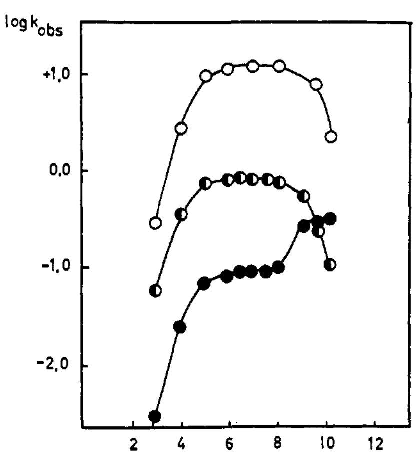


Figure 2. pH-rate profiles for catechol monosuccinate (**2a**, filled circles), catechol mono-*dl*-2,3-dimethylsuccinate (**2b**, semifilled circles), and catechol monotetramethylsuccinate (**2c**, open circles) at 25.0° in water containing 11% (by volume) acetonitrile.

mental error, which strongly supports the assumption that **2a** and **3** hydrolyze according to the same mechanism at pH > 8. Catechol monobenzoates **4** and **3** have previously been shown to undergo hydrolysis with intramolecular general base catalysis from the adjacent ortho phenolate group.[5] Furthermore, the solvent deuterium isotope effects for **2a** and **4** are identical (k_{H_2O}/k_{D_2O} = 1.8[6]), which points to a similarity in mechanism.

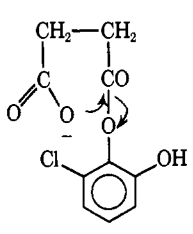
The absence of general acid catalysis in the hydrolysis of the catechol monosuccinates is evident from the small variation in the hydrolysis rates of the monosuccinates of phenol, *o*-methoxyphenol, and catechol (**2a**) (Table I). As can be seen from the pH-rate profiles of esters **2b** and **2c** (Figure 2), methyl substitution in the succinic acid moiety increases the rate of the intramolecular carboxylate ion catalyzed reaction (k_α) and decreases the rate of the intramolecular general base catalyzed reaction (relevant rate constants are summarized in Table I). The increase in k_α is caused by the accommodation of alkyl substituents in the carbon chain, the geminate dimethyl effect, which operates strongly in the cyclization of succinic acid derivatives,[7] while the retardation of the second mechanism is due to increased steric hindrance for the general base catalyzed attack of a water molecule at the ester carbonyl carbon atom. In addition, the pH-rate profile for **2a** shows that the intramolecular carboxylate catalysis must be unimportant when intramolecular general base catalysis by the adjacent ortho phenolate group is operating. This is not unexpected in view of the electrostatic repulsion introduced in the dianion of **2a**. It is, however, possible that the degree of intramolecular carboxylate ion participation at pH >8 increases as the succinic acid moiety becomes more substituted, which of course will make the participation of the adjacent ortho phenolate group less efficient.

Table I. Values of k_α[a] for the Hydrolysis of Substituted Aryl Hydrogen Succinates

Ester	k_α, min^{-1}
2a	0.093 (0.076[b])
2b	0.84
2c	12.3
Phenyl hydrogen succinate	0.085[b]
o-Methoxyphenyl hydrogen succinate	0.065 (0.072[b])

[a] k_α is the rate constant for hydrolysis *via* intramolecular carboxylate ion attack, *i.e.*, at the plateau of the pH-rate profile. [b] Reference 2a.

Thus, we have presented strong evidence for *competing* intramolecular nucleophilic and general base catalyzed mechanisms in the hydrolysis of catechol monosuccinates **2a**, **b**, and **c**. These mechanisms can be represented by formulas **5** and **6**. We believe that the difference in hydrolysis behavior between **1** and **2** can be rationalized in terms of a much weaker hydrogen bond between the free OH group and the ether oxygen of the ester group in **5** than in the corresponding anion of **1**.[8]



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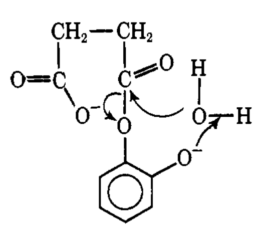

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[5] B. Capon and B. C. Ghosh, *J. Chem. Soc. B*, 472 (1966).

