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REACTIONS OF 1-HALOCYCLOHEPTENES WITH POTASSIUM t-BUTOXIDE AND WITH SODIUM PYRROLIDIDE

A. T. BOTTINI,* K. A. FROST II, B. R. ANDERSON and V. DEV
Department of Chemistry, University of California, Davis, California 95616

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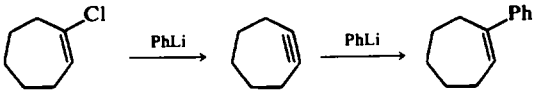
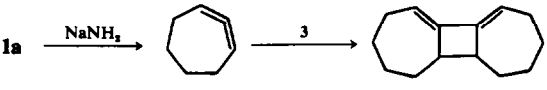
Abstract—Reactions of 1-halocycloheptenes with KO-t-Bu in DMSO and THF were studied. The principal products obtained could be accounted for on the basis of two competing dehydrohalogenation mechanisms. These are: dehydrohalogenation across the C_1–C_2 bond to give cycloheptyne; and dehydrohalogenation across the C_1–C_7 bond to give 1,2-cycloheptadiene. One or both of these intermediates react with KO-t-Bu to give 1-t-butoxycycloheptene in poor yield. The principal product from the three 1-halocycloheptenes in both solvents is tricyclo[7.5.0.0^{2,8}]tetradeca-2,14-diene (**4**), the dimer of 1,2-cycloheptadiene. Also formed are **5**, the 2(8), 14-diene isomer of **4**, presumably by cycloaddition of 1,2-cycloheptadiene and cycloheptyne, and **6**, the 2,13-diene isomer of **4**, by rearrangement of **4** effected by KO-t-Bu.

Also studied were rections of 1 chloro- and 1-iodocycloheptene with sodium pyrrolidide (Na-NC_4H_8) in THF. These reactions give 1-(1-pyrrolidino)cycloheptene in fair yield together with smaller amounts of the 14-carbon hydrocarbons. Reactions of 1-chlorocycloheptene-1-^{14}C and 4-chloro- and 4-iodobicyclo[5.1.0]oct-3-ene leading to (1-pyrrolidino)cycloheptenes were found to occur *via* both the corresponding cycloheptyne and 1,2-cycloheptadiene.

Montgomery and Applegate[1] found that 1-chlorocycloheptene (**1a**) reacts with PhLi to give 1-phenylcycloheptene predominantly and probably exclusively *via* the intermediacy of cycloheptyne (**2**). In contrast, Ball and Landor[2] treated **1a** with sodamide in liquid ammonia and obtained a 32% yield of tricyclo[7.5.0.0^{2,8}]tetradeca-2,14-diene (**4**), which they rationalized as being formed by dimerization of the intermediate 1,2-cycloheptadiene (**3**). It should also be noted that Wittig and Meske-Schüller[3] obtained a 69% yield of a mixture of two



1a **2**



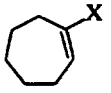
3 **4**

isomeric 14-carbon hydrocarbons from the reaction of 1-bromocycloheptene with KO-t-Bu in DMSO, and the major product was identified as **4**. Also, they were able to trap an intermediate, which they presumed to be **3**, with 1,3-diphenylisobenzofuran. Further, when 1,2-dibromocycloheptene was treated with KO-t-Bu in DMSO in the presence of 1,3-diphenylisobenzofuran, two trapped products were isolated and their formation was rationalized as having occurred *via* 1-bromo-1,2-cycloheptadiene.

A study of reactions of 1-halocyclohexenes with KO-t-Bu in DMSO and THF was completed recently in our laboratory.[4] This study revealed that 1-halocyclohexenes react with KO-t-Bu by three dehydrohalogenation mechanisms: (a) *via* cyclohexyne (b) *via* 1,2-cyclohexadiene, and (c) *via* prototropic rearrangement to 3-halocyclohexene followed by elimination to 1,3-cyclohexadiene; and the direction of the reaction is a sensitive function of the halide and the solvent. Both strained intermediates react with KO-t-Bu to give 1-t-butoxycyclohexene. In addition, 1,2-cyclohexadiene undergoes cycloaddition with either 1,2- or 1,3-cyclohexadiene to give an array of 12-carbon hydrocarbons.

