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THE STRUCTURES OF THE DICHLOROCARBENE ADDUCTS OF HEXAMETHYLDEWARBENZENE

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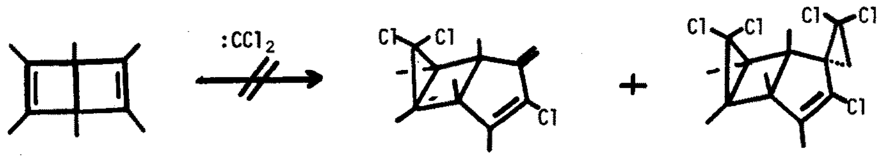
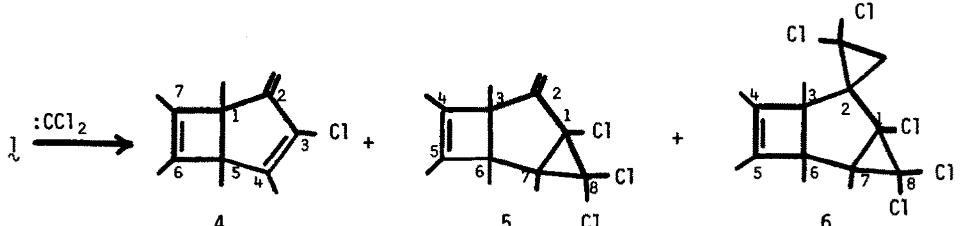
It was reported[1] that dichlorocarbene gives two adducts with hexamethyldewarbenzene (1); the structures were formulated as 2 and 3. We wish to report that both structures were incorrectly assigned, that there is a third adduct, and that one of the adducts serves as an excellent precursor of the bicyclic ketone 7.



1 2 3

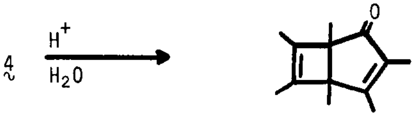
Treatment of 1 (810 mg) in chloroform (1.19 g) containing ethanol (32 µl) and triethylbenzylammonium chloride (16 mg) with 50% aqueous sodium hydroxide (3.3 ml) for 1 hr at room temperature[2] gave, after hydrolysis, methylene chloride extraction, and column chromatography (Alcoa F-1 alumina, petroleum ether eluent) three products to which we assign structures 4, 5 and 6.



4 5 6

The compound to which we assign structure 4 appears to be the same compound previously assigned structure 2. It had a mp of 25° (reported[1] 24°), gave analytical data corresponding to $C_{13}H_{17}Cl$[3] and its mass spectrum showed a molecular ion peak at m/e 210, 208.[4] The pmr spectrum of 4 (CCl_4) was almost identical with that previously reported for 2[6]: δ1.10, 1.13 (3H each, s, C1 and C5 methyls), 1.50-1.54 (6H, m, homoallylically coupled methyls at C6 and C7), 1.85 (3H, s, C4 methyl), 4.70, 5.01 (1H each, vinyl protons).

Acid hydrolysis of **4**[7] gave **7**, mp 62-63°, in 65% yield. The structure of **7** follows from its spectral data[8], independent synthesis[9], and chemical transformations.[10] The formation of **7** from **4** clearly requires that **4** be derived from a 1:1 adduct of dichlorocarbene and **1**. Presumably **4** arises from the undetected adduct **8**.[11]



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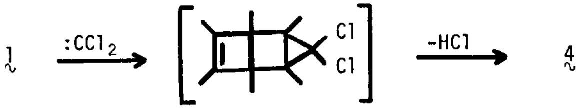

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From the results shown in the Table, it is clear that **5**[12] is formed by addition of dichlorocarbene to **4**. Consequently it must have either structure **5** or **2**, since the spectral data[13] show that the terminal methylene group is still present. The chemical shift data and expected homoallylic coupling between adjacent methyls on the C4-C5 double bond are only consistent with structure **5**. The difference in the uv spectra of **4** and **5** provides further confirmation of the structural assignment (in methanol, **4** has a λ_{max} at 241 nm (log ε4.10) whereas **5** showed a shoulder at 235 nm, and end absorption at 210 nm).

The compound to which we assign structure **6** is identical with the compound previously[1] assigned structure **3**. The data in the Table show that **6** is formed by the addition of dichlorocarbene to **5**. Since the spectral data[14] show that the vinyl methylene protons are no longer present, structure **6** must be correct. The observed coupling between the adjacent methyls on C4

Table 1. Yields of Adducts as a Function of Reaction Conditions

Starting Material	Mol Ratio of $CHCl_3$ to Starting Material	Reaction Time (hr)	Products (%)[15]		
			4	**5**	**6**
1	2	1	47	26	1
1	3	2	13	36	32
1	10	3	-	30	59
4	2	3	-	35	29
5	3	2	-	-	57
6	5	10	-	-	85

and C5 is expected and there is no need to call upon unusual long-range coupling[1] to rationalize the pmr spectrum. As the Table shows, the remaining double bond in **6** is inert to further attack by dichlorocarbene.

