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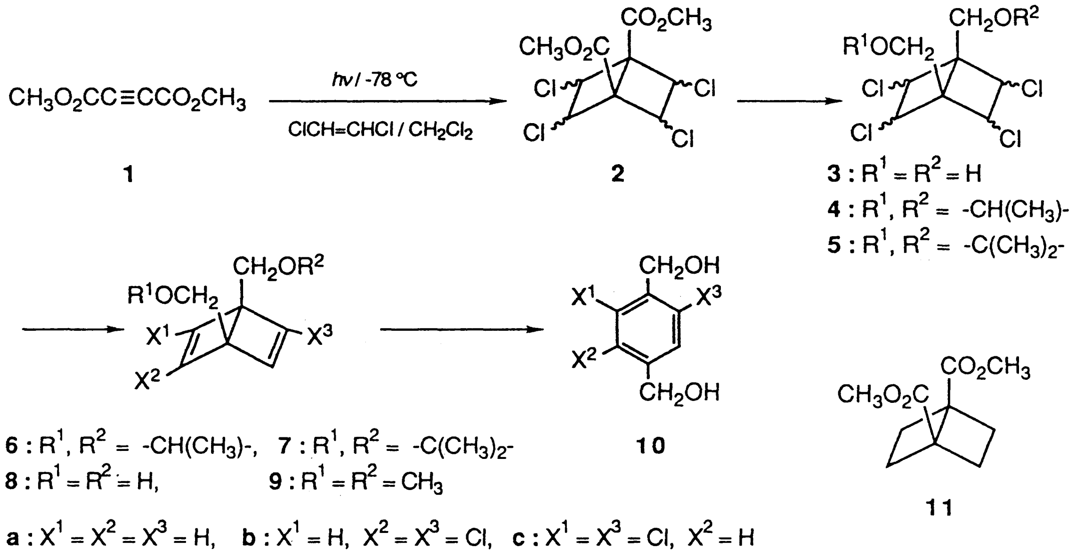
Convenient Synthesis of Some Functionalized Dewar Benzenes and Effect of Chlorine Substitution on the Rates of Their Aromatization

Takashi TSUJI,* Harumi WATANABE, Jun TANAKA,
Mari INADA, and Shinya NISHIDA
Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060

1,4-Bis(hydroxymethyl) Dewar benzenes were prepared in five steps from dimethyl acetylenedicarboxylate in ca. 10% overall yield and rates of their aromatization were measured: dichloro substitution at both the 2,5- and 2,6-positions led to substantial deceleration of the isomerization.

Dewar benzene is of considerable interest in preparative and physical organic chemistry. By exploiting its high strain energy and ready isomerization to benzene upon heating or irradiation of light, a variety of structurally distorted benzene derivatives have been synthesized from the corresponding Dewar derivatives.[1)] It is also known that electronically excited benzene is thermally accessible from the Dewar isomer, owing to the high heat of formation of the latter[2)] and chlorinated derivatives exhibit increased chemiexcitation efficiencies.[3)] Although a variety of synthetic methods for Dewar benzene have been developed so far,[1a,4)] further exploration of easy access routes to variously functionalized derivatives is highly desirable. Herein we report a simple, efficient preparation method for some functionalized Dewar benzenes.

Irradiation of dimethyl acetylenedicarboxylate (**1**) in a 1:1 mixture of (E)-1,2-dichloroethene and dichloromethane with a high pressure mercury lamp through Pyrex at -78 °C afforded a mixture of bicyclo[2.2.0]hexanes **2** in 68% yield, from which five out of seven possible stereoisomers were subsequently isolated and identified.[5)] The high thermal stability of these adducts as compared with **11**[6)] was rather unexpected but quite welcome, since **2** could be readily purified by distillation under reduced pressure. $LiAlH_4$ reduction of the mixture followed by treatment of resultant diols **3** with 1,1-dimethoxyethane or 2,2-dimethoxypropane in the presence of a catalytic amount of p-toluenesulfonic acid (TsOH) in benzene provided the corresponding acetals **4** or **5** in 45-50% yield. Reductive



Scheme 1.

dechlorination of **4** with five mol equivalents of disodium-phenanthrene7) in 1,2-dimethoxyethane afforded **6a** in 40% yield, while dehydrochlorination of **4** with three equivalents of sodium amide in liquid ammonia produced **6b** and **6c** in a ratio of 2:3 in 37% yield in total, which were subsequently isolated by preparative GLPC. Deacetalization of these products in TsOH-methanol provided the corresponding diols **8a-c** in 55-75% yield.8) Differentiation between **8b** and **8c** was readily made by examining their ^{1}H NMR spectra; methylene protons in **8b** gave rise to an AB quartet signal, while those in **8c** two singlet signals.

