Tetrahedron Vol. 37, pp. 953 to 956

0040-4020/81/050953-04$02.00/0

TRANSFORMATIONS OF HALOCYCLOPROPANES—*VI*

REACTIONS OF 7,7-DICHLOROBICYCLO[4.1.0]HEPTANE WITH SOME ORGANIC ANIONS IN NONPOLAR MEDIA

J. ARCT* and B. MIGAJ
Institute of Organic Chemistry and Technology, Warsaw Technical University,
00:662 Warsaw, Koszykowa 75, Poland

(*Received in UK* 12 *June* 1980)

Abstract—The reactions of 7,7-dichlorobicyclo-[4.1.0]heptane, **1** with organic bases were carried out in benzene and THF. The reaction course of **1** in nonpolar media is different from that in DMSO; the rearrangements of cyclopropene **3** taking place in the former. **8** is produced by the shift of double bond into the C_6 ring. The cyclopropene-carbene isomerization and reactions of carbenes **14** and **15** with alkoxide anions are the probable route leading to the other products.

Reactions of 7,7-dichlorobicyclo[4.1.0]heptane, **1** with a variety of organic anions and potassium t-butoxide in DMSO have been reported.[1]

Generally they lead to the carbon 1 substituted derivatives of 7-chlorobicyclo[4.1.0]heptane **2**. Apart from frequently appearing products of further rearrangements of **2**, a significant amount of aromatic hydrocarbons C_8–C_9, mostly *o*-ethyltoluene and ethylbenzene, were found in the post-reaction mixture. These are believed to be formed by the reaction of the transient 7-chlorobicyclo[4.1.0]heptene-7, **3** with potassium dimsyl.[2] The reaction course of **1** with potassium isopropoxide is similar to that of with t-BuOK.

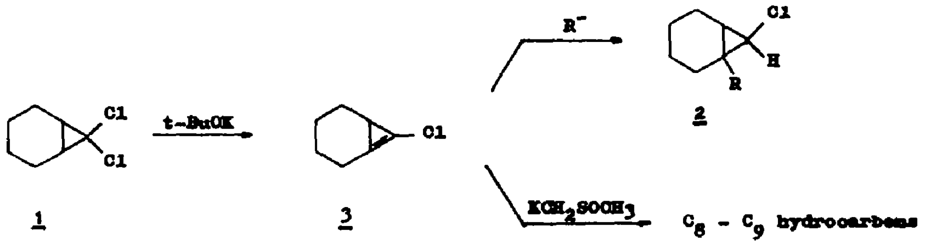
In solvents of lower than DMSO polarity, e.g. THF, **1** did not react with t-BuOK, while treatment of some other gem-dichlorobicyclo[n.1.0]alkanes with t-BuOK in THF afforded products of dehydrochlorination-isomerization sequence.[3,4] Nevertheless the suggested[3,4] mechanism of the reaction requires further clarification. We report here the transformations of **1** with various organic bases in nonpolar solvents. The results point to the possibility of the existence of carbene intermediates in the sequence of reaction leading to the final products.

RESULTS

The reaction of **1** with t-BuOK in benzene containing catalytic amounts of crown ether (18-crown-6, 10% molar) gives t-butoxy(2-cyclohexene-1-ylidene)methane **4** in 70% yield. Addition of 10% of DMSO to the mixture alters the reaction course. Previously reported[2] aromatic hydrocarbons C_8–C_9 are now formed as major products accompanied by only a small amount of **4**.

Introduction of the methoxide anion as an additional nucleophile to the initial system results in a mixture of products arising from the dehydrohalogenation–isomerization–substitution reaction sequence. The isomeric methoxy(cyclohexenylidene)-methanes, **5** and **6**, chloro(2-methoxycyclohexenylidene)methane, **7** and 7-chlorobicyclo[4.1.0]heptene-2, **8** are formed under such conditions.

