

ture of concerted paths cannot be determined by the present examination. However, to be ruled out for fragmentation of 1–3 are simple concerted paths controlled exclusively by either least motion dynamics or orbital symmetry or a mechanism involving a common diradical intermediate (for 2 and 3).

The earlier proposals concerning substituted cyclobutanes<sup>1,2</sup> rested on the observed 5–9 kcal/mol stabilization of the transition state for cracking achieved by substitution of a cyclobutane by acyl or carbomethoxy groups<sup>11</sup> and on the evidence that these groups do not confer that amount of stabilization by delocalization or other means on adjacent radical (and presumably diradical) centers. The latter rests with the determination of bond energies from iodination kinetics data; for example, the  $\alpha$  C–H bond dissociation energy for acetone is just that found for the primary C–H bond in propane (*i.e.*, stabilization energy for the acetyl radical =  $0 \pm 2$  kcal/mol).<sup>14</sup> Analysis of the secondary C–H bond dissociation energy in methyl ethyl ketone likewise reveals a low ( $2.7 \pm 1.7$  kcal/mol) resonance stabilization for the methylacetyl radical.<sup>15</sup>

On the other hand these experimentally determined bond dissociation energies for acyl systems may be artificially high since they depend on the virtual equivalency of activation energy and the enthalpy for abstraction (presumed to be homolytic) by iodine at an appropriate hydrogen. That abstraction by halogen atoms (Cl and Br) is in fact electrophilic has been shown by a number of Hammett studies.<sup>16</sup> Considering that abstraction by iodine has similar polar character ( $\rho = -1$  to  $-3$ ), pure homolytic C–H bond dissociation in acetone and analogous systems may be less energetic than previously determined by 2–4 kcal/mol and the attendant stabilization energy in the resulting radical larger by the same amount. This is tantamount to acknowledging that a “repulsion polar effect”<sup>17</sup> (for hydrogen transfer between two electrophilic radicals) may raise the activation energy for reaction of HI and

(11) That the decompositions of 1–3 are accelerated relative to a non-carbonyl substituted model is confirmed by comparison of the Arrhenius parameters for static pyrolysis of 1 ( $E_a = 52 \pm 2$  kcal/mol,  $\log A = 15 \pm 1$ ) in diphenyl ether solvent at 319–359° with those for cracking of bicyclo[3.2.0]heptane ( $E_a = 61.0$  kcal/mol,  $\log A = 15.02^{12}$ ). This comparison reveals a transition state stabilization of about 7 and 2 kcal/mol for the acyl and chlorine<sup>13</sup> substituents, respectively.

(12) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 4184 (1964).

(13) E. N. Cain and R. K. Solly, *J. Amer. Chem. Soc.*, **94**, 3830 (1972).

(14) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 11 (1970).

(15) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 381 (1970).

(16) W. A. Pryor, T. H. Lin, J. P. Stanley, and R. W. Henderson, *J. Amer. Chem. Soc.*, **95**, 6993 (1973), and references cited therein.

(17) (a) J. A. Kerr and D. M. Timlin, *Int. J. Chem. Kinet.*, **3**, 1, 69 (1971); (b) J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, **62**, 1662 (1966).

the acetyl radical above the  $1 \pm 1$  kcal/mol assumed in the iodination kinetics treatment.<sup>18</sup> Along with the evidence implicit from the energetics<sup>1,2</sup> and stereochemical losses<sup>19</sup> associated with small ring decompositions, a variety of epr spectral determinations<sup>20</sup> confirm that acyl substituted radicals enjoy significant delocalization stabilization.<sup>21</sup>

Finally, “stereoretention,” the olefin product ratio for decomposition of 1–3 which very likely reflects the partition between cleavage and bond rotation in an initially formed diradical intermediate (or the equivalent partitioning of a family of concerted paths), may be compared with the accumulated literature values for systems potentially involving 1,4-diradicals.<sup>9</sup> The present values (3–4) compare favorably with those for systems involving diyls with moderate substituent stabilizing and low ponderal influences at the diradical termini.

**Acknowledgment.** We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

(18) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

(19) G. Jones, II, and M. E. Fantina, *J. Chem. Soc., Chem. Commun.*, 375 (1973).

(20) D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, **95**, 7978 (1973), and references cited therein.