Reductive dechlorination of 1,2-dichlorocyclobutanes with sodium in liquid ammonia is an established procedure for the synthesis of cyclobutene derivatives1a,9) and resultant cyclobutenes are generally inert toward excess sodium under the reaction conditions. Attempts to apply this methodology to **4** and **5**, however, met with difficulty. Thus, the addition of **5** to ten equivalents of sodium in liquid ammonia at -60 °C produced none of **7a**, but led instead to the formation of **12** and p-methylbenzyl alcohol (**13**) in 9% and 53% yields, respectively. The formation of **12** and **13** suggests that **7a** readily suffers overreduction. Treatment of **7a** with sodium in liquid ammonia, in fact, afforded a 1:6 mixture of **12** and **13** in good yield. Thus, the reduction potential of **7a** is substantially more anodic, compared with that of a simple cyclobutene, probably owing to electronic interactions between the two π bonds and/or increased bond-angle strain.10)

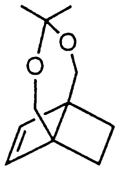
Breslow and coworkers reported sometime ago that substitution of a bridgehead proton of Dewar benzene by chlorine as in **14b** made its isomerization to benzene much faster, but that a second chlorine reversed the effect.11) They rationalized the former accelerating effect in terms

Table 1. Rates and Activation Parameters for the Thermal Rearrangement of Dewar Benzenes

Compound	10^4k_1 at 75 °C s^{-1}	Rel. Rate at 75 °C	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}
8aa)	1.22	1.0	107 ± 1.0	-12 ± 2.8
8ba)	0.0199	0.016	122 ± 4.2	-3.6 ± 11
8ca)	0.0505	0.041	120 ± 0.8	-3.1 ± 1.8
9ab)	2.40	2.0		

a) In 1-butanol. b) In octane.

of push-pull stabilization of an antiaromatic transition state leading to benzene. In order to gain a further insight into substituent effect on the thermal stability of Dewar benzene with respect to isomerization to benzene, rates of the isomerization of **8a-c** were measured in 1-butanol by monitoring the development of electronic absorptions due to **10a-c**, which followed first-order kinetics up to at least 80% conversion. As summarized in Table 1, the substitution of olefinic carbons with chlorine led to retardation of the isomerization irrespective of substitution pattern.12) Thus, chlorine substituents on the olefinic carbons of Dewar benzene appear to exert only decelerating effect on its thermal rearrangement to benzene. Although the reason why **8b,c** are thermally stabilized by the chlorine substituents is not quite clear, increment in torsional strain caused by the chlorine substitution on going from **8** to a transition state might be responsible for the increased thermal stability of **8b,c** compared with **8a**. The fact that the difference in the thermal stability of **8a-c** is primarily due to difference in activation enthalpy is consistent with the above rationalization.



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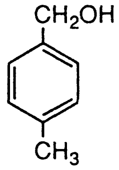

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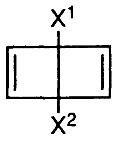

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a : $X^1 = X^2 = H$
b : $X^1 = H$, $X^2 = Cl$
c : $X^1 = X^2 = Cl$

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8) **8a**: mp 30.3-32.5 °C; ^{1}H NMR($CDCl_3$) δ = 1.96 (br s, 2H), 4.02 (s, 4H), 6.56 (s, 4H). **8b**: mp 75.5-77 °C; ^{1}H NMR($CDCl_3$) δ = 2.16 (br s, 2H), 4.02 (d, J = 13.2 Hz, 2H), 4.05 (d, J = 13.2 Hz, 2H), 6.32 (s, 2H). **8c**: mp 85-86 °C; ^{1}H NMR($CDCl_3$) δ = 1.75 (br s, 2H), 4.05 (s, 2H), 4.07 (s, 2H), 6.28 (s, 2H).

9) E. L. Allred, B. R. Beck, and K. J. Voorhees, J. Org. Chem., **39**, 1426 (1974).

10) The reduction of **7a** is considered to proceed by initial electron transfer from sodium followed by protonation (H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, California (1972), Chap. 3). Probable mechanism for the formation of **12** and **13** will be discussed in a full paper.

11) R. Breslow, J. Napierski, and A. H. Schmidt, J. Am. Chem. Soc., **94**, 5906 (1972). Rates of the rearrangement of **14a-c** have been reported to be 5.18×10^{-6}, 4.64×10^{-4}, and 8.4×10^{-9} s^{-1}, respectively, at 24.3 °C. According to given activation parameters, however, that of **14c** should be 8.4×10^{-8} s^{-1} at 24.3 °C, hence k_1(**14a**)/k_1(**14c**) = 60 rather than 600.

12) The similar thermal stability of **8a** and **9a** suggests that hydrogen bonding in the former does not exert appreciable effect on the rate of aromatization under the present conditions.

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