Research (Grant No. AF-AFOSR-69-1769) is gratefully acknowledged.

(20) National Institutes of Health Predoctoral Fellow, 1963–1965.
* Address correspondence to this author.

G. Büchi,* K. M. Snader, J. D. White[20]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

J. Zanos Gougoutas, Sarjant Singh
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received August 18, 1970

Tricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene[1]

Sir:

The title compound (**1**, isobullvalene)[2] appears to have revived interest in some transformations of (CH)$_{10}$ hydrocarbons and has been proposed as an unstable intermediate of some chemical reactions.[3,4] We have recently developed techniques which enable us to purify and characterize thermally unstable compounds such as [10]annulenes[1,5] and oxonins,[6] and the application to the present problem has led to the isolation of **1** without difficulty. We wish to outline briefly the apparatus employed for purification at cold temperatures and further to report the intriguing chemistry of **1** and its related compounds.

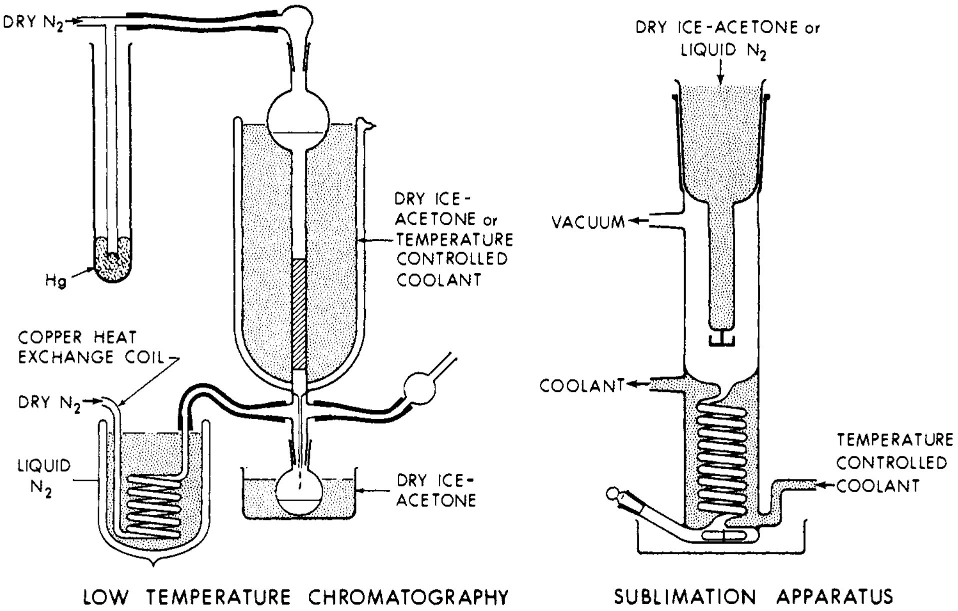


Figure 1. Equipment for low-temperature separation.

Figure 1 shows our typical equipment utilized for precisely temperature-controlled distillation (or sublimation) and low-temperature (down to −80°) chromatography and it is self-explanatory. This apparatus allows one to perform the entire work-up process below −50° and therefore most of the compounds which are surrounded by, at minimum, a 15 kcal/mol energy barrier, can be isolated.

Thus, reaction of cyclononatetraenide (**2**) with methylene chloride and *n*-butyllithium,[3,7] performed at −60° (1.25 hr) and quenched by methanol at −80°, provided a new (CH)$_{10}$ hydrocarbon by distillation at −13° (10^{-4} mm) and alumina chromatography at −80°. Its nmr spectrum (100 MHz, CDCl$_3$ at −40°) is shown in Figure 2 and is obviously compatible with the structure of **1** and corresponds well to that of its 3,4-benzo analog.[4] Catalytic hydrogenation of **1** with Rh-on-carbon at −80°[5,6] afforded three fully saturated compounds, the major product being the tricyclic compound (80%, *m/e* 136) corresponding to **1** and identical with that synthesized through an independent route.[8] The other two minor products were bicyclic (9 and 9%, *m/e* 138). These results clearly demonstrate that compound **1** is tricyclo[5.3.0.0^{2,10}]decatriene, and this structural assignment was further substantiated by its thermal conversion to **4** (*vide infra*). The synthesis is illustrated in Scheme I.