Use of bromoform in place of chloroform gave mono- and pentabromo adducts which correspond in structure to **4** and **6**.

In summary, hexamethyldewarbenzene reacts with dichlorocarbene to give **4** which reacts further with dichlorocarbene to give **5**, then **6**. Compound **4** can be hydrolyzed to **7**. The stereochemistry of **5** and **6** remains to be elucidated.

Acknowledgement. We are indebted to the National Institutes of Health (GM 15997) for financial support of this research.

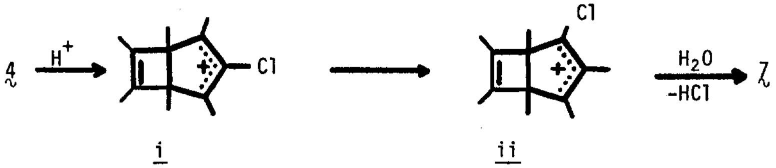
REFERENCES AND FOOTNOTES

1. E. V. Dehmlow, *Tetrahedron*, **28**, 175 (1972).
2. M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.*, 4659 (1969); M. Makosza and M. Fedorynski, *Synth. Commun.*, **3**, 305 (1973).
3. The compound decomposes (darkens) quickly on standing, as reported;[1] consequently our best analytical data[5] are 1% off of theory. However the data are clearly more consistent with **4** than with **2** [Calcd for **4**: C, 74.44; H, 6.28; Calcd for **2**: C, 57.65; H, 5.88; Found: C, 73.30; H, 7.58].
4. One may well ask how it would be possible to mistake **4** for **2**; no analytical data were reported, but a parent peak in the mass spectrum was reported at m/e 290. One possible explanation for the discrepancy in mass spectra would be if the sample used previously[1] for the mass spectrum was contaminated with **5**.
5. *Spang Microanalytical Laboratory, Ann Arbor, Michigan.*
6. The only discrepancy is the singlet at δ1.13 which was previously reported[1] at δ1.34. We have no explanation for the difference.
7. **4** (546 mg) in methanol (15 ml) was treated with concentrated sulfuric acid (5 ml) at 0° for 3 hr, then hydrolyzed and worked up.
8. Ir (KBr) 1680, 1635 cm^{-1}; $\lambda_{\mathrm{max}}^{\mathrm{MeOH}}$ 231 nm (ε4790), 340 (60); pmr (CCl_4) δ1.07, 1.16 (3H each, s, C1 and C5 methyls), 1.57 (9H, m, C3, C6 and C7 methyls), 1.95 (3H, q, *J*=1.2Hz, C4 methyl); m/e (rel intensity) 190 (10), 147 (100).

9. **7** was one (31% yield) of four products isolated from the methylation with methyl iodide of 4,5,6,7,8-pentamethylbicyclo[3.2.0]hepta-3,5-dien-2-one [H-N. Junker, W. Schäfer and H. Niedenbrück, Chem. Ber., **100**, 2508 (1967)] in DMSO containing t-BuOK; H. Hart and M. Nitta, unpublished results.

10. H. Hart and M. Nitta, Tetrahedron Lett., see following paper.

11. The mechanism for the conversion of **4** to **7** is not yet established. One possibility is shown. The conversion of i to ii may involve a chlorohexamethyltropylium ion, or may involve a sequence of 1,2-shifts.



12. This product was not previously[1] observed.

13. **5** is a colorless oil; ir (neat) 880 cm^{-1}; pmr (CCl_4) δ1.08, 1.28, 1.38 (3H each, s, C3, C6 and C7 methyls), 1.43, 1.65 (3H each, q, J=1.5Hz, C4 and C5 methyls), 5.05, 5.38 (1H each, s, vinyl protons); λ_{max}^{MeOH} 235 nm (sh), end absorption at 210 nm; m/e (rel intensity) 292 (1), 290 (2), 119 (100). Calcd for $C_{14}H_{17}Cl_3$: C, 57.65; H, 5.88. Found:[5] C, 57.42; H, 5.71.

14. We find mp 124-125°; ir (KBr) 2960, 1700, 1452, 1420, 1235, 1075, 1050, 905, 885, 862, 795 765, 742 cm^{-1}; pmr (CCl_4) 1.15, 1.27, 1.40 (3H each, s, C3, C6 and C7 methyls), 1.50, 1.63 (3H each, q, J=1.5Hz, C4 and C5 methyls), 1.69, 2.07 (1H each, d, J=8.2Hz, methylene); λ_{max}^{MeOH} end absorption only; m/e (rel intensity) 341 (24), 339 (47), 337 (38), 241 (100); Calcd for $C_{15}H_{17}Cl_5$: C, 48.24, H, 4.42; Found:[5] C, 48.25; H, 4.50.

15. All yields are of isolated, purified product.