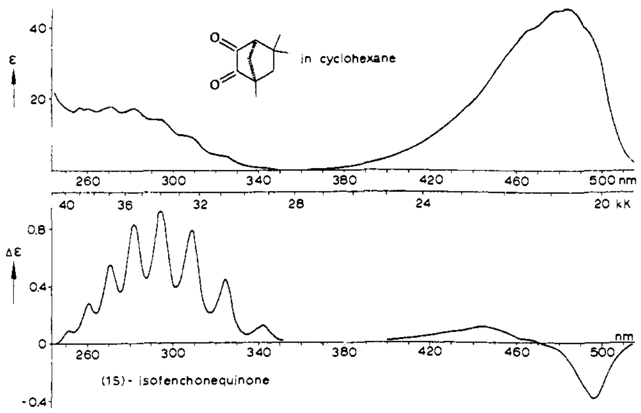

Figure 3.

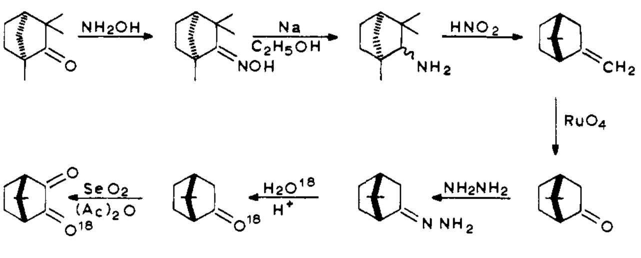

Figure 4. The synthesis of compound I from (+)-(1*S*)-fenchone.

in expecting the same sense of twist to be present in the dicarbonyl group of II. However, the opposite sense of twist has been suggested on the basis of conformational analysis.[6]

Theoretical analysis of the CD of compound I, which will be published elsewhere, may contribute to clear up these antitheses.

Details of the synthesis of I will be published separately by one of the authors (Kokke). A scheme of the route followed is given in Figure 4.

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[3] S. Englard, J. S. Britten, and I. Listowsky, *J. Biol. Chem.*, **242**, 2255 (1967); L. Verbit, *J. Amer. Chem. Soc.*, **89**, 167 (1967).

[4] From ORD measurements of III (H.-P. Gervais and A. Rassat, *Bull. Soc. Chim. Fr.*, 745 (1961)) it has been concluded[5,6] that the absorption band around 480 nm gives rise to a normal Cotton effect in CD, which is at variance with our results.

[5] W. Hug and G. Wagnière, *Helv. Chim. Acta*, **54**, 633 (1971); W. Hug, J. Kuhn, K. J. Seibold, H. Labhart, and G. Wagnière, *ibid.*, **54**, 1451 (1971).

[6] A. W. Burgstahler and N. C. Naik, *ibid.*, **54**, 2920 (1971).

[7] E. Charney and L. Tsai, *J. Amer. Chem. Soc.*, **93**, 7123 (1971).

[8] One of the authors (W. C. M. C. Kokke) is indebted to the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) for the sponsoring of this work. A NATO grant for the purchase of ^{18}O is gratefully acknowledged.

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Test of Bond-Order Methods for Predicting the Position of the Minimum-Energy Path for Hydrogen Atom Transfer Reactions

Sir:

The bond-energy–bond-order method (BEBO) of Johnston and Parr can be used to predict a narrow curving parabolic potential energy channel between reactants and products in reactions of the form A + HB → AH + B.[1,2] The predicted properties of the saddle point have been tested in conjunction with transition state theory and the combination of theories has

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[1] H. S. Johnston and C. Parr, *J. Amer. Chem. Soc.*, **85**, 2544 (1963).

[2] H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966.