(21) For further discussion and an interesting survey of substituent effects for thermal chemistry in the bicyclo[2.2.0]hexane series, see E. N. Cain, *Tetrahedron Lett.*, 1865 (1971); E. N. Cain and R. K. Solly, *J. Amer. Chem. Soc.*, **95**, 4791 (1973); the assessment in the latter of 1.0 kcal/mol for the resonance energy of the carbomethoxymethyl radical should be revised upward in light of the recent evaluation<sup>22</sup> of the effect of alkyl group substitution in the same series.

(22) E. N. Cain and R. K. Solly, *J. Amer. Chem. Soc.*, **95**, 7884 (1973).

Guilford Jones, II,\* Marvis H. Williamson, Jr.

Department of Chemistry, Boston University  
Boston, Massachusetts 02215

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## Transannular Interactions in the Acyloin Reaction.

### I. Interactions with the Terminal Methylene Group

Sir:

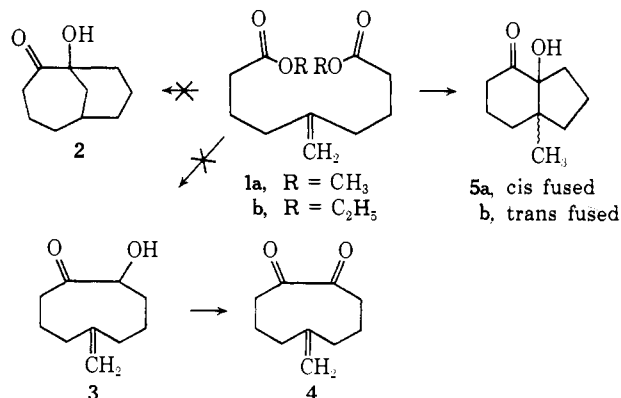
As part of our investigation of transannular interactions in both the ground and excited states,<sup>1</sup> we have been interested in obtaining 2-hydroxy-6-methylenecyclononane (3) and the corresponding dione 4. A previous attempt to synthesize compound 3 *via* the acyloin reaction of dimethyl 5-methylenonane dicarboxylate (1a) reportedly<sup>2</sup> did not give the desired product 3 but gave instead a compound tentatively identified as 1-hydroxybicyclo[4.3.1]decan-2-one (2). As we felt this reaction might be modified to give 3, we have undertaken a study of the acyloin reaction of diester 1 and related systems. Our initial studies involving the chlorotrimethylsilane modification<sup>3</sup> of the acyloin reaction of diester 1b showed that neither 2 nor 3 was obtained after hydrolytic work-up but rather hydroxy ketone 5 was the major product (Scheme I). We have now found that 5 is the major product of this

(1) (a) P. Y. Johnson, J. Zitsman, and C. Hatch, *J. Org. Chem.*, **38**, 4087 (1973); (b) P. Y. Johnson, *Tetrahedron Lett.*, 1991 (1972); (c) P. Y. Johnson, E. Koza, and R. Kohnman, *J. Org. Chem.*, **38**, 2967 (1973).

(2) J. Panzer, dissertation, Cornell University, 1956; *Diss. Abstr.*, **17**, 39 (1957). See K. T. Finley, *Chem. Rev.*, **64**, 573 (1964).

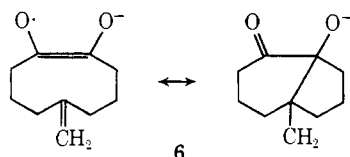
(3) See J. J. Bloomfield, *Tetrahedron Lett.*, 587 (1958).

Scheme I. Product of the Acyloin Reaction of Diester 1

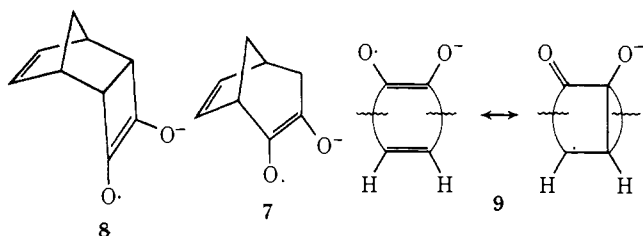


reaction under a variety of conditions, including those originally reported (Na in refluxing toluene). To our knowledge this is the first known acyloin reaction in which an acyclic diester has been shown to give a bicyclic system.

