

mole is consistent with the above discussion if the resonance energy in  $R-CO-CH_2\cdot$  radicals is assigned a value of about 7 kcal. This is a few kcal. higher than we would expect from bond energy considerations but not outside the limits of error of the available data. On the other hand, the very low  $E_{act}$  of 32.5 kcal. observed<sup>10</sup> for the first order isomerization of cyclobutene to butadiene cannot be reconciled with the present discussion unless one assumes that the strain energy in cyclobutene exceeds that in cyclobutane by about 15 to 20 kcal. This seems rather unreasonable.

(10) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).

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### CESIUM SALTS CONTAINING THE $ClHCl^-$ SPECIES

Sir:

The report of West<sup>1</sup> on the preparation of  $CsClHCl$  has stimulated much interest and some further study of this compound (including this work). Our work indicates that the compound prepared by West is not an anhydrous salt but contains an amount of water equivalent to the amount of  $HCl$  contained. This explains the failure of Sharp<sup>2</sup> to find the stretching frequency characteristic of the  $ClHCl^-$  species. We wish to report the preparation of anhydrous  $CsClHCl$ .

On exposure of anhydrous  $CsCl$  to anhydrous  $HCl$  at  $-78.5^\circ$ , rapid absorption of  $HCl$  initially takes place and then slow absorption for several days to form the stoichiometric compounds. Pressure-composition diagrams indicate the presence of  $CsCl \cdot 0.75HCl$  and  $CsCl \cdot 1HCl$ , the product being determined by the final pressure of  $HCl$ . No interaction of  $CsCl$  with  $HCl$  gas at one atmosphere could be detected at  $0^\circ$ . From pressure measurements at two temperatures the indicated pressures at  $30^\circ$ , the temperature of West's work, would be *ca.* 4.4 atmospheres and  $>400$  atmospheres for the  $CsCl \cdot 0.75HCl$  and  $CsCl \cdot 1HCl$  compounds, respectively. Both of these anhydrous compounds were colorless.

Since these compounds appeared to be different from the compound reported by West, his preparative scheme was followed to obtain a sample for comparison. Four grams of Fisher purified grade  $CsCl$  were dissolved in 3 cc. of water, and the solution alternately treated with  $HCl$  gas and cooled. Approximately 2 g. of very pale yellow crystals were recovered and dried. Analysis for water using a Karl Fischer titration,  $HCl$  by titration with  $NaOH$  and total chloride by gravimetric determination as  $AgCl$  are all consistent with the compound  $CsCl \cdot 0.74HCl \cdot 0.74HOH$ . The compound prepared by West thus appears to be the hydrated  $CsCl \cdot 0.75HCl$  or the hydrated  $CsCl \cdot 1HCl$  or a mixture of the two.

(1) R. West, *J. Am. Chem. Soc.*, **79**, 4568 (1957).

(2) D. W. A. Sharp, *J. Chem. Soc.*, 2558 (1958).

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### TRICYCLO[4.4.0.0<sup>3,8</sup>]DECANE

Sir:

Consideration of the structure and reactivity of the highly symmetrical molecule adamantane has prompted us to synthesize its twist<sup>1</sup> boat isomer tricyclo[4.4.0.0<sup>3,8</sup>]decane (Fig. 1), a convenient trivial name for which is "twistane." Inspection



Fig. 1.

of models reveals that twistane, in contrast to adamantane, is dissymmetric and composed exclusively of twist boat cyclohexane rings, but is