[6] Ratio of the rate constants based on the concentration of the ionized forms of the esters.

[7] L. Eberson and H. Welinder, *J. Amer. Chem. Soc.*, in press, and references cited therein.

[8] M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965); V. S. Korobkov, *Russ. J. Phys. Chem.*, **38**, 795 (1964).

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Cyclobutenes by Ring Expansion of Cyclopropenes

Sir:

We wish to report a new and general cyclobutene synthesis, in which lithium aluminum hydride mixed with aluminum chloride reductively expands the ring of readily accessible cyclopropenes. Our approach complements the known methods for obtaining cyclobutenes.[1] The following synthesis of 1,2-dipropyl-

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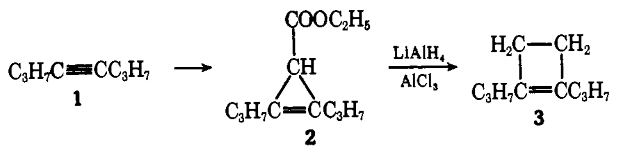
[1] One such scheme depends on the availability of properly substituted acylcyclopropanes, the tosylhydrazones of which are heated with alkoxide [*cf.* C. D. Gutsche and D. Redmore "Carbocyclic Ring Expansions," Academic Press, New York, N. Y., 1968, p 111; I. D. R. Stevens, H. M. Frey, and C. L. Bird, *Angew. Chem., Int. Ed. Engl.*, **7**, 646 (1968)]. Another preparation requires 1,3-butadienes, which can be photochemically cyclized [*cf.* K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965); W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Amer. Chem. Soc.*, **88**, 2742 (1966); H. M. Frey, *Trans. Faraday Soc.*, **59**, 1619 (1963)]. Other useful though less general methods have also been reported [*cf.* R. Fuks and H. G. Viehe in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, p 435].

cyclobutene (**3**) from ethyl 1,2-dipropyl-1-cyclopropene-3-carboxylate (**2**) exemplifies the method.



Lithium aluminum hydride (1.5 g; 38 mmol) was added to a stirred solution of aluminum chloride (5.2 g; 38 mmol) in absolute ether (40 ml) at $-80°$. The mixture was allowed to warm to room temperature and then boiled for 15 min. Ethyl 1,2-dipropyl-1-cyclopropene-3-carboxylate (**2**) (5.0 g; 25 mmol), obtained from 4-octyne (**1**) and ethyl diazoacetate[2] and dissolved in 30 ml of dry ether, was added dropwise to the stirred boiling solution. After another 15 min of warming, the mixture was brought to $-80°$ and was hydrolyzed with water and dilute sulfuric acid. The usual processing, including distillation, afforded homogeneous,[3] water-white 1,2-dipropylcyclobutene (**3**) in 80% yield.[4] Similarly, 1,2-diethylcyclobutene[5,6] was obtained from 1,2-diethyl-3-carbethoxycyclopropene[2] in 60% yield, and 1,2-dibutylcyclobutene[6] from 1,2-dibutyl-3-carbethoxycyclopropene[2] in 73% yield.

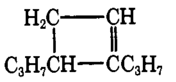
3-Acylcyclopropenes, accessible by treating the corresponding 3-carboxylic acids with organolithium reagents, or preferably by coupling the 3-acid chloride with organocadmium derivatives,[7] gave trisubstituted cyclobutenes. For example, 1,2-diethyl-3-benzoylcyclopropene[8] furnished 1,2-diethyl-3-phenylcyclobutene (54%), 1,2-dipropyl-3-butanoylcyclopropene[8] furnished 1,2,3,-tripropylcyclobutene (64%), and 1,2-dibutyl-3-pentanoylcyclopropene[8] furnished 1,2,3-tributylcyclobutene (61%).

Cyclopropenyl-3-carbinols also served as precursors. Thus, the primary carbinol 1,2-dipropyl-3-hydroxymethylcyclopropene[9] was reductively rearranged to 1,2-dipropylcyclobutene (40%) and the tertiary carbinol 1,2-dipropyl-3-(1'-hydroxy-1'-propyl)-butylcyclopropene[10] was reductively rearranged to 1,2,3,3-tetrapropylcyclobutene (61%).

