Tetrahedron Vol 37, No. 21, pp 3689 to 3692, 1981
Printed in Great Britain

0040-4020/81/213689-04$02.00/0
Pergamon Press Ltd.

TRANSFORMATIONS OF HALOCYCLOPROPANES—VII

REACTIONS OF 7,7-DICHLOROBICYCLO[4.1.0] HEPTANE WITH CARBANIONS

J. ARCT*, B. MIGAJ and A. LEONCZYNSKI

Institute of Organic Chemistry and Technology, Warsaw Technical University, Koszykowa 75, 00-622 Warsaw, Poland

(*Received in the UK 10 November 1980*)

Abstract—The reactions of 7,7-dichlorobicyclo[4.1.0] heptane **1** were carried out with C-H acids in the presence of t-BuOK in DMSO. The respective syn-7-chlorobicyclo[4.1.0] heptane derivatives **3** were the major products of the reactions with diethyl malonate and ethyl cyanoacetate. The dehydrochlorinated material α-bicyclo[4.1.0] hepten-5-yl-α-phenylpropionitrile **5c**, was obtained in good yield in the reaction with α-phenylpropionitrile.

Treatment of 7,7-dichlorobicyclo[4.1.0] heptane **1** with t-BuOK in DMSO affords a mixture of dehydrochlorinated, rearranged and dimsyl anion methylated products.[1] Ethylbenzene, o-ethyltoluene, isomeric ethylidenecyclohexenes, toluene and cycloheptatriene-1,3,5 were found as major products of this reaction. Reaction of 7,7-dichlorobicyclo[4.1.0] heptane **1** with t-BuOK in the presence of less basic but stronger nucleophilic anions, i.e. alcoholates, thioalcoholates or phenolates, apart from the listed hydrocarbons, yielded the products with preserved carbon skeleton substituted at carbon 1 by the nucleophile. The elimination-addition mechanism was proposed for these reactions[2] supported by deuterium exchange experiments.

Other gem-dihalocyclopropanes undergo similar transformations.[3]

Up to now only the reactions with oxygen or sulphur centered nucleophiles were reported in the literature. In this paper preliminary results of the reaction of 7,7-dichlorobicyclo-[4.1.0] heptane **1** with anions of C-H acids are described.

The reaction of **1** with 'BuOK and diethyl malonate was carried out in DMSO for various reaction time and at different temperatures. 18-Crown-6 was used in some experiments. Reaction mixtures were analysed by GLC. Their partial separation was achieved by distillation. Products not isolated as pure material were identified by means of mass spectrometry, and in some cases (ethylbenzene and o-ethyltoluene) by comparison with the authentic samples.

The results of these investigations are summarized in Table 1 and in Figs. 2 and 3.

The reaction of **1** with excess of t-BuOK and diethyl malonate is exothermic. The conversion of **1** reaches 60% within a few minutes at 25°C. Further prolonged heating of the reaction mixture at 45–50°C does not change the conversion of **1**. At 80–90°C the overall conversion of **1** increases to about 80%. With a larger excess of 'BuOK **1** might be totally reacted albeit mostly to a mixture of C_7–C_{10} hydrocarbons. For 2 hr at 45–50°C the reaction gives predominantly diethyl syn-7-chlorobicyclo[4.1.0] heptylmalonate **3a**. Upon increasing the reaction time diethyl bicyclo[4.1.0] heptene-5-ylmalonate **5a** and high molecular weight unidentified material is formed at the expense of **3a**. At higher temperature two other products were found, i.e. ethyl syn-7-chlorobicyclo[4.1.0]heptylacetate **6** and ethyl bicyclo-[4.1.0] heptene-5-ylacetate **8**. The yield of **3a** diminishes under such conditions.

Compounds **5a**, **6** and **8** were not isolated pure (even using preparative GLC and column chromatography) and they were identified by means of mass spectrometry. The structures of these compounds are given on the grounds of literature data[4] and results described in this paper (compound **5c**). The syn-7-chlorobicyclo[4.1.0] heptane derivatives are easy dehydrochlorinated in the presence of t-BuOK in DMSO[4] and it is the most probable route leading to the **5a** ($M^+ - 252 = C_{14}H_{20}O_4$). The compounds **6** ($M^+ - 216 = C_{11}H_{17}O_2Cl$) and **8** ($M^+ - 180 = C_{11}H_{16}O_2$) are probably the respective products of decarboxylation[5] and decarboxylation and dehydrochlorination of **3a**. Both were formed at higher temperatures and it may well prove this reaction route.

