Tetrahedron Letters No.14, pp. 1113-1116, 1969. Pergamon Press. Printed in Great Britain.

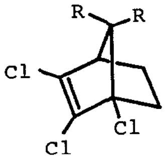
THE SYNTHESIS OF 1,2,3-TRICHLORO- AND 2,3-DICHLOROBICYCLO[2.2.1]HEPT-2-EN-7-ONE.

A SELECTIVE REDUCTION OF BRIDGEHEAD CHLORINE.

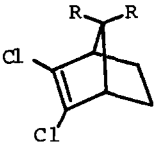
William H. Okamura,[±] James F. Monthony[+] and Curtis M. Beechan
Department of Chemistry, University of California
Riverside, California 92502

(Received in USA 19 December 1968; received in UK for publication 19 February 1969)

We wish to report the synthesis of 1,2,3-trichlorobicyclo[2.2.1]hept-2-en-7-one (1a) and 2,3-dichlorobicyclo[2.2.1]hept-2-en-7-one (2a). The ketones, 1a and 2a, and ketals, 1b and 2b, are of interest to us in connection with studies related to substituent effects on the thermal and photochemical behavior of bicyclo[2.2.1]hept-2-en-7-one derivatives and their corresponding ketals.



1a (R,R=O)
1b (R=OCH_3)



2a (R,R=O)
2b (R=OCH_3)

Reduction of 7,7-dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene (1) (3) with chromous perchlorate-ethylenediamine complex (32 equivalents Cr^{II} per mole of 3) in aqueous N,N-dimethylformamide for 24-48 hours according to the method of Kochi and co-workers (2,3) resulted in a good yield (~90%; 63% after recrystallization) of dichloroketal 2b, m.p. 54.0-54.5°C. (4). Similar reduction

---

[±] To whom correspondence should be addressed.

[+] NDEA Predoctoral Fellow, 1967-1968

of **3** but using 6 equivalents of Cr^{II} per mole of **3** resulted in *ca*. 90% yield of a 4 to 1 mixture (by v.p.c.) of trichloroketal **1b** and dichloroketal **2b** respectively. **1b** is easily purified by preparative v.p.c. (Varian Aerograph 90P, 5 ft. 20% diethylene glycoladipate on 60/80 firebrick, 197°C, 70 ml helium/minute), m.p. 47.0-47.5°C.

Sulfuric acid treatment at 0°C (5) for 1-2 hours of the mixture of **1b** and **2b** described above produced, after fractional recrystallization, the trichloroketone **1a** in 40-50% yield (based on **1b**), m.p. 55.4-56.0°C. Treatment of pure **2b** in a similar manner produced the dichloroketone **2a** in 75% yield, m.p. 54.0-55.0°C.

Spectral data for **1a**, **1b**, **2a**, and **2b** are summarized in the Table and are consistent with the structures assigned. Particularly noteworthy are the infrared carbonyl stretching frequencies of **1a** (1808 cm^{-1}) and **2a** (1795 cm^{-1}). For comparison, the carbonyl absorption of 1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-en-7-one (4) and bicyclo[2.2.1]hept-2-en-7-one (5) appear at 1833 and 1790 cm^{-1} (film) respectively (1,5a).

The chromous-ethylenediamine reagent developed by Kochi and co-workers (2) has proven to be an excellent reagent for the preparation of other 2,3-dichlorobicyclo[2.2.1]hept-2-ene derivatives from the corresponding 1,2,3,4-tetrachloro compounds (6). It is especially interesting that the bicyclo[2.2.1]hept-2-enyl bridgehead chlorine is selectively removed in preference to the vinylic chlorine (2, 7, 8).

The chemical behavior of **1a**, **2a**, and related derivatives is under investigation.

Acknowledgements

We gratefully acknowledge support by grants from the Petroleum Research Fund (#3369-A1) administered by the American Chemical Society, the Research Corporation (Frederick G. Cottrell Grant), and the Intramural Fund of the University of California at Riverside. We thank Professor C. E. Castro for interesting and helpful discussions.