In order to understand better the behavior of 1-halocycloheptenes when treated with strong base, we undertook a study of reactions of 1-halocycloheptenes with KO-t-Bu and sodium pyrrolidide ($NaNC_4H_8$), which we describe here.

1-Chlorocycloheptene (**1a**) was converted smoothly to 1-lithiocycloheptene by reaction with lithium in ether, and reaction of the organolithium reagent with bromine in pentane gave 1-bromocycloheptene (**1b**) in 60% yield. The organolithium reagent also reacted smoothly with iodine in THF solution to give a 42% yield of 1-iodocycloheptene (**1c**).



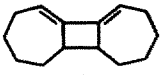
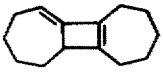
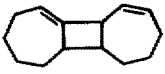
1a: X = Cl
1b: X = Br
1c: X = I
1d: X = O-*t*-Bu
1e: X = NC_4H_8

Reaction of the 1-halocycloheptenes with KO-t-Bu in DMSO and THF gave mainly 14-carbon hydrocarbons together with small amounts of 1-t-butoxycycloheptene (**1d**). Traces of 7-carbon hydrocarbons were detected, and these were identified tentatively as cycloheptene and 1,3-cycloheptadiene by comparison of VPC retention times. Products and yields from these reactions are summarized in Table 1.

nm assigned to 4,[2] the spectrum showed an absorption at 250 nm, $\epsilon = 14{,}500$. The isomer, therefore, must be conjugated. Comparison of the UV absorption of 1-methylene-3-methylcyclobutene (λ_{max} 224 nm, $\epsilon = 15{,}000$)[7] with that of 1,2-dimethylenecyclobutane (λ_{max} 246 nm, $\epsilon = 11{,}000$)[8] shows that the shift of λ_{max} to the blue and the greater extinction coefficient are consistent with the assignment of the methylenecyclobutene structure. This compound could not be isolated pure because it could either not survive the detector conditions or exposure to air. Roberts and coworkers[7a] reported that 1-methylene-3-methylcyclobutene decomposes rapidly in air.

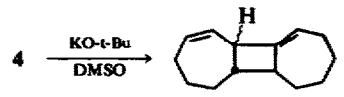
When tricyclo[7.5.0.0^{2,8}]tetradeca-2,14-diene (**4**) was treated with 0·2 equivalents of KO-t-Bu in DMSO it rearranged rapidly to give a 30% yield of two isomeric compounds (*m/e* 188) in a ratio of

Table 1. Products and yields from reactions of 1-halocycloheptenes with KO-t-Bu[a]

Halocycloheptene	Solvent	Time, hr.	Yields, %				
			1d	 **4**	 **5**	 **6**	Residue[b]
1a	THF	2	3	54	—	—	—
1b	THF	2	3	30	16	—	35
1c	THF	2	5	23	10	—	47
1a	DMSO	1	0·3	47	—	21	10
1c	DMSO	1	trace	43	—	—	29

[a]All reactions were performed under nitrogen at 65° with 2·2 equiv of KO-t-Bu in THF and 1·1 equiv of KO-t-Bu:t-BuOH complex in DMSO.
[b]Residue yield was based on complete dehydrohalogenation.

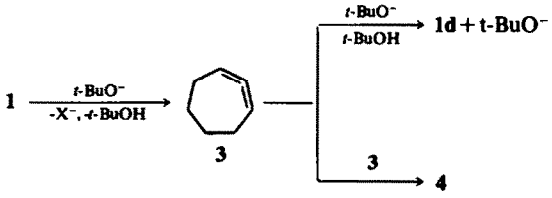
The structure of 1-t-butoxycycloheptene (**1d**) was established by its spectral properties, its acid hydrolysis to cycloheptanone,[5] and its elemental analysis. The structure of the principal dimeric product, tricyclo[7.5.0.0^{2,8}]tetradeca-2,14-diene (**4**), was determined by Ball and Landor[2] and confirmed by Wittig and Meske-Schüller,[3] and its stereochemistry was established as *trans* by Criegee and Reinhardt.[6] The structural assignment of tricyclo[7.5.0.0^{2,8}]tetradeca-2(8),14-diene (**5**) was based on examination of spectra of mixtures of it and **4**, which were obtained as distillation fractions from the reaction of 1-bromo- or 1-iodocycloheptene with KO-t-Bu in THF. VPC analysis established that there were two compounds in these fractions in the ratio of *ca* 2:1, and the main compound was **4**. The mass spectrum showed only peaks up to a parent ion of *m/e* 188, and the NMR spectrum showed a vinyl-to-alkyl-proton ratio of 1:12. The latter suggested the presence of an isomer with only one vinyl hydrogen. The UV spectrum provided the best evidence for the position of the double bonds in the second substance. In addition to those absorptions at λ 269 and 259 > 2:1. Only a trace amount of the starting diene remained unchanged. The NMR spectrum of the rearranged mixture indicated a vinyl:alkyl proton ratio of 3:17. By analogy with the behavior of tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene when treated with KO-t-Bu in DMSO,[4] the rearranged products are assigned diastereomeric tricyclo[7.5.0.0^{2,8}]-tetradeca-2,13-diene (**6**) structures.