Introductions of crown ether (18-crown-6) rises the conversion of **1** at 25°C up to about 75% with simultaneous increase of the yield of **3a**. With prolonged reaction time large amounts of ethyl syn-7-chlorobicyclo[4.1.0] heptylacetate, **6** are formed. Without crown ether this product requires extended heating at elevated temperatures. Significant amounts of ethylbenzene and o-ethyltoluene accompany **3a** or **6** in all these reactions.

The reaction of **1** with ethyl cyanoacetate in the presence of 'BuOK analogously to previously described reaction with diethyl malonate gave ethyl syn-7-chlorobicyclo[4.1.0]heptylcyanoacetate, **3b**. Large amounts of dehydrochlorinated product **5b** are present in the post reaction mixture besides **3b** already at 45–50°C.

With a much weaker C-H acid, α-phenylpropionitrile, no α - syn - 7 - chlorobicyclo[4.1.0]heptyl - α - phenylpropionitrile **3c** was detected. Instead the dehydrochlorinated material α - bicyclo[4.1.0]hepten - 5 - yl - α-phenylpropionitrile **5c** was obtained in good yield. Significant amounts of o-ethyltoluene were also formed, but no ethylbenzene as well as other products of the reaction of **1** with 'BuOK and DMSO.

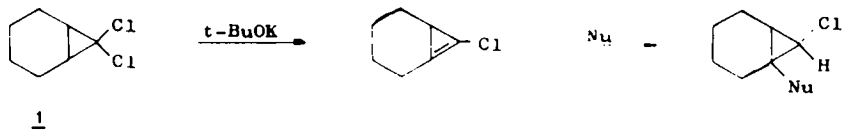
Based on the presented results the reaction course is shown in the scheme (Fig 2). The first stage of the reaction consists of fast conversion of **1** into unstable cyclopropene derivative **2**. This, attacked by the anion of C-H acid, affords the primary product **3**. The product **3** might undergo subsequent dehydrochlorination to un-

*Author to whom correspondence should be addressed.

Table 1. Reactions of 7,7-dichlorobicyclo[4.1.0] heptane with C–H acids in the presence of t-BuOK

C–H acid	Temp. °C	Time	Degree of conversion	Mixture ratio (%) a) 3	5	6	8	ethyl-benzene	o-ethyl-toluene	unidentified compounds
diethyl malonate	45–50	5 min.	58%	28	-	-	-	21	51	-
		2 hr	61%	60	-	-	-	18	16	6
		38 hr	62%	11	20	-	-	26	22	21
		5 min. b)	48%	48	-	-	-	15	19	18
		2 hr b)	72%	84	-	-	-	5	2	9
		30 hr b)	76%	25	5	46	-	7	3	14
	80–90	16 hr	80%	42	2	25	3	8	12	8
ethyl cyanoacetate	45–50	2 hr	66%	51	16	-	-	9	7	17
α-phenyl-propionitrile	50	4 hr	95%	-	81	-	-	-	15	4

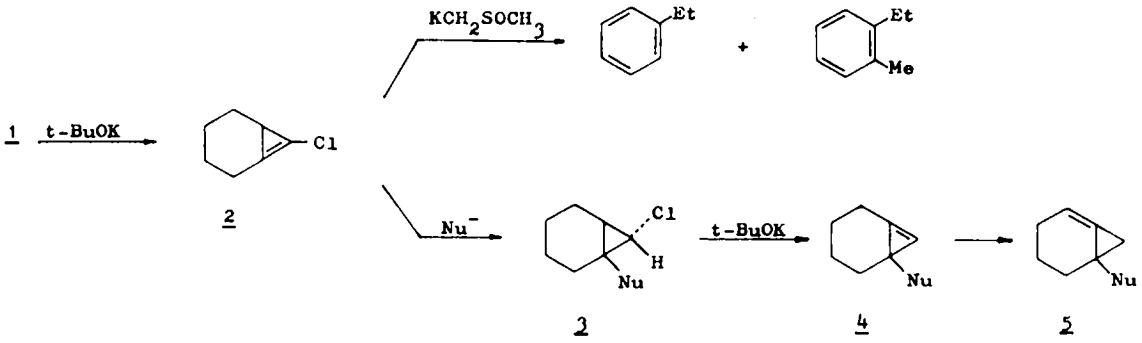
a) without uncreated 1 b) in the presence of 18-crown-6



1

Nu = MeS, MeO, ArO

Fig. 1.



a) Nu = $CH(COOEt)_2$ b) Nu = CH(CN)COOEt c) Nu = CMe(CN)Ph

Fig. 2.