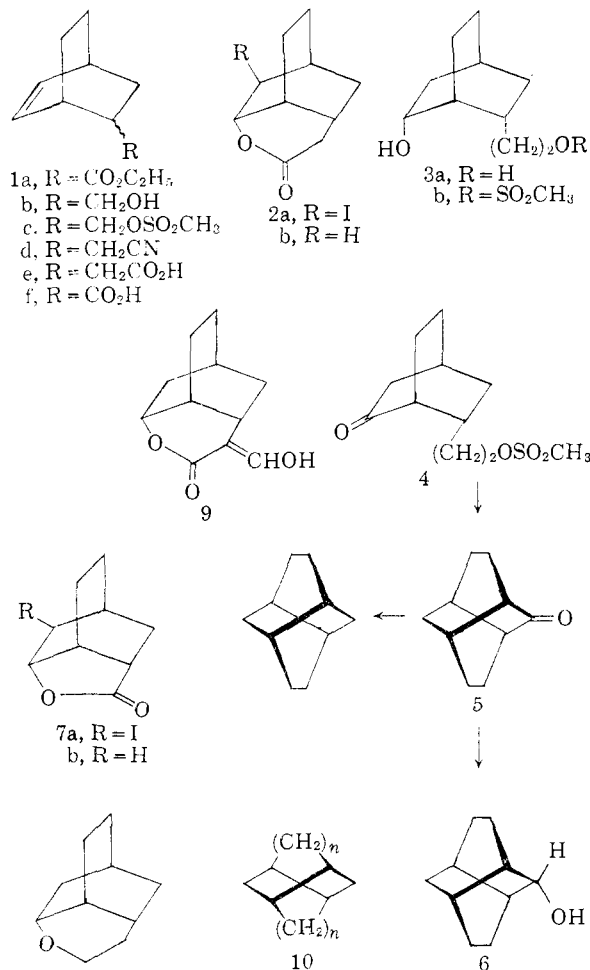


Fig. 2.

(1) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *J. Am. Chem. Soc.*, **83**, 606 (1961).

not completely free of angle strain.<sup>2</sup> The synthesis employed was chosen on the basis of its *not* proceeding *via* carbonium ions (with their concomitant uncertainty as to the occurrence of skeletal rearrangements).

Lithium aluminum hydride reduction of **1a**<sup>3</sup> (Fig. 2) afforded a quantitative yield of **1b**,<sup>4</sup> b.p. 109–110° (10 mm.),  $n_D^{25}$  1.5060, which on reaction with methanesulfonyl chloride in pyridine to afford methanesulfonate **1c**, then reaction of **1c** with sodium cyanide in dimethylformamide (110°, 12 hr.) gave an 85% yield of nitrile **1d**, b.p. 115–118° (9 mm.),  $n_D^{25}$  1.4943. Hydrolysis of **1d** with potassium hydroxide in ethylene glycol (155°, 1.5 hr.) gave a 92% yield of a pasty mixture of stereoisomers of **1e**, m.p. 39.0–40.8° after repeated recrystallization from pentane at –70°. Iodolactonization<sup>5</sup> of **1e** afforded a 68% yield of iodolactone **2a**, m.p. 127–129°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.80  $\mu$ , which on catalytic hydrogenolysis (platinum plus one equivalent of triethylamine in ethyl acetate, 40 p.s.i. of hydrogen) afforded a 79% yield of  $\delta$  lactone **2b**, m.p. 67–69°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.80  $\mu$ . Similarly,  $\gamma$  lactone **7b**, m.p. 205–206°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.86  $\mu$ , was prepared by hydrogenolysis of **7a**,<sup>6</sup> m.p. 80–81°. Structural correlation of the two lactones **2b** and **7b** was achieved by conversion of **2b** into its hydroxymethylene derivative (**9**), m.p. 109–110°, then ozonization of **9** to afford **7b**. Lithium aluminum hydride reduction of **2b** afforded diol **3a**, m.p. 82.2–83.1°, in

90–92% yield. Esterification of **3a** with one equivalent of methanesulfonyl chloride in pyridine gave the oily diol monomesylate (**3b**)<sup>7</sup> which was directly oxidized<sup>8</sup> to **4**, m.p. 62.8–64.3°, in 87% yield. Cyclization of **4**, effected by treatment with an excess of sodium hydride in anhydrous dimethylformamide at 60° for 8 hr., afforded a 90% yield of tricyclo[4.4.0.0<sup>3,8</sup>]decan-2-one (**5**), m.p. 198–199.5°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  5.79  $\mu$ , which afforded a 2,4-dinitrophenylhydrazone, m.p. 186–187°, and except for a trace of **8** was homogeneous by vapor phase chromatography. Consistent with this formulation is the observation that reduction of **5**, employing either lithium aluminum hydride or sodium and alcohol, afforded high yields of a single alcohol (**6**), m.p. 214.4–216.4°. Wolff-Kishner reduction of **5** afforded a 23% yield of tricyclo[4.4.0.0<sup>3,8</sup>]decane (twistane), m.p. 163–164.8°, characterized by its elemental analysis, very simple infrared spectrum, n.m.r. spectrum<sup>9</sup> (three peaks at 8.37, 8.45 and 8.65 tau in the expected ratio of 1:2:1), and great volatility.<sup>10,11</sup>