For the latter system the addition of an equimolar amount of DMSO to **1** or replacement of benzene by



R = MeS, MeO, i-PrO, PhO, PhC(Me)CN, $HC(COOEt)_2$, HC(CN)COOEt

Fig. 1.

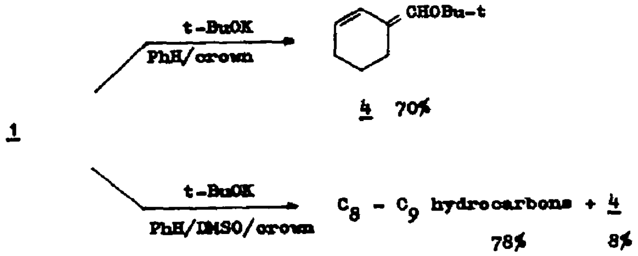


Fig. 2.

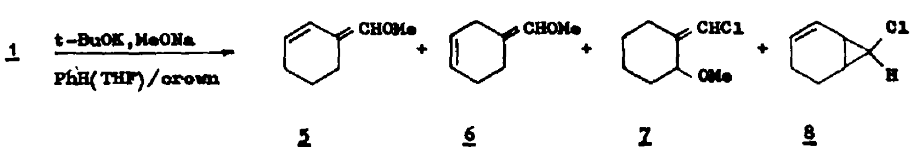
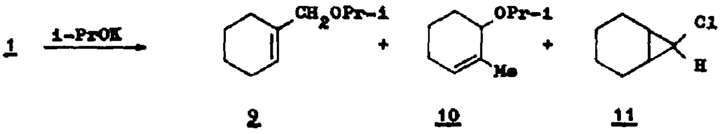


Fig. 3.



	9	10	11
benzene	38%	25%	37%
THF	45%	44%	5%

Fig. 4.

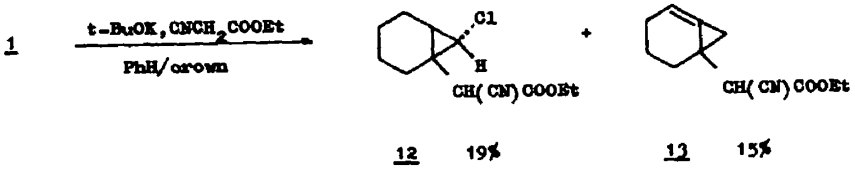


Fig. 5.

Table 1. Influence of the solvent on the transformation of 1 with t-BuOK/MeONa/18-crown-6

Solvent	Mixture ratio 5+6	7	8	Degree of conversion
benzene	54%	20%	26%	73%
benzene + 2.5% DMSO	45%	30%	25%	45%
THF	44%	31%	9%	70%

THF has no substantial influence on the reaction course.

Detailed results of these experiments are presented in Table 1.

Reaction of **1** with i-PrOK in a solvent of lower than DMSO polarity, in the presence of crown ether proceeds differently compared with that previously reported[1b] reaction in DMSO. Products of the expected dehydrohalogenation-isomerization-substitution sequence are accompanied by a substantial amount of hydrogenated material. The work-up of the resulting mixture gave 1-cyclohexenylmethyl-isopropyl ether, **9**, 3-isopropoxy-2-methylcyclohexene-2, **10** and the mixture of *endo* and *exo*-7-chlorobicyclo[4.1.0]heptanes, **11**. The reaction of **1** with i-PrOK in benzene or THF gives similar products as those obtained from **1** with t-BuOK/methoxide anion in solvents of low polarity. Also in this case more of the unsubstituted compound **11** is formed in benzene than in THF.

The reaction of **1** in DMSO with t-BuOK and anions derived from C-H acids has been reported previously.[1c] Analogous transfer reaction of **1** in the system benzene/18-crown-6 with t-BuOK and ethyl cyanoacetate gave a mixture of products **12** and **13** formed via dehydrochlorination-addition reaction sequence, similarly as in DMSO.