Formation of **5** is believed to involve transannular interaction of the terminal olefin and the radical anion formed from dione **4** (see semidione<sup>4</sup> **6**). Transannular



interactions related to that shown for semidione **6** have been observed by Russell and coworkers.<sup>4,5</sup> They observed moderate splittings in the epr signal of semidiones such as **7** and **8** due to the vinyl protons. These splittings were attributed to interactions of the type shown in structure **9**.



Compound **5** which was obtained by distillation (bp 70–75° (0.05 mm)) in nearly 50% yield was identified<sup>6</sup> by its spectra: ir (CCl<sub>4</sub>) 3494, 1706, and 856 cm<sup>-1</sup>; mass spectrum (70 eV) *m/e* (relative intensity) 168 (13, M<sup>+</sup>), 150 (3), 112 (6), 98 (100), 69 (15); uv<sub>max</sub> (EtOH) 287 nm (ε 45). The nmr<sup>7</sup> spectrum of **5** in CDCl<sub>3</sub> showed two methyl singlets occurring at δ 0.98 and 1.08, in a ratio of 2.3 to 1.0, respectively, indicating that **5** exists as a mixture of the cis and trans fused isomers. In order to determine which methyl absorption corresponded to which isomer, the nmr of **5** was obtained in the presence of 0.3 molar equiv of the lanthanide shift reagent tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-

(4) Semidiones have been proposed as intermediates in the acyloin reaction. See G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 6782 (1967).

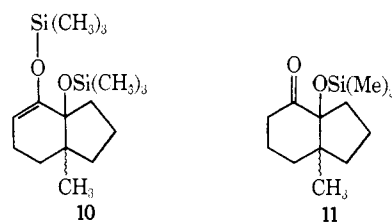
(5) (a) G. A. Russell, E. T. Strom, E. R. Taty, K.-Y. Chung, R. D. Stephens, and M. C. Young, *Rec. Chem. Progr.*, **27**, 3 (1966); (b) G. A. Russell, G. W. Holland, and K.-Y. Chung, *J. Amer. Chem. Soc.*, **89**, 6629 (1967).

(6) Satisfactory spectra and elemental analysis were obtained on all major compounds.

(7) All nmr spectra were taken on a JOEL MH100 instrument.

octane-4,6-dionatoeuropium (Eu(fod)<sub>3</sub>). Binding of the shift reagent was presumed to occur preferentially at the hydroxyl oxygen, as has been reported for other hydroxy ketones.<sup>8</sup> Models of the cis and trans isomers (**5a** and **5b**) show that the hydroxyl oxygen is forced quite close to the methyl group in **5a**, while they are on opposite sides of the molecule in isomer **5b**. In the presence of Eu(fod)<sub>3</sub> both methyl absorptions are shifted downfield, the larger by δ 0.46 and the smaller by δ 1.41. The relatively large downfield shift of the smaller methyl absorption clearly identifies it as belonging to the cis isomer.

When the acyloin reaction was run in the presence of chlorotrimethylsilane and a nonhydrolytic work-up employed, the disilylated acyloin **10** was obtained. Compound **10** was found to be labile, and hydrolyzed readily to the monosilylated acyloin **11**. The nmr

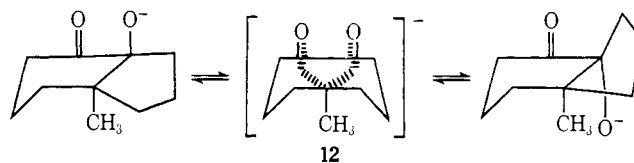


spectrum of **11** showed only a single methyl absorption. Upon addition of 1 equiv of Eu(fod)<sub>3</sub> to the sample, however, the methyl absorption was resolved into two peaks occurring in the same ratio as previously observed. Acid hydrolysis of silane **11** gave acyloin **5** in the same isomer ratio as was previously noted.

An attempt to convert a mixture of **5a** and **5b** to a single epimer by isomerizing one of the epimers under basic conditions (refluxing methanol with a trace of sodium methoxide) resulted in no change in the isomer ratio. However, when the experiment was repeated in methanol-*d*, 84% of the sample recovered after aqueous work-up contained four deuteriums.<sup>9</sup> No specific cation effect on the final isomer ratio<sup>10</sup> of **5** was observed as the same isomer ratios were obtained when either lithium or potassium methoxide was employed in this reaction instead of sodium methoxide.