Our results make it likely that the new method opens a convenient way to a variety of 1,2-dialkyl-, 1,2,3-trisubstituted, and 1,2,3,3-tetrasubstituted cyclobutenes. Where the groups in the starting cyclopropene are different, the derived disubstituted cyclobutene as in **3** will still appear as a single isomer, whereas derived tri- and tetrasubstituted cyclobutenes, *a priori*, should emerge as a pair of isomers. The method should be applicable also to the preparation of cyclobutenes carrying functional groups on the substituents so long as the functional group (*e.g.*, Cl or OH) is not affected by the mixed reagent or when reduction of the functional group is not critical.

The ring methylene units in all the cyclobutenes encountered here showed nmr signals at δ 2.18–2.19 ppm;[11] the lone ring methine hydrogen in the 1,2,3-trisubstituted cyclobutenes showed signals at δ 2.20–2.24 ppm. All the cyclobutenes absorbed in the infrared at 1675 cm^{-1}.

Structures analogous to that of cyclobutene **3** were assigned in preference to those of the *a priori* possible cyclobutene as in **4** or cyclopropene as in **5**. The choice rested on nmr and infrared evidence. For example, the nmr spectrum of the 1,2-dipropylcyclobutene (**3**) is fully consistent in chemical shifts, multiplicities, and integration values with the assigned structure. Of significance also is the absence of signals at lower field corresponding to the absence of olefinic protons[12] as in **4**. Since cyclopropene **5** was not available for direct comparison, we made use of the structurally related 1,2,3-tripropylcyclopropene.[2] This cyclopropene shows a four-proton signal at δ 2.3 ppm attributable to the two methylene groups directly attached to the ring unsaturation.[13] In contrast, in the curve for 1,2-dipropylcyclobutene (**3**), for example, the signal for two acyclic methylene groups next to the double bond appears at δ 1.93 ppm. Also, the infrared absorption spectra for 1,2,3-tripropylcyclopropene as well as for 1,2,3-tributylcyclopropene show characteristic maxima at 1855 and 1015–1005 cm^{-1}, whereas none of the cyclobutene products encountered in this work has these peaks.



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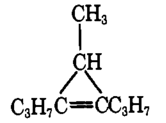

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As far as mechanism is concerned, a simple rationalization would call for reducing the cyclopropene

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(2) An adaptation of the directions of R. Breslow, H. Höver, and H. W. Chang [*J. Amer. Chem. Soc.*, **84**, 3168 (1962)] and P. F. Wolf [Ph.D. Dissertation, Columbia University, 1964, through University Microfilms (order no. 65-14014, *Diss. Abstr.*, **26**, 4251 (1966)] gave the dipropylcyclopropene in 86% yield (70% conversion). In the same way, 1,2-diethyl-3-carbethoxycyclopropene was prepared in 86% yield (43% conversion), and 1,2-dibutyl-3-carbethoxycyclopropene [*cf.* R. R. Kostikov and I. A. D'Yakanov *J. Gen. Chem. USSR*, 32, 2358 (1962)] in 87% yield (69% conversion).

(3) The compounds used in this work were homogeneous according to gas–liquid or thin-layer chromatography and showed the expected spectroscopic properties. New compounds had the correct carbon and hydrogen content.

(4) In most of the examples reported here no attempt was made to develop optimal conditions.

(5) *Cf.* T. C. Shields D. W. Peck, and A. N. Kurtz, *Chem. Ind.* (*London*), 269 (1969).

(6) The diethyl and the dibutyl reductive rearrangements were performed by adding a mixture of the cyclopropene with an equimolar amount of aluminum chloride to the lithium aluminum hydride–aluminum chloride combination. This procedure, used at first, was abandoned when the simpler method was found to be effective.

(7) *Cf.* R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967); R. Breslow and M. Douek, *ibid.*, **90**, 2698 (1968); M. Vidal, E. Chollet, and P. Arnaud, *Tetrahedron Lett.*, 1073 (1967); I. Moritani and N. Obata, *ibid.*, 2817 (1965).