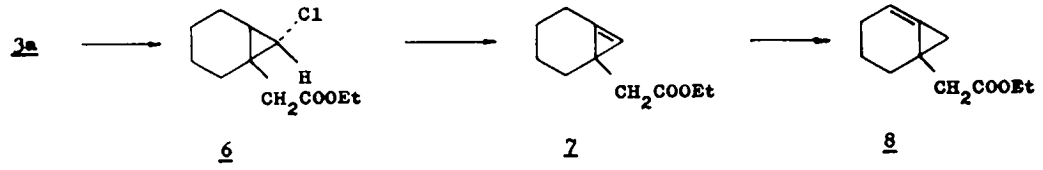


Fig. 3.

stable cyclopropene **4** which undergoes facile rearrangement[4] to bicyclo[4.1.0] hept-5-enes **5**. In case of derivatives of diethyl malonate and ethyl cyanoacetate the formation of **4** is more difficult, most probably due to their ionization in the reaction medium. For **3a** the decarboxylation also proceeds (Fig 3) e.g. according to the mechanism given by Hunter *et al.*[5]

Simultaneously to the formation of **3**, the rearrangements, dehydrochlorination and methylation reactions[1] of **2** leading to o-ethyltoluene and ethylbenzene are taking place. In the presence of crown ether the enhanced nucleophilicity[6] of anions facilitates their reaction with **2** thus affording higher yields of **3**, when o-ethyltoluene and ethylbenzene are formed in only small amounts.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a JEOL-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. A. Varian 2868 and a Chromatron type GCHF with a steel 6 m × 6 mm column packed with 15% OV-17 on Chromosorb P were used for preparative separations. Elemental analyses were performed on a Perkin–Elmer 240 microanalyzer. Bps are uncorrected.

Materials

7,7-Dichlorobicyclo[4.1.0] heptane **1** was prepared by Makosza method.[7]

Potassium t-butoxide (Fluka) was used without purification. Dimethyl sulphoxide was distilled from CaH_2 and stored over 4A molecular sieves prior to use.

General procedure

All reactions were carried out in the atmosphere of dry, oxygen free nitrogen. C–H acid (0.045 mol) was added to a solution of t-BuOK (10.0 g, 0.09 mol) and 18-crown-6 (3.0 g, 0.0115 mol) in 50 cm^3 DMSO. The mixture was cooled to room temperature and **1** (3.75 g, 0.0225 mol) was added. Reaction conditions are given in Table 1. 100 cm^3 of water was added to the reaction mixture and it was extracted with n-hexane (8 × 15 cm^3). The extract was washed with water (3 × 15 cm^3), dried over $MgSO_4$ and concentrated. Products were analyzed by GLC and separated by preparative GLC.

(a) *Reaction of* **1** *with diethyl malonate.* Products were identified as diethyl syn-7-chlorobicyclo[4.1.0] heptylmalonate **3a**: IR (film): 1760, 1740 cm^{-1} (C = O); ^{1}H NMR (CCl_4): δ 1, 21 (m, 6H, $2CH_3$), 1.63–2.63 (m, 8H, H2, H3, H4, H5), 3.01 (m, 1H, H6), 3.61 (d, 1H, H7, J = 11.3 Hz), 4, 10 (2q, 4H, 2 $COOCH_2CH_3$), 5.84 (s, 1H, -CHCOOEt); MS *m/e*: 288 (M^+, 4%), 179 (100), 161 (40), 160 (53), 151 (52), 133 (36), 93 (51), 91 (37), 79 (39), 77 (33), 29 (71). Diethyl bicyclo[4.1.0] heptene-5-ylmalonate, **5a**: MS *m/e*: 252 (M^+, 18%), 179 (74), 161 (65), 151 (25), 133 (59), 105 (100), 92 (32), 91 (45), 79 (48), 29 (93), 27 (26). Ethyl syn-7-chlorobicyclo[4.1.0] heptylacetate **6**: MS *m/e*: 216 (M^+, 1%), 107