The reaction of 1-chlorocycloheptene (**1a**) with KO-t-Bu in THF gave a small amount (3%) of 1-t-butoxyclcloheptene (**1d**) and a good yield (54%) of pure **4**. When the reaction of the chloride was carried out in DMSO, a 0·3% yield of **1d** was obtained together with a 68% yield of dimeric material. The dimeric material was a 70:30 mixture of the tricyclo[7.5.0.0^{2,8}]tetradeca-2,14-diene (**4**) and its 2,13-diene (**6**) isomer. When 1-iodocycloheptene

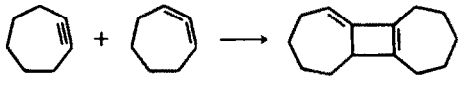
was treated with KO-t-Bu in the same solvent, only a trace (< 0·1%) of substitution product was obtained together with a 43% yield of pure **4**. The fact that the iodide in DMSO gave pure **4** whereas the chloride gave 30% rearranged 2,13-diene (**6**) together with the 2,14-diene (**4**) indicated that KO-t-Bu must react with the iodide much more readily than with **4** so that all the base is consumed before it can effect rearrangement of **4**. Also, the reactivity of KO-t-Bu with the chloride must be only slightly greater than with the initially formed dimer **4**.

By analogy with the behavior of the 1-halocyclohexenes, it appears that the most important initial reaction with KO-t-Bu of the 1-halocycloheptenes in DMSO and 1-chlorocycloheptene in THF is dehydrohalogenation to 1,2-cycloheptadiene (**3**). The strained cyclic allene then dimerizes to give **4** or, at a slower rate, reacts with KO-t-Bu to give 1-t-butoxycycloheptene (**1d**).



The reactions of 1-bromo- and 1-iodocycloheptene with KO-t-Bu in THF are of particular interest because they gave evidence of cycloheptyne involvement. The reaction of the iodide gave a 5% yield of 1-t-butoxycycloheptene together with a 33% yield of dimeric material that consisted of 70% **4** and 30% tricyclo[7.5.0.0^{2,8}]tetradeca-2(8), 14-diene (**5**). The bromide gave a lower yield (3%) of ether and a higher yield of dimeric product, but the composition of the dimeric fraction was much the same.

As **5** does not appear as a product from the base-induced isomerization of **4**, it must be formed by another mechanism. An attractive alternative is 1,2-cycloaddition of 1,2-cycloheptadiene and cycloheptyne.



Change of solvent from DMSO to THF results in a greater amount of cyclohexyne formation in reactions of the 1-halocyclohexenes with KO-t-Bu, and it appears that this solvent change has similar consequences with the 1-halocycloheptenes. As with the reaction of two molecules of 1,2-cycloheptadiene (**3**) that forms **4**, the reaction of the 1,2-diene with cycloheptyne must have a much larger rate constant than that for the reaction of **3** with KO-t-Bu because the concentration of these highly strained intermediates must be very low throughout the reaction.

Low yields of 1-t-butoxycycloheptene were obtained from all reactions of the 1-halocycloheptenes with KO-t-Bu. Yields were slightly greater in THF, and this appears to parallel the increase in importance of the cycloheptyne mechanism. Significantly, Caubere and Brunet[9] found that 1-chlorocyclohexene gives a larger amount of substitution product *via* cyclohexyne when treated with an alkali metal amide than when treated with KO-t-Bu in tetrahydrofuran (THF).

Reactions of 1-chloro- and 1-iodocycloheptene with $NaNC_4H_8$ in THF were carried out to see if yields of substitution products would be increased over those obtained with KO-t-Bu. The results are summarized in Table 2.