We felt the incorporation of four deuteriums suggested that a ring homologation rearrangement of the type shown in Chart I was occurring, and the constant

Chart I. Ring Homologation Reaction of Acyloin 5



cis-trans isomer ratio observed in the experiments suggested that this rearrangement might occur *via* the

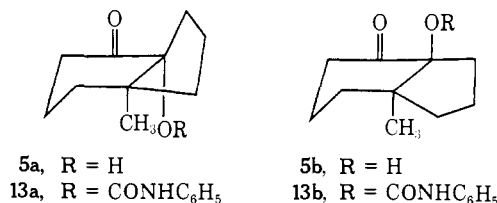
(8) C. C. Hinckley, M. R. Klotz, and F. Patil, *J. Amer. Chem. Soc.*, **93**, 2417 (1971).

(9) Deuterium content was determined using a Hitachi RMU6D mass spectrometer at 70 eV. Of the remainder of the sample, 13% was trideuterated and 1% was pentadeuterated. The latter is not significant in view of the accuracy limits of mass analysis and the probable existence of a small amount of OD remaining after the aqueous work-up.

(10) While it is possible that the rate of interconversion of **5a** and **5b** (see Chart I) was effected by the cation (See P. T. Lansbury and F. D. Saeva, *J. Amer. Chem. Soc.*, **89**, 1890 (1967)), we were concerned only with the isomer ratio.

breakdown of a common intermediate<sup>11</sup> such as **12**, leading to the thermodynamic mixture of **5a** and **5b**.

In order to provide additional evidence concerning the nature of this rearrangement, we sought a base labile derivative of **5** which would allow isolation of a single epimer.<sup>12</sup> To this end the mixture of *cis*- and *trans*-**5** obtained from the acyloin reaction was converted to phenylcarbamate **13** by treatment with phenyl isocyanate. The nmr spectrum of **13** showed two methyl singlets occurring at  $\delta$  0.90 and 1.19 in a ratio of 2.1 to 1, respectively, and were attributed to the *trans* and *cis* carbamates. Recrystallization of the carbamate mixture from  $\text{CHCl}_3$ -hexane gave a 15% yield of pure **13b** (mp 108–109°) as determined by nmr. Hydrolysis of **13b** in refluxing methanol-water con-



taining potassium hydroxide for 7 hr gave, after workup a 76% yield of a mixture of **5a** and **5b** in a ratio of 1 to 2.3. The isolation of a mixture of epimers of **5** from the hydrolysis of a single epimer of **13** shows that the *cis* and *trans* forms of **5** are interconvertible under the basic conditions of the hydrolysis and supports the existence of intermediate **12**.

Further work is now in progress on the reactions of acyloins **5a** and **5b**, and studies of the scope of this type of acyloin interaction are in progress.

**Acknowledgment.** This work was partially supported by the National Institutes of Health Grant No. AI 10389.

(11) Similar intermediates have been implicated in rearrangement of bicyclo[2.2.1]heptane systems. See A. Nickon, T. Nishida, and Y. Lin, *J. Amer. Chem. Soc.*, **91**, 6860 (1969), and references cited therein.

(12) Attempts to isolate epimers **5a** and **5b** by gas chromatography under a variety of conditions were unsuccessful.

Peter Y. Johnson,\* Matthew A. Priest

*Chemistry Department, The Johns Hopkins University  
Baltimore, Maryland 21218*

*Received April 4, 1974*

### Allenic Boranes. Their Preparation and Conversion into Alkylallenes<sup>1</sup>

Sir:

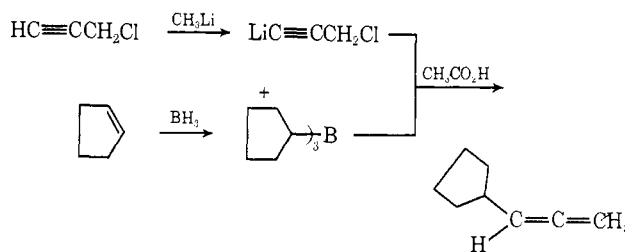
In our continuing investigations of the chemistry of organoboranes derived from functionally substituted acetylenes,<sup>2</sup> we have now uncovered a novel procedure for the preparation of allenic boranes<sup>3</sup> and, *via* their reaction with acetic acid, an operationally simple method for addition of the allene moiety to olefinic

(1) This research was supported by the National Science Foundation through Grant No. GP-26369.