(51), 106 (60), 105 (35), 93 (69), 91 (42), 88 (100), 79 (40), 77 (30), 61 (30), 29 (45). Ethyl bicyclo[4.1.0] heptene-5-ylacetate **8**: MS *m/e*: 180 (M^+, 30%), 107 (99), 106 (16), 105 (20), 102 (16), 92 (46), 91 (54), 76 (100), 41 (26), 29 (36). Double bond position in these compounds is not certain, but we suggest these structures on the grounds of literature data[4] and our results (compound **5c**).

(b) *Reaction of* **1** *with ethyl cyanoacetate.* Products were identified as ethyl syn-7-chlorobicyclo[4.1.0] heptylcyanoacetate, **3b**: IR (film): 2250 (C ≡ N), 1745 cm^{-1} (C=O); ^1H NMR (CCl_4): δ 1, 27; 1, 28 (t, 3H, CH_3), 1, 34 – 3.00 (m, 9H, H2, H3, H4, H5, H6), 3.63: 3.69 (d, 1H, H7, J = 10.3 Hz), 4.18; 4.19 (q, 2H, OCH_2CH_3), 5.84: 6.05 (s, 1 H, –CH(CN)COOEt); MS *m/e*: 243 (M^+, 0.2%), 241 (M^+, 0.4%), 129 (23), 114 (30), 93 (100), 91 (32), 79 (22), 77 (32), 41 (24), 39 (27), 29 (58), 27 (30). The asymetric carbon atom in the compound **3b** (CH(CN)COOEt) and **5c** (CMe(CN)Ph) is the reason of the double values in the NMR spectra. Ethyl bicyclo[4.1.0] heptene-5-ylcyanoacetate **5b**: MS *m/e*: 205 (M^+, 36%), 177 (86), 160 (62), 159 (66), 132 (100), 130 (62), 77 (77), 41 (77), 39 (81), 27 (99).

(c) *Reaction of* **1** *with α-phenylpropionitrile.* The major product (3.26 g, 65%) was isolated by vacuum distillation (b.p. 140–146°C/0.3 mm Hg) and identified as α-bicyclo[4.1.0] heptene-5-yl-α-phenylpropionitrile **5c**: IR (film): 2200 (C≡N), 1635 cm^{-1} (C=C); ^1H NMR (CCl_4): δ 0.9–2.2 (m, 8H, H2, H3, H4, H7), 1.65 (2s, 3H, CH_3), 5.35; 5.90 (m, 1H, H5), 7.20 (m, 5H, arom); MS *m/e*: 223 (M^+, 1%), 131 (26), 94 (7), 93 (100), 91 (33), 78 (7), 77 (38), 65 (7), 51 (8), 41 (7), 39 (10). (Found: C, 85.85; H, 7.80; N, 6.35. Calc. for $C_{16}H_{17}N$: C, 86.05; H, 7, 70;N, 6.30%).

REFERENCES

[1]J. C. Ranson and C. B. Reese, *Chem. Commun.* 970 (1975).
[2]T. C. Shields and P. D. Gardner, *J. Am. Chem. Soc.* **89**, 5425 (1967); J. Arct and B. Migaj, *Bull. Acad. Sci. Polon., Ser. Sci. Chim.* **25**, 697 (1977).
[3]T. C. Shields, B. A. Shoulders, J. G. Krause, C. L. Osborn and P. D. Gardner, *J. Am. Chem. Soc.* **87**, 3026 (1965); W. E. Billups, L. P. Lin and W. Y. Chow, *Ibid.* **96**, 4026 (1974); W. E. Parham, W. D. McKown, V. Nelson, S. Kajigaeshi and N. Ishikawa, *J. Org. Chem.* **38**, 1361 (1973).
[4]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).
[5]D. H. Hunter, M. Hamity, V. Patel and R. A. Perry, *Can. J. Chem.* **56**, 104 (1978).
[6]S. A. DiBiase and G. W. Gokel, *J. Org. Chem.* **43**, 447 (1978).
[7]M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.* 4659 (1969).