Table 2. Products and yields from reactions of 1-halocycloheptenes with $NaNC_4H_8$ in THF[a]

Halocycloheptene	Yields, % 1e	4	5	6	Residue[b]
1a	28	8	—	3	22
1c	24	5	2	—	50

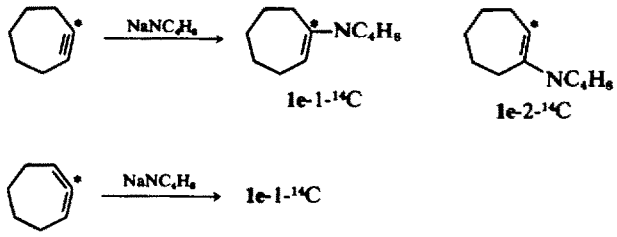
[a]Reactions were performed with 2·2 equiv of $NaNC_4H_8$ under nitrogen at 65°.

[b]Residue yield was based on complete dehydrohalogenation.

Comparison of Tables 1 and 2 shows that use of $NaNC_4H_8$ in place of KO-t-Bu results in significant increases in yield of substitution product and substantial reductions in yield of 14-carbon hydrocarbons. Interestingly, the major dimer obtained is that formed apparently by dimerization of 1,2-cycloheptadiene. With $NaNC_4H_8$, 1-iodocycloheptene gave a small amount of the 1,2-cycloheptadiene-cycloheptyne addition product **5**, and 1-chlorocycloheptene gave a low yield of **6**, the rearrangement product from **4**.

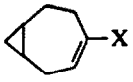
In an attempt to determine the relative importance of the 1,2-cycloheptadiene and cycloheptyne pathways in the substitution reaction of **1a** with $NaNC_4H_8$, we prepared 1-chlorocycloheptene-1-^{14}C and converted it to 1-(1-pyrrolidino)-cycloheptene-x-^{14}C (**1e**-x-^{14}C). By analogy with the behavior of the 6-membered ring homologs, cycloheptyne-1-^{14}C can be expected to give equal amounts of **1e**-1-^{14}C and **1e**-2-^{14}C, whereas 1,2-cycloheptadiene-2-^{14}C can be expected to give only **1e**-1-^{14}C.

Acid hydrolysis of **1e**-x-^{14}C gave cycloheptanone-x-^{14}C, which was subjected to the conditions used by Roberts *et al*[10] to degrade cyclohexanone to 1,5-diaminopentane and carbon dioxide. The procedure gave poor (< 10%) yields of 1,6-diaminohexane and carbon dioxide. Unexplainably, the carbon dioxide, which should be formed from C_1 of



1e-x-^{14}C, had a specific activity equal to only 5–10% that of the cycloheptanone-x-^{14}C. However, the specific activity of the diamine, which should contain C_2-C_7 of 1e-x-^{14}C, was 35 ± 2% that of the cycloheptanone-x-^{14}C. Although this latter result indicated that 70 ± 4% of the radioactive 1e was formed *via* cycloheptyne and 30 ± 4% was formed *via* 1,2-cycloheptadiene, the poor material balance of radioactivity cast serious doubt on its reliability.

As a further effort to determine the relative importance of the two elimination–addition mechanisms in the conversion of 1-chlorocycloheptene to 1-(1-pyrrolidino)-cycloheptene, we prepared 4-chlorobicyclo[5.1.0]octanone (7a) from 4-bicyclo-[5.1.0]octanone and treated it with $NaNC_4H_8$ in THF. Note that if 7a reacts in the same manner as its 6-membered ring analogs, the corresponding cycloheptyne will give equal amounts of 3- and 4-(1-pyrrolidino)bicyclo[5.1.0]oct-3-ene, whereas the corresponding cyclic allene will give only the latter substitution product.



7a: X = Cl 7b: X = I

The mixture of pyrrolidinobicyclo[5.1.0]oct-3-enes obtained from 7a was converted to the corresponding mixture of ketones by acid hydrolysis. Analysis by vpc showed that the ketone mixture consisted of 66% 4-bicyclo[5.1.0]octanone and 34% 3-bicyclo[5.1.0]octanone, which confirmed the result obtained with 1a-1-^{14}C.