TABLE

NMR,[±] IR,[+] AND MASS SPECTRAL* DATA

1a	τ	6.7-6.8 (1H, bridgehead, multiplet) 7.5-8.5 (CH_2CH_2, multiplet)
	$\nu_{max}^{CCl_4}$	1589 (m) cm^{-1} (C=C) and 1808 (s) cm^{-1} (C=O)
	m/e	210 (M; not detectable), 188 (M+6-CO; 3.1%), 186 (M+4-CO; 22.6%), 184 (M+2-CO; 73.3%), 182 (M-CO; 74.9%), 147 (base peak; 100%)
2a	τ	6.8-7.1 (2H, bridgehead, multiplet) 7.7-8.8 (CH_2CH_2, multiplet)
	$\nu_{max}^{CCl_4}$	1593 (m) cm^{-1} (C=C) and 1795 (s) cm^{-1} (C=O)
	m/e	178 (M+2; 1.0%), 176 (M; 1.4%), 152 (M+4-CO; 3.9%), 150 (M+2-CO; 17.6%), 148 (M-CO; 27.7%), 77 (base peak; 100%)
1b	τ	6.60, 6.67 (2 CH_3 groups, singlets) 7.10 (1H, bridgehead, broad doublet, J $\approx$ 3Hz) 7.7-8.9 (CH_2CH_2, multiplet)
	$\nu_{max}^{CCl_4}$	1610 (m) cm^{-1} (C=C)
	m/e	260 (M+4; 9.5%), 258 (M+2; 27.2%), 256 (M; 27.2%), 59 (base peak; 100%)
2b	τ	6.81, 6.84 (2 CH_3 groups, singlets) 7.1-7.2 (2H, bridgehead, multiplet) 7.8-8.9 (CH_2CH_2, multiplet)
	$\nu_{max}^{CCl_4}$	1613 (m) cm^{-1} (C=C)
	m/e	226 (M+4; 4.6%), 224 (M+2; 21.4%), 222 (M; 32.7%), 59 (base peak; 100%)

[±] Varian A-60 Spectrometer; CCl_4 as solvent with tetramethylsilane as an internal standard; the resonances showed the appropriate relative intensities for the structures assigned.

[+] Perkin-Elmer 621 Infrared Spectrophotometer.

* Hitachi-Perkin Elmer Model RMU-6D Spectrometer; 80 ev. at chamber temperature of 80°C; m/e based on ^{35}Cl.

REFERENCES

1. P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964) and references cited.

2. a) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968).
   b) J. Kochi and P. Macadlo, *J. Am. Chem. Soc.*, 88, 4094 (1966).

3. We thank Professor Kochi for informing us of a recent publication (2a). Professor Kochi has also informed us that certain other bridgehead and vinyl halides can be reduced with this Cr^{II} reagent.

4. In control experiments monitored by vapor phase chromatography, we have found that as little as 10 equivalents of chromous reagent per mole of **3** is necessary for nearly complete disappearance of **3** and **1b** after 1-2 days. However, on a preparative scale, a very large excess of chromous reagent gave more reproducible yields of **2b**.

5. a) P. E. Hoch, *J. Org. Chem.*, **26**, 2067 (1961).
   b) P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965); P. E. Eaton, private communication.

6. W. Okamura, J. F. Monthony, and C. M. Beechan, unpublished results.

7. It has been suggested (2) that this reduction proceeds through a radical-like mechanism. The 1-bicyclo[2.2.1]heptyl radical was the least stable of the alkyl radicals studied by D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 2194 (1965). The stability of the vinyl radical was not compared to that of the bridgehead radicals. Although the bridgehead positions of **3** and **1b** are allylic, allylic resonance stabilization would be expected to be minimal. Inductive factors, however, may be important.

8. K. Williamson, Y. Fang li Hsu, and E. I. Young, *Tetrahedron*, **24**, 6007 (1968) recently reported the chromous acetate reduction of 1,2,3,4,7,7-hexachloro-5-*endo*-acetoxybicyclo[2.2.1]hept-2-ene in refluxing acetic acid. Mainly mono-dechlorination of the *anti*-7-chlorine was observed. We have found that reduction of other hexachloro-derivatives as well as 1,2,3,4-tetrachloro-derivatives with the Cr^{II}-ethylenediamine complex (2) produces 2,3-dichlorobicyclo[2.2.1]hept-2-ene derivatives, but more slowly than the ketals reported in this communication.