A more intriguing finding in the above reaction (**2** + CH$_2$Cl$_2$) was that the cold (−60°) reaction mixture con-

---

(1) Presented on June 17, 1970 before the Gordon Conference (Hydrocarbon) at Andover, N. H., as a part of the general subject entitled "The chemistry of some cyclic systems." The synthesis of pure (*cis*)^5-[10]annulene was also announced.

(2) This name was suggested for this hydrocarbon by L. A. Paquette and J. R. Malpass, *J. Amer. Chem. Soc.*, 90, 7151 (1968).

(3) T. J. Katz and J. J. Cheung, *ibid.*, 91, 7772 (1969). Compound **2** did not react with CH$_2$Cl$_2$ in the absence of butyllithium even at −25° (3 hr). The condensation occurred only after the addition of the last reagent to the reaction mixture.

(4) E. Vedejs, R. A. Shepherd, and R. P. Steiner, *ibid.*, **92**, 2158 (1970).

(5) S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969).

(6) S. Masamune, S. Takada, and R. T. Seidner, *J. Amer. Chem. Soc.*, **91**, 7769 (1969).

(7) Treatment of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene with lithium at −65° for 3 hr [*cf.* T. J. Katz and P. J. Garratt, *ibid.*, **86**, 5194 (1964); G. LaLanatte and R. E. Benson, *ibid.*, **87**, 1941 (1965)] provided a lithium salt mixture of mono-*trans*-cyclononatetraenide [**3**, 70%, see G. Boche, D. Martens, and W. Danzer, *Angew. Chem., Int. Ed. Engl.*, **8**, 984 (1969)] and all-cis compound (**2**, 30%). Geometrical isomerization of **3** to **2** proceeded at 10°. Addition of excess methanol to the cold mixture effected protonation of only anion **3** at −80°, producing *all-cis*-cyclononatetraene, whereas **2** remained anion up to −10°. These results indicate that **3** is far more basic than **2**, as expected, and the site of protonation of **3** is specific.

(8) From 3-bromocycloheptene, using conventional methods: W. von E. Doering, *et al.*, *Tetrahedron*, **21**, 25 (1965).

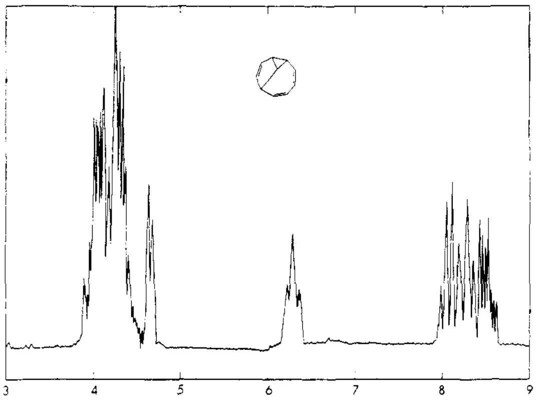
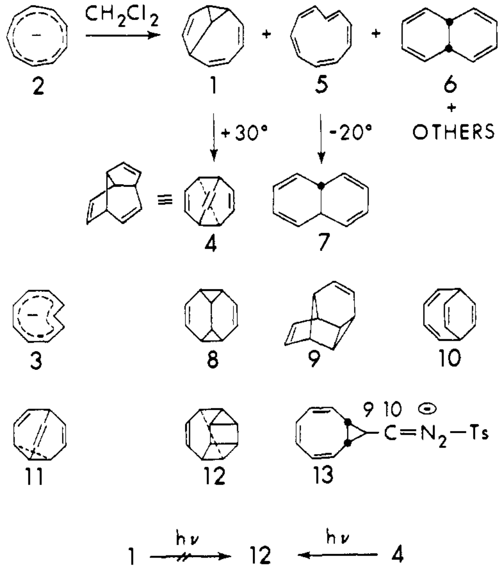


Figure 2. Nmr spectrum of **1**.