DISCUSSION

The reaction course of 7,7-dichlorobicyclo-[4.1.0]heptane with t-BuOK, i-PrOK or methoxide anion and t-BuOK in nonpolar media differ from that in DMSO. It appears, however that in both polar as well as nonpolar media dehydrochlorination of **1** leading to the cyclopropene derivative **3** takes place in the first step. Formation of products **8** and **11**, the transformations occuring in the presence of ethyl cyanoacetate and experiments carried out with **1** and t-BuOK in DMSO-d_6 support this assumption. The latter reaction produced deuterated **4**, hydrocarbons C_8-C_9 containing deuterium label, but no incorporation of deuterium into the unreacted **1** has been detected.

Reactive intermediate **3** might undergo two kinds of solvent controlled transformation. In DMSO, due to firm solvation of the polar transition state, the addition to the double bond predominates, leading to the derivatives of the type **2**. In weakly solvating media the rearrangements of **3** take place. The shift of the double bond into the C_6 ring[5] produces 7-chlorobicyclo-[4.1.0]heptene-2, **8**. Another type of rearrangement most probably consists of the isomerization cyclopropene-carbene yielding carbenes **14** and **15**. These carbenes with alkoxide anions give alkoxycyclohexylidenemethanes **16** and **17** as well as derivatives of chloro(2-alkoxycyclohexylidene)methane **18**. The carbene **14** appears to be thermodynamically more stable. The latter is suggested by the formation of **4** with weakly nucleophilic t-butoxide anion and the predominance of compounds of structure **16** in the reactions of **1** with MeO^- and $i\text{-}PrO^-$. In the reaction of **1** with potassium isopropoxide initially formed compounds **8**, **16**, **17** and **18** are reduced, producing a mixture of products **9**, **10** and **11**.

Only in the case of rather strongly nucleophilic anions derived from C-H acids (i.e. ethyl cyanoacetate) the reaction in nonpolar media as well as in DMSO proceeds without the rearrangement of cyclopropene **3**.

Presented results suggested the need of reformulation of the mechanism[7] of the known reactions of dichlorobicyclo[n.1.0]alkanes with t-BuOK in THF. The latter will form the subject of further studies.

EXPERIMENTAL

^1H NMR spectra were recorded on a JEOL JNM-MH-100 spectrometer using TMS as internal standard. IR spectra were recorded on a Perkin-Elmer 577 IR spectrophotometer. Mass spectra were taken on a LKB-900 mass spectrometer operating at 70 eV. Analytical glc was performed with a Chrom 41 gas chromatograph using a 3.5 m × 3 mm steel column packed with 3% OV-17 on Chromosorb W. Varian 2868 and Chromatron type GCHF with a steel 6 m × 6 mm column packed with 15% OV-17 on Chromosorb P was used for preparative separations. Bps are uncorrected.

Materials. Compound **1** was prepared by the Makosza method.[8] BuOK and NaOMe (Fluka) were used without purification. K i-PrOK was prepared by the reaction of the metal with i-PrOH and dried under vacuum (100°/0.1 mm Hg). Benzene was dried and purified by distillation from Na; THF was dried and purified by distillation from LAH_4.

General procedure. All reactions were carried out in the atmosphere of dry, oxygen free N_2. The alcoholate (0.5 mol t-BuOK or i-PrOK; 0.25 mol of t-BuOK and 0.25 mol of MeONa) was suspended in 300 ml dry solvent (benzene or THF) and 18-crown-6 (3.0 g, 0.0115 mol) was added. The mixture was heated for 1 hr at 60°, cooled to room temp and **1** (16.5 g, 0.1 mol) was added. The mixture was kept 20 hr at 65° and the solvent was evaporated. 400 ml water was added to the residue, extracted with n-hexane (5 × 30 ml), washed with water and dried over $MgSO_4$. After concentration the mixture of products was analysed by glc and separated by distillation or preparative glc. Products were identified by ^1H NMR, IR and MS spectra or by glc/MS identity method with the comparison samples prepared by other methods.