We also prepared 4-iodobicyclo[5.1.0]oct-3-ene (7b) and investigated its reaction with $NaNC_4H_8$ in THF. Acid hydrolysis of the resulting pyrrolidinobicyclo[5.1.0]oct-3-enes gave a 65:35 mixture of 4- and 3-bicyclo[5.1.0]octanones. Thus, as with the chlorocycloheptenes, 70% of the substitution reaction of the iodocycloheptene 7a with $NaNC_4H_8$ in THF occurs *via* the cycloheptyne, and the remainder occurs *via* the 1,2-cycloheptadiene.

In summary, reactions of 1-halocycloheptenes with KO-t-Bu are similar to those of the 1-halocyclohexenes[4] in that they appear to take place mainly by initial dehydrohalogenation to the corresponding cycloalkyne and 1,2-cycloalkadiene. Compared with their 6-membered ring homologs, these intermediates yield relatively little substitution product, *i.e.*, 1-t-butoxycycloalkene. 1,2-Cycloheptadiene dimerizes to tricyclo[7.5.0.$0^{2,8}$]-tetradeca-2,14-diene (4) and reacts with cycloheptyne to yield 5, the 2(8), 14-diene isomer of 4. In addition, 4 is rearranged under the reaction conditions to 6, the 2,13-isomer of 4. Reactions similar to those leading to 4 and 6 also take place on reaction of the 1-halocyclohexenes; however, the homolog of 5 was not observed, presumably because of its lesser stability. Unlike the 1-halocyclohexenes with KO-t-Bu, particularly in DMSO, the 1-halocycloheptenes undergo very little prototropic rearrangement to the corresponding 3-halocycloalkene and subsequent dehydrohalogenation to the 1,3-cycloalkadiene. Reactions of 1-chloro- and 1-iodocycloheptenes with $NaNC_4H_8$ in THF give somewhat better yields of substitution product, and cycloheptyne and 1,2-cycloheptadiene are both important intermediates in these reaction.

EXPERIMENTAL

Sublimed KO-t-Bu was obtained from MSA Research Corp. and resublimed before use. All DMSO used had been passed through a column of basic alumina, activity grade one, and distilled from 3 Å molecular sieves at reduced pressure. THF was distilled from LAH before use. As the 1-halocycloheptenes decompose slowly on standing, they were redistilled at reduced pressure immediately before use.

Temps are uncorrected. IR spectra were obtained with either a Beckman IR-8 or Perkin Elmer 237B spectrophotometer. NMR spectra were obtained at 60 MHz with a Varian Associates A60A spectrometer or 100 MHz with a Jeolco Minimar. Unless noted otherwise, spectra were taken of 10–20% solns in CCl_4, and resonance frequencies in NMR spectra were determined relative to internal TMS. UV spectra were obtained with a Cary Model 14 recording spectrophotometer. Mass spectra were determined with a Consolidated Electrodynamics Corp. Type 21-104 mass spectrometer; an ionizing voltage of 70 eV was used. Gas chromatograms were obtained with an Aerograph Model 600-D, an Aerograph Model A-700, a Varian-Aerograph Model 90-P, or an F. and M. Model 810. ^{14}C assays were made using a Nuclear-Chicago Corp. Model GWI ^{14}C glassware system and an Applied Physics Corp. Cary 31 vibrating reed electrometer. Samples for radioassay were weighed with a Cahn Electrobalance Model M-10. Elemental analyses were carried out by the Microanalytical Laboratory, University of California, Berkeley, or Chemalytics, Inc. Tempe, Arizona.

1-*Bromocycloheptene*. To a vigorously stirred suspension of 7·63 g (1·1 mole) of Li wire in 1 l. of ether under N_2 was added dropwise 65·2 g (0·55 mole) of 1-chlorocycloheptene.[2] The mixture was stirred overnight, cooled

with a dry ice–acetone bath, and 66 g (0·825 mole) Br_2 in 200 ml pentane was added dropwise. The mixture was allowed to come slowly to room temp, and 125 ml water was added dropwise to destroy the unreacted Li. The mixture was added to 300 ml water, and the phases were separated. The aqueous phase was extracted with ether (2 × 100 ml), and the organic solns were combined, washed successively with sat sodium thiosulfate soln (2 × 250 ml) and water (2 × 200 ml), dried, and distilled to give 45 g (60%) 1-bromocycloheptene: b.p. 80–81° (20 mm); $n^{23}D$ 1·5151 [lit.[3] b.p. 76–77° (20 mm), $n^{23}D$ 1·5150]; IR 1675 cm^{-1} (C=C); NMR δ 6·17 (t, 1, J = 6 Hz, C<u>H</u>=CBr), 2·65 (m, 2, =CBrC<u>H</u>$_2$), 2·1 (m, 2, C<u>H</u>$_2$CH=) and 1·65 ppm (m, 6, —CH$_2$[C<u>H</u>$_2$]$_3$CH$_2$—); ms, *m/e* (rel intensity) 176(12), 174(12), 96(8), 95(100), 79(10), 77(8), 67(27), 66(7), 65(10), 55(17), 54(15), 53(31), 52(6), 51(11), 41(25), 39(29).

1-*Iodocycloheptene*. As described for the preparation of 1-bromocycloheptene, 1-lithiocycloheptene was prepared from 1·42 g (0·24 mole) of Li wire and 13·3 g (0·103 mole) freshly distilled 1-chlorocycloheptene. I_2 (29 g, 0·114 mole) in 60 ml THF was added dropwise, and the mixture was allowed to come slowly to room temp. Work-up similar to that described for the preparation of 1-bromocycloheptene gave 9·7 g (42%) 1-iodocycloheptene: b.p. 79–80° (7 mm), $n^{23}D$ 1·5611; IR 1625 cm^{-1} (C=C); NMR δ 6·45 (t, 1, J = 7 Hz, C<u>H</u>=CI), 2·75 (m, 2, =CIC<u>H</u>$_2$), 2·1 (m, 2, C<u>H</u>$_2$CH=), and 1·65 ppm (m, 6, —CH$_2$[C<u>H</u>$_2$]$_3$CH$_2$—); ms, *m/e* (rel intensity) 222(55), 128(4), 127(16), 96(8), 95(100), 93(7), 79(10), 77(12), 67(47), 66(11), 65(12), 55(36), 54(7), 53(35), 52(9), 51(14), 41(47), 40(7), 39(39). (Found: C, 37·82; H, 4·72; I, 56·98. $C_7H_{22}I$ requires: C, 37·86: H, 4·99; I, 57·15.)

4-*Chlorobicyclo*[5.1.0]*oct-3-ene* (**7a**). A soln of 19·8 g (0·159 mole) bicyclo[5.1.0]octan-4-one[11] dissolved in 50 ml ether was added dropwise to a stirred slurry of 66·5 g (0·318 mole) PCl_5 in 300 ml ether. When the addition was complete, the mixture was heated under reflux for 5 hr, cooled, and added cautiously to 500 g crushed ice. The phases were separated, and the aqueous phase was extracted with ether. The ether solns were combined, washed successively with sat. $NaHCO_3$ aq (2 × 200 ml) and sat NaCl aq (2 × 200 ml), dried ($MgSO_4$), and distilled to give 16·2 g (72%) 4-chlorobicyclo[5.1.0]oct-3-ene: b.p. 100–103° (35 mm); $n^{24}D$ 1·5071; IR 1640 cm^{-1} (C=C); NMR δ 5·88 (m, 1, C=C<u>H</u>), 2·6–0·02 ppm (multiplets, ≫ 100 lines, 10); ms (in part), *m/e* (rel intensity) 144(8), 142(25), 114(21), 113(19), 107(71), 101(38), 91(59), 88(24), 80(14), 79(100), 78(23), 77(49), 67(50), 65(82), 54(96), 53(51), 52(23), 51(54), 50(29). (Found: C, 67·46; H, 7·78; Cl, 25·08. $C_8H_{11}Cl$ requires: C, 67·37: H, 7·77; Cl, 24·86%).

4-*Iodobicyclo*[5.1.0]*oct-3-ene* (**7b**). A procedure similar to that used to prepare 1-iodocycloheptene was used. From 10·0 g (0·070 mole) **7a**, 0·97 g (0·14 mole) Li, and 17·8 g (0·070 mole) I_2 was obtained 3·4 g (20%) 4-iodobicyclo[5.1.0]oct-3-ene: b.p. 109–111° (12 mm); $n^{24}D$ 1·5817; IR 1618 cm^{-1} (C=C); δ 6·20 (m, 1, C=C<u>H</u>), 2·80 (m, 2, =CI—C<u>H</u>$_2$—), 2·44–0·52 (multiplets, 6, C<u>H</