Reaction Between 7,7-Dichlorobicyclo[4.1.0]heptane and Potassium t-Butoxide in Dimethyl Sulphoxide Solution: Dimethyl Sulphoxide as a Methylating Agent

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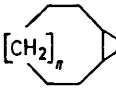
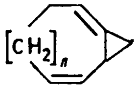
Summary Reaction between (**6a**) and $\mathrm{KOBu^t}$ in $\mathrm{Me_2SO}$ gives *o*-ethyltoluene (**7b**), ethylbenzene (**7a**), and 3-ethylidenecyclohexenes (**8**) and (**9**) as the main products; under similar conditions, (**6b**) also gives (**7a**) and (**7b**) while (**14a**) and (**14b**) give homofulvene (**16**) in modest yield.

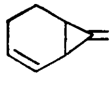
RECENTLY, Billups *et al.*[1] have demonstrated that 9,9-dichlorobicyclo[6.1.0]nonane (**1**) reacts with $\mathrm{KOBu^t}$ in $\mathrm{Me_2SO}$ to give the diene (**2**). This reaction appears to be general for dichlorocarbene adducts of larger ring cycloalkenes. Under the same conditions, 8,8-dichlorobicyclo-[5.1.0]octane (**3**) is converted[1] into (**4**) which is a possible rearrangement product of (**5**). We now report that 7,7-dichlorobicyclo[4.1.0]heptane (**6a**) reacts with KOBu^t in Me$_2$SO at 20 °C to give a mixture of volatile hydrocarbons† containing toluene (*ca.* 5%), cyclohepta-1,3,5-triene (*ca.* 2%),



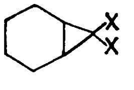
(1) n = 2
(3) n = 1



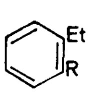
(2), n = 2
(5), n = 1



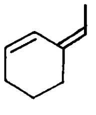
(4)



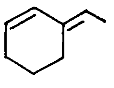
(6) a; X = Cl
b; X = Br



(7) a; R = H
b; R = Me



(8)

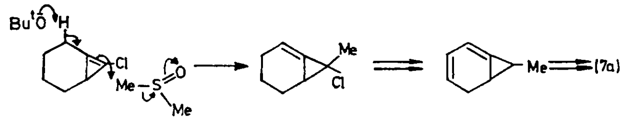


(9)

ethylbenzene (**7a**; *ca.* 25%), *Z*- and *E*-ethylidenecyclohexenes‡ (**8** and **9**, respectively; *ca.* 15%), and *o*-ethyltoluene (**7b**; *ca.* 50%). The combined yields of all the volatile hydrocarbons isolated account for *ca.* 50% of the starting material (**6a**). After 5 min, the starting material is more than half consumed (as indicated by g.l.c.) and the product distribution is virtually the same as it is after 18 h when no starting material (**6a**) remains. Even after 5 s, when only *ca.* 10% of (**6a**) has been consumed, (**7a**), (**7b**), (**8**), and (**9**) are the main products.

The reaction between (**6b**) and KOBu^t (5 mol. equiv.) in Me$_2$SO [11 ml/mmol (**6b**)] under similar conditions, gives volatile products (*ca.* 30%) which consist of *o*-ethyltoluene (**7b**; *ca.* 60%), ethylbenzene (**7a**; *ca.* 20%), and several unidentified minor products. This reaction is extremely rapid; little starting material (**6b**) remains even after 10 s and the reaction is virtually complete after 1 h. In more concentrated solution [2 ml Me$_2$SO/mmol (**6b**)], ethylbenzene (**7a**, *ca.* 40%) is the major product but *o*-ethyltoluene (**7b**, *ca.* 30%) and toluene (*ca.* 10%) are also obtained.

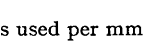
A possible mechanism for the formation of ethylbenzene (**7a**) from (**6a**) is outlined in the Scheme. It is suggested that intermediate (**10**), which has previously been trapped as its methanethiol adduct,[2] is methylated at C(7) by Me$_2$SO under the basic reaction conditions to give (**11**) which is a possible precursor of (**7a**). Both (**11**) and (**12**) could conceivably undergo further methylation at C(1) and hence be precursors of *o*-ethyltoluene (**7b**). The evidence for Me$_2$SO being a methylating agent under these conditions is twofold. Firstly, more extensive methylation occurs in the reaction between (**6b**) and KOBu^t in which the ratio of Me$_2$SO to (**6b**) is higher. Secondly, when (**6b**) is treated with KOBu^t in (CD$_3$)$_2$SO [1·6 ml/mmol (**6b**)], the average numbers of deuterium atoms located (as calculated from a combination of ^{1}H and ^{2}H n.m.r. spectroscopic data) in the Me and CH$_2$ groups and in the aromatic nucleus of the isolated ethylbenzene are as indicated in (**13**). Ethylbenzene (**7a**) does not undergo exchange to a detectable extent in the reaction medium. Presumably methylation has not been observed in the reactions of (**1**) and (**3**) with KOBu^t in Me$_2$SO because the corresponding intermediate cyclopropene and methylene cyclopropane derivatives are less strained and hence less reactive.



(10) (11) (12)

SCHEME

Finally in none of the experiments involving (**6a**) or (**6b**) was (**15**) or a product obviously derived from (**15**) observed. However, treatment of a mixture of *exo*- and *endo*-7-chloro- or -bromo-bicyclo[4.1.0]hept-2-enes, (**14a**) or (**14b**), with KOBu^t in Me$_2$SO gives homofulvene[3] (**16**) in *ca.* 8% isolated yield.



(13)

(14) a; X = Cl
b; X = Br

(15) (16)

One of us (C.J.R.) thanks the S.R.C. for a research studentship.

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† In a typical experiment, 5 mmol of base and 5 ml of solvent was used per mmol of substrate (**6a**); the products were isolated by preparative g.l.c. (silicone grease), identified spectroscopically, and their structures confirmed by comparison with authentic samples,

‡ These isomers were obtained in the ratio of 1 : 4. The minor and major isomers were assigned structures (**8**) and (**9**), respectively. on the basis of the chemical shifts (δ 5·07 and 5·18, respectively) of their ethylidene olefinic protons (C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, 1966, **49**, 164). The mixture of 3-ethylidenecyclohexenes obtained by heating 4-vinylcyclohexene with KOBu^t in Me$_2$SO (S. Bank, C. A. Rowe, Jr., A. Schriesheim, and L. A. Naslund, *J. Org. Chem.*, 1968, **33**, 221) is also rich in the putative *E*-isomer (**9**).

[1] W. E. Billups, B. A. Baker, W. Y. Chow, K. H. Leavell, and E. S. Lewis, *J. Org. Chem.*, 1975, **40**, 1702.
[2] T. C. Shields and P. D. Gardner, *J. Amer. Chem. Soc.*, 1967, **89**, 5425.
[3] M. Rey, U. A. Huber, and A. S. Dreiding, *Tetrahedron Letters*, 1968, 3583.