(8) The benzoyl compound was obtained from the cyclopropene ester by saponification, conversion of acid to acid chloride, and organocadmium coupling in 60% overall yield. The butanoyl compound was obtained similarly in 71%, the pentanoyl compound in 49% yield.

(9) Obtained in 90% yield by reducing the acid chloride of 1,2-dipropylcyclopropene-3-carboxylic acid with lithium aluminum hydride. Wolf[2] prepared the same carbinol from the corresponding ester in 65% yield.

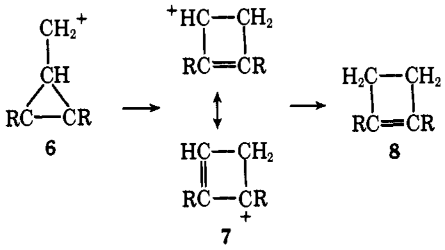
(10) Addition of 2 mol of propylmagnesium bromide to ethyl 1,2-dipropyl-1-cyclopropene-3-carboxylate gave this compound in 74% yield.

(11) R. Srinivasan [*J. Amer. Chem. Soc.*, **84**, 4141 (1962)] reported a chemical shift of δ 2.2 ppm for the ring protons of 1,2-dimethylcyclobutene.

(12) The cyclobutene olefinic protons absorb at δ 5.6–6.0 ppm; *cf.* J.-L. Ripoll and J.-M. Conia, *Bull. Soc. Chim. Fr.*, 2755 (1965); E. Gil Av and J. Shabtai, *J. Org. Chem.*, **28**, 2893 (1963); **29**, 257 (1964).

(13) This chemical shift corresponds to those observed for other analogously constituted cyclopropenes. Thus, 1-chloro-7,8-methano-7-hexadecene absorbs at δ 2.39, methyl malvalate at 2.36, and malvalonitrile at 2.42 ppm [W. J. Gensler, K. W. Pober, D. M. Solomon, and M. B. Floyd, *ibid.*, **35**, 2301 (1970)].

ester or ketone function by action of the reagent pair[14] to the alcohol stage. Thereafter, development of electron deficiency at the external carbon (*cf.* **6**) would lead to a Wagner–Meerwein rearrangement with ring expansion to the cyclobutene cation (*cf.* **7**). Delivery of hydride ion would complete the processes and form the cyclobutene product (*cf.* **8**). The **6**–**7** ring expansion has been reported before,[15] though without trapping the four-membered ring system as we have done here. Questions about the nature of the ionic intermediates[15] and why only product **3** and none of **4** or **5** is obtained will be reserved for a more detailed treatment.



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[14] According to E. C. Ashby and B. Cooke (*J. Amer. Chem. Soc.*, **90**, 1625 (1968)), E. C. Ashby and J. Prather (*ibid.*, **88**, 729 (1966)), and E. L. Eliel (*Rec. Chem. Progr.*, **22**, 129 (1961)), a 1:1 mixture of lithium aluminum hydride and aluminum chloride may be regarded as monochloroaluminum dihydride (H_2AlCl), which is an effective reducing agent as well as a strong Lewis acid.

[15] R. Breslow and M. Battiste, *J. Amer. Chem. Soc.*, **82**, 3626 (1960); R. Breslow, J. Lockhart, and A. Small, *ibid.*, **84**, 2793 (1962).

[16] NASA Predoctoral Trainee, 1967–1970.

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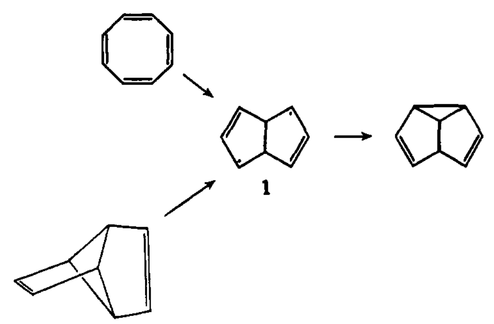
Synthesis and Thermal Reorganization of 1,2,5,6-Tetramethyl-3,4,7,8-tetramethylenecyclooctadiene

Sir:

The diradical **1** has recently been implicated in a number of thermal reorganizations. It is a probable intermediate in both the thermal rearrangement of octamethylcyclooctatetraene to octamethylsemibullvalene[1,2] and of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene to semibullvalene.[3,4]

If **1** is indeed a common intermediate in these two rearrangements leading to semibullvalene, it ought to prove possible to observe the equilibration *via* **1** of an appropriate cyclooctatetraene derivative with the corresponding tricyclo[3.3.0.0^{2,6}]octadiene, provided that the exit to semibullvalene is blocked. Indeed, Stiles has postulated just such an equilibration to account for the thermal isomerization of 5,6- to 5,11-substituted dibenzocyclooctatetraenes.[5] In these benzocyclooctatetraenes the incorporation of the radical stabilizing double bonds of **1** into benzene rings renders unfavorable the conversion to semibullvalene, which would necessitate destruction of the aromaticity of one of the benzene rings.



Another mode of foiling the conversion of the diradical to semibullvalene would be to position the stabilizing double bonds exocyclic to the bicyclo[3.3.0]ring system. This should allow equilibration of a dimethylene-substituted cyclooctadiene with the corresponding tricyclo[3.3.0.0^{2,6}]cyclooctane, while making semibullvalene formation inpossible. We herein report the experimental realization of this expectation in the thermal reorganization of 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenecyclooctadiene (**3**) to 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (**4**).

Synthesis of a 1,2,5,6-tetramethylenecyclooctadiene was of interest to us as an extension of our studies of the chemistry of 1,2,5,6-tetramethylenecyclooctane.[6] Employing an approach to a member of the former class of compounds which had proven successful in our synthesis of the latter,[7] we carried out the benzophenone-sensitized irradiation of 1,2-dimethyl-3,4-dimethylenecyclobutene. From the crude photolysate a single photodimer[8] was obtained in 50% yield. The nmr spectrum of this material showed three sharp singlets at ($CDCl_3$) δ 1.05, 4.70, and 5.27 in the ratio 3:1:1, indicating the gross structure **2** for the product.[9,10] The anti stereochemistry of **2** was established by reduction to the octamethyltricyclooctadiene,[9] either catalytically[11] or using lithium in ammonia–tetrahydrofuran-*tert*-butyl alcohol. The nmr spectrum of the product was similar to but distinguishable from that of authentic *syn*-octamethyltricyclo[4.2.0.0^{2,5}]-octa-3,7-diene[12] and the melting point was in acceptable agreement with that reported for the anti compound.[13]

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[1] R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **7**, 537 (1968).

[2] Diradical **1** has also been proposed as an intermediate in the rearrangement of cyclooctatetraene to dihydropentalene; M. Jones, Jr., and L. O. Schwab, *J. Amer. Chem. Soc.*, **90**, 6549 (1968).

[3] (a) J. Meinwald, D. Schmidt, and H. Tsuruta, *ibid.*, **91**, 5877 (1969); (b) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

[4] Photochemical interconversion of $(CH)_8$ isomers has also been studied: (a) H. E. Zimmerman and G. L. Grunwald, *ibid.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968); (d) J. Meinwald and H. Tsuruta, *ibid.*, **92**, 2579 (1970).

[5] (a) M. Stiles and U. Burckhardt, *ibid.*, **86**, 3396 (1964); (b) M. Stiles (19th National Organic Symposium, Tempe, Ariz., June 1965, p 62) has also presented strong evidence for the intermediacy of the biradical in these reactions.

[6] W. T. Borden, I. L. Reich, L. A. Sharpe, and H. Reich, *J. Amer. Chem. Soc.*, **92**, 3808 (1970).

[7] W. T. Borden, L. A. Sharpe, and I. L. Reich, *Chem. Commun.*, 461 (1970).

[8] The crystalline photodimer decomposes rapidly unless stored at Dry Ice temperature.

[9] Spectral and analytical data were in accord with this proposed structure.

[10] It is of some interest that the photodimerization takes place exclusively at what is the most sterically hindered double bond.

[11] 1,2-Dimethylenecyclobutanes generally add hydrogen 1,4 when a 5% palladium on carbon catalyst is used; R. Stafford, Ph.D. Thesis, Harvard, 1971.

[12] Prepared by the procedure of R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).