(a) *Reaction of* **1** *with* t-BuOK *in benzene*. The product was separated by distillation, b.p. 47-48°/0.3 mm Hg; 5.5 g (33% yield) and identified as **4**: ^1H NMR (CCl_4) δ: 1.23 (s, 9 H, 3 CH_3), 1.69 (m, 3 H, H5, H6), 2.09 (m, 3 H, H4, H6), 5.44 (m, 1 H, H3), 5.77 (s, 1 H, =C$\underline{H}$OBu-t), 6.33 (d, 1 H, H2); IR (film): 1650 cm^{-1} (C=C), 1608 cm^{-1} (C=C), 1130-1170 cm^{-1} (C-O); MS *m/e* (% int): M^+ 166 (9.1), 110 (100.0), 95 (34.2), 57 (33.8), 81 (29.0), 41 (28.7), 79 (27.5), 29 (16.1), 92 (14.6), 37 (14.4), 67 (10.9).

(b) *Reaction of* **1** *with* t-BuOK *in benzene in the presence of 10% DMSO*. The reaction was carried out for 1 hr at 60°. The mixture of products was identified by glc/MS; it contained 77.6% of hydrocarbons-toluene, ethylbenzene, *o*-ethyltoluene, *o*-xylene and 3-ethylidenecyclohexenes, 6.5% of **4**, 1% of **1** and about 15% of unidentified products with high mass weight, which were not analysed.

(c) *Reaction of* **1** *with* t-BuOK *in benzene in the presence of 10% DMSO-d_6*. The mixture contained deuterated hydrocarbons and deuterated **4**: MS *m/e* (% int): M^+ 168 (10.3), 57 (100.0), 112 (62.7), 41 (22.4), 111 (18.9), 29 (13.8), 94 (11.8), 56 (11.4), 58 (6.9), 130 (6.5).

(d) *Reaction of* **1** *with* MeONa *and* t-BuOK (*in benzene or THF*). Products were separated by preparative glc and identified as **5**: MS *m/e* (% int): M^+ 124 (66.7), 91 (100.0), 92 (78.7), 77 (61.9), 79 (55.2), 45 (46.3), 39 (33.0), 93 (31.0), 81 (27.4), 109 (24.3); **6**: MS *m/e* (% int): M^+ 124 (100.0), 109 (98.4), 81 (89.9), 79 (73.3), 39 (56.9), 91 (56.9), 92 (49.5), 53 (47.8), 41 (41.7); **7**: ^1H NMR (CCl_4) δ: 1.17-2.60 (m, 8 H, H3, H5, H6), 3.17 (s, 3 H, OCH_3), 3.55 (m, 1 H, H2), 5.90 (s, 1 H, =C$\underline{H}$$OCH_3$); MS *m/e* (% int): M^+ 160 (10.2), 125 (100.0), 93 (38.1), 39 (26.3), 77 (18.3), 45 (17.9), 41 (17.0), 91 (14.9), 27 (12.4), 71 (12.0) and **8**: ^1H NMR (CCl_4) δ: 1.5-2.7 (m, 6 H, H1, H4, H5, H6), 3.25 (2d, 1 H, H7), 5.30 (m, 2 H, H2, H3); MS *m/e* (% int): M^+ 128 (39.4), 130 (13.1), 93 (100.0), 91 (98.8), 77 (93.5), 79 (75.2), 39 (53.8), 128 (39.4), 65 (35.7), 51 (27.2), 63 (18.2), 92 (17.3).

