

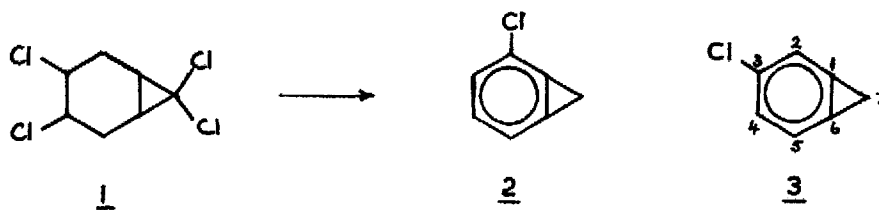
ON THE SUPPOSED '2-CHLOROBENZOCYCLOPROPENE'

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(Received in UK 7 September 1976; accepted for publication 27 September 1976)

Recently Devaprabhakara and his co-workers¹ have reported the interesting observation that when 3,4,7,7-tetrachlorobicyclo[4.1.0]heptane (1) is treated with excess KOt-Bu in DMSO then 2-chlorobenzocyclopropene (2) is obtained and not 3-chlorobenzocyclopropene (3), as would have been expected on the basis of the Billups-Günther mechanism.^{2,3} This result was very surprising, in that only the compound 2, and none of 3 appeared to have been formed. Further, there have been no previous cases in which benzocyclopropenes have arisen via a skeletal rearrangement; thus although Browne *et al.*⁴ have observed that formation of cycloheptatriene derivatives in related base eliminations, these compounds did not close to the corresponding benzocyclopropenes. Devaprabhakara and co-workers¹ formulated a mechanism to account for their product, which was



again unusual in that it suggested a 1,5-dehydrohalogenation involving the migration of a cyclopropyl ring.

From an inspection of the data provided for compound 2 we were unable to discern why structure 2 had been preferred to structure 3 for the product isolated. We have therefore re-investigated this reaction and would like to present evidence which, we believe, characterises the product of this reaction as 3-chlorobenzocyclopropene (3) and not 2-chlorobenzocyclopropene (2), as previously formulated.

Treatment of 1 with KOt-Bu in DMSO as described^{1,5} gave, after flash distillation of the black mixture, extraction (pentane, H₂O) and distillation, a colourless oil, bp 42-44°, 3.0 mm 15%, m.s. m/e 124, 126.

The FMR spectrum in CCl_4 showed singlets at δ 7.12 and at 3.23 while in pentane the lower field singlet was resolved as a multiplet (δ 7.14 - 7.04). The electronic spectrum (cyclohexane) had maxima at 274 ($\log \epsilon$ 2.20), 278 (2.29), and 286 nm (2.21) and the ir spectrum showed a band at 1665 cm^{-1} (C=C stretch). The ^{13}C NMR spectrum showed signals at 128.3 (C-1), 124.2 (C-6), 117.2 (C-2, 170 Hz), 115.8 (C-5, 176 Hz), 133.4 (C-3), 129.3 (C-4, 164 Hz), 21.4 (C-7, 172 Hz), compatible only with structure 3.⁶ Treatment of 3 with HCl gave a mixture (ca 35:1) of 3-chlorobenzyl chloride and 4-chlorobenzyl chloride, with no 2-chlorobenzyl chloride.⁷

We therefore conclude that the product of the base elimination of 1 is 3, and that the Billups-Günther mechanism is probably operative in this reaction.

References and Notes

1. A. Kumar, S.R. Tayal, and D. Devaprabhakara, Tetrahedron Letters, 863 (1976).
2. W.E. Billups, A.J. Blakeney, and W.Y. Chow, J. Chem. Soc. D, 1461 (1971).
3. J. Prestien and H. Günther, Angew. Chem. Int. Ed. Eng., 13, 276 (1974).
4. A. Browne, B. Halton, and C.W. Spangler, Tetrahedron, 30, 3289 (1974).
5. The use of twofold, rather than fourfold, excess of KOtBu also gave the same product. Browne et al.⁴ have shown that the smaller the excess of base the more is cycloheptatriene formation favoured.
6. H. Günther, G. Jikeli, H. Schmickler, and J. Prestien, Angew. Chem. Int. Ed. Eng., 12, 762 (1973).
7. Using the benzylic resonance, it is possible to detect <2% of 2-chlorobenzyl chloride in a 3.5:1 mixture of the other isomers.

(Note added by Editor: Professor Devaprabhakara has informed us that, in further work using ^{12}C labelling, he and A. Kumar have shown that C-7 of the tri- and tetrachlorobicycloheptanes becomes C-7 of the derived benzocyclopropenes, and that he agrees with the reassignments of structure proposed above.)