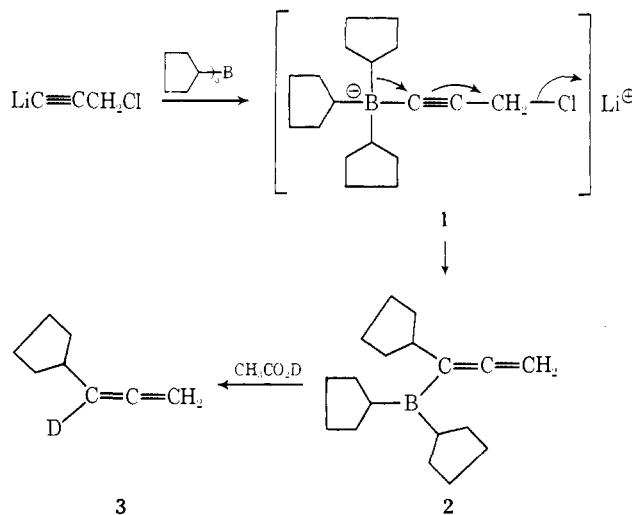
(2) G. Zweifel and H. Arzoumanian, *J. Amer. Chem. Soc.*, **89**, 5086 (1967); J. Plamondon, J. T. Snow, and G. Zweifel, *Organometal. Chem. Syn.*, **1**, 249 (1971); G. Zweifel and A. Horng, *Synthesis*, 672 (1973); *J. Amer. Chem. Soc.*, **96**, 316 (1974).

(3) It has been reported that sequential treatment of propargyl bromide with magnesium and trimethylborate produces a 36% yield of dimethoxyallenylborate [ $\text{CH}_2=\text{C}=\text{CHB}(\text{OCH}_3)_2$ ]. E. Favre and M. Gaudemar, *C. R. Acad. Sci., Ser. C*, **262**, 1333 (1966).

double bonds,<sup>4</sup> as represented by the specific example shown below.



Thus, addition of an equimolar amount of methyl-lithium in ether to propargyl chloride in tetrahydrofuran at  $-70$  to  $-60^\circ$  resulted in quantitative metalation of the acetylenic group. This was evidenced by the amount of methane evolved. The resultant lithium salt of propargyl chloride<sup>5</sup> was immediately treated with a solution of tricyclopentylborane in tetrahydrofuran while maintaining the temperature during the addition between  $-70$  to  $-60^\circ$ . The reaction was allowed to warm up to room temperature, then was examined by nmr and ir. The nmr spectrum revealed only a singlet at  $\delta$  5.65 in the vinyl proton region, and the ir spectrum exhibited an absorption band at  $1950\text{ cm}^{-1}$ . Thus both the nmr and the ir data point to formation of the 1,1-disubstituted 1,2-propadiene **2**.<sup>6</sup> Additional support for the proposed structure of the allenic borane **2** was obtained by its treatment with  $\text{CH}_3\text{COOD}$ . Nmr examination of the 1-cyclopentyl-1,2-propadiene formed indicated nearly exclusive incorporation of one deuterium at the 1-position of the 1,2-diene moiety (**3**).



The reactions leading to **2** may be depicted as follows. The ate complex **1**, formed by the reaction of tricyclopentylborane with the lithium chloropropargylide, undergoes a spontaneous anionotropic rearrangement in which one alkyl group migrates from boron to the

(4) Allenes may also be obtained by aqueous sodium hydroxide treatment of  $\beta$ -chlorovinylboranes, derived from the reaction of dialkylboranes with 1-chloro-2-alkynes. G. Zweifel, A. Horng, and J. T. Snow, *J. Amer. Chem. Soc.*, **92**, 1427 (1970).

(5) Addition of acetone to lithium chloropropargylide at  $-70^\circ$  produced a 90% yield of 1-methyl-5-chloro-3-pentyne-1-ol. Metalation of propargyl chloride with butyllithium has been described by L. Brandsma "Preparative Acetylenic Chemistry," Elsevier, New York, N. Y., 1971, p 77.

(6) Due to the complexity of the nmr and ir spectra resulting from the presence of THF and ether, no additional information as to other structural features of the allenic borane could be obtained.