(e) *Reaction of* **1** *with* i-PrOK (*in benzene or THF*). Products were separated by preparative glc and identified as **9**: ^{1}H NMR (CCl_4) δ: 1.10 (d, 6 H, 2 CH_3), 1.64 (m, 4 H, H4, H5), 1.98 (m, 4 H, H3, H6), 3.46 (septet, 1 H, $OC\underline{H}(CH_3)_2$), 3.68 (s, 2 H, $-OCH_2$), 5.50 (s, 1 H, H2); MS *m/e* (% int): M^+ 154 (9.4), 41 (100.0), 79 (91.4), 112 (82.3), 81 (80.0), 43 (76.7), 67 (63.8), 95 (63.3), 39 (56.6), 94 (55.7), 27 (51.3); **10**: ^{1}H NMR (CCl_4) δ: 1.12 (d, 6 H, 2 CH_3), 1.28–2.25 (m, 7 H, H3, H4, H5, H6), 3.03 (septet, 1 H, $OC\underline{H}(CH_3)_2$), 5.55 (s, 1 H, H1); MS *m/e* (% int): M^+ 154 (0.8), 109 (100.0), 67 (76.8), 43 (49.6), 41 (35.5), 81 (32.5), 111 (30.1), 55 (26.4), 39 (24.7), 27 (18.3), 79 (17.2); and **11**: MS *m/e* (% int): M^+ 130 (9.4), 132 (2.4), 81 (100.0), 67 (82.6), 88 (80.9), 68 (68.3), 95 (64.1), 39 (63.6), 53 (62.6), 55 (49.7), 41 (46.9), 27 (37.2)

(f) *Reaction of* **1** *with ethyl cyanoacetate and* t-BuOK *in benzene*. Products were separated by preparative glc and identified as **12**: ^{1}H NMR (CCl_4) δ: 1.27; 1.28 (t, 3 H, CH_3), 1.34–3.00 (m, 9 H, H2, H3, H4, H5, H6), 3.63; 3.69 (d, 1 H, H7), 4.18; 4.19 (q, 2 H, OCH_2), 5.89; 6.05 (s, 1 H, $-C\underline{H}(CN)COOEt$); IR (film): 2250 cm^{-1} (CNN), 1745 cm^{-1} (C=O); MS *m/e* (% int): M^+ 241 (0.4), 243 (0.2), 93 (100.0), 29 (58.0), 77 (32.3), 91 (31.6), 114 (30.1), 27 (29.3), 39 (26.9), 41 (23.9), 129 (22.8), 79 (22.2); and **13**: MS *m/e* (% int): M^+ 205 (36.3), 132 (100.0), 27 (99.0), 29 (98.5), 177 (85.5), 39 (81.3), 77 (77.2), 41 (76.6), 159 (65.6), 160 (62.3), 130 (61.9)

REFERENCES

[1a] T. C. Shields and P. D. Gardner, *J. Am. Chem. Soc.* **89**, 5425 (1967); [b] J. Arct and B. Migaj, *Bull. Sci. Polon., Ser. sci. chim.* **25**, 697 (1977); [c] J. Arct and B. Migaj, in press.
[2] J. C. Ranson and C. B. Reese, *Chem. Comm.* 970 (1975).
[3] A. R. Browne and B. Halton, *Tetrahedron* **33**, 345 (1977).
[4] W. E. Billups and L. E. Reed, *Tetrahedron Letters* 2239 (1977).
[5] T. C. Shields and W. E. Billups, *J. Am. Chem. Soc.* **90**, 4749 (1968); W. E. Billups, T. C. Shields, W. Y. Chow and N. C. Deno, *J. Org. Chem.* **37**, 3676 (1972); T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn and P. D. Gardner, *J. Am. Chem. Soc.* **87**, 3026 (1965).
[6] W. E. Billups, L. P. Lin and W. Y. Chow, *Ibid.* **96**, 4026 (1974); C. Wentrup, *Topics in Current Chem.* **62**, 173 (1976).
[7] W. E. Parham, H. E. Reiff and P. Swartzentruber, *J. Am. Chem. Soc.* **78**, 1437 (1956).
[8] M. Makosza and M. Mawrzyniewicz, *Tetrahedron Letters* 4659 (1969).