Solvolysis of suitable derivatives of **6**, with their interesting multiplicity of possible Wagner-Meerwein rearrangements, extension of the intramolecular alkylation reaction to give more highly strained *trans*-bridged systems of the general type **10**, and less lengthy (although more ambiguous), syntheses of tricyclo[4.4.0.0<sup>3,8</sup>]decane are currently being investigated.

(2) This unfortunately renders twistane of uncertain value for determination of the energy difference between chair and twist boat cyclohexane rings by comparison of its heat of combustion with that of adamantane. The angle strain can be seen clearly by bridging bicyclo[2.2.2]octane (Dreiding models) between C-2 and C-5 with a two carbon unit.

(3) R. Skeda and O. Tramposch, *Chem. Ber.*, **75**, 1379 (1942), 85% *endo*-carbethoxy as shown by vapor phase chromatography.

(4) K. Alder, S. Hartung and O. Netz, *Chem. Ber.*, **90**, 1 (1957). All new compounds were characterized by spectral data and, except for **3b** and **4**, by elemental analyses.

(5) C. S. Rondestvedt and C. D. Ver Nooy, *J. Am. Chem. Soc.*, **77**, 3583 (1955).

(6) W. Boehme, E. Schipper and W. E. Scharpf, *ibid.*, **80**, 5188 (1958), have reported the formation of two iodolactones from **1f**. In our hands this reaction invariably afforded only the one isomer, m.p. 80–81°.

(7) Diol monomesylate **3b** was unstable, cyclizing to ether **8** on standing.

(8) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

(9) Obtained at 60 Mc. on a Varian Associates A-60 nuclear magnetic resonance spectrometer purchased with funds provided by the National Science Foundation, grant G19108.

(10) An alternative structure for the hydrocarbon, 2,6-ethanobicyclo[2.2.2]octane, which would arise if the original iodolactonization proceeded abnormally, is rendered unlikely by the data contained herein.

(11) Molecular weight 136 by mass spectroscopy. The author thanks Professor C. Djerassi of Stanford University for this determination.

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## BOOK REVIEWS

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Biological Structure and Function. Proceedings of the First IUB/IUBS International Symposium Held in Stockholm, September 12–17, 1960. Volume I. Edited by T. W. GOODWIN, Department of Agricultural Biochemistry, Institute of Rural Science, Penglais, Wales, and O. LINDBERG, The Wenner-Gren Institute for Experimental Biology, University of Stockholm, Sweden. Academic Press Inc., (London) Ltd., 17 Old Queen Street, London, S. W. 1, England. 1961. xii + 363 pp. 16 × 23.5 cm. Price, \$10.50.

This volume is in three sections of quite widely different nature. The first, Macromolecular Structure and Function, contains nine papers, most of which are quite short but of high quality. A brief review by Kendrew on myoglobin structure is accompanied by discussion, followed by a re-

view of nucleic acid structure as derived from X-ray diffraction studies (Wilkins). Several other papers in this section deal with nucleic acids: nucleotide sequence (Chargaff), polynucleotide sequence (Davidson), and synthesis of soluble RNA (Canellakis and Herbert). Of particular interest was the paper by P. Reichard on the Enzymic Formation of DNA from Ribonucleotides, in which it is suggested that the reduction of ribose to deoxyribose (as nucleotide) may be a rate-controlling step in DNA synthesis.

The second section is the largest, containing 12 papers, and represents more closely the primary objective of the symposium. It is entitled Microsomes and Protein Synthesis. An excellent review of the Endoplasmic Reticulum and its functions is presented by Keith R. Porter, with numerous electron micrographs. This is followed by a