tained *trans,(cis)*^{4}-[10]annulene (**5**, 14%), *cis*-9,10-dihydronaphthalene (**6**, 14%), and other unidentified compounds in addition to the major product **1** (55%). At this temperature *(cis)*^{5}-[10]annulene is stable,[1,5] but was not found in the reaction mixture. Compound **5** exhibited uniquely temperature-dependent nmr spectra between −30 and −80° and was isomerized around −20° to *trans*-9,10-dihydronaphthalene (**7**).[5] Upon further warming to 30°, the signals due to **4** began to appear at the expense of those of **1**. Hydrogenation of the cold mixture performed in a manner similar to that applied to other systems[5,6] confirmed the composition of the products mentioned above, yielding cyclodecane (15%), the hydrogenation products (*vide supra*) of **1** (combined yield, 45%) and *cis*-decalin (18%).[9]

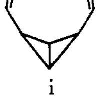
Scheme I



Thermolysis of **1** in $CDCl_3$ was readily followed by nmr spectroscopy and as expected **1** was converted to **4** quantitatively: k at 11.1° = $(7.15 \pm 0.33) \times 10^{-5}$ sec^{-1}, k at 30.8° = $(6.90 \pm 0.15) \times 10^{-4}$, $\Delta H^{\ddagger} = 19.3 \pm 0.8$ kcal/mol, and $\Delta S^{\ddagger} = -10 \pm 2.8$ eu. A constant-temperature liquid bath was employed to control the temperatures, and the integration of nmr signals was performed at −30°. Photochemical reaction of **1** in THF-d_8 at −85° (where no thermolysis of any photoproducts occurred) was rather inefficient, and after irradiation for 5 hr by a low-pressure mercury lamp[10] provided **8** (14%), **9** (10%), **7** (9%), and **6** (7%) (nmr and glc analysis) in addition to 60% recovery of **1**. Comparing the structure of **1** with those of the products, explanations can be offered by invoking diradical species derived from **1** or concerted, photoinduced bond reorganization, but the actual pathways are undoubtedly very complex.

Finally brief comments are made concerning the explanations offered recently[3] for photoisomerizations of some $(CH)_{10}$ compounds. In contrast to the previous reports on room-temperature irradiation of **10** and **11** (2537 Å),[11] photolysis of these compounds (0.25 *M*, THF-d_8) at −100° reached, within 90 min under our standard conditions,[10] a photostationary mixture, consisting of **8** (40–*ca.* 50%), **11** (30%), and four minor products (all known compounds and identified), and this composition changed only slightly upon further irradiation (6 hr). Examination of the minor products revealed that, while **1** existed in minute quantities (2–3%), **9** and **12**[11] were also present. Since **4** photoisomerized readily to give **12** under the conditions used but **1** did not (*vide supra*), the above results would indicate (at least, would not eliminate) the possibility of the direct pathway from **11** to **4**.[12] Similarly, although we confirmed the formation of **1** by photodecomposition of the sodium salt of **13**,[13] repeated[14] deuterium-labeling experiments using the 9,10-dideuterated derivative of **13** showed the presence of deuterium in not only the aliphatic but also the olefinic positions of **4** after room-temperature work-up, and the mechanistic pathway leading to **4** has not yet been made conclusive, possibly dual in nature. We have studied extensively the photochemistry of most of the known $(CH)_{10}$ hydrocarbons and plan to present detailed discussions in full papers.

(9) A pathway leading to **5** might involve another intermediate i,



i

which could be formed by carbene addition to the appropriate double bonds of the ring and is expected to be extremely thermally unstable to provide **5**. However, this mechanism is nothing more than speculative at the present time.

(10) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 5286 (1968).

(11) M. Jones, Jr., *ibid.*, **89**, 4236 (1967); W. von E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967); M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970).

(12) A referee suggested we add the following explanation to clarify this sentence: (a) **4** gives **12**; (b) **1** gives *very* little **12** if any; (c) **11** gives **12**, probably *via* **4**; (d) **1** does not go to **4** under the conditions. Therefore **11** probably goes directly to **4**, not to **4** *via* **1**.

(13) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Amer. Chem. Soc.*, **89**, 4804 (1967); S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 2727 (1968).

(14) Presumably because this product distribution was very sensitive to the reaction temperature and because of the formation of insoluble sodium tosylsulfinate during the photolysis, we have so far failed to obtain very consistent results.

* Address correspondence to this author.

K. Hojo, R. T. Seidner, S. Masamune*

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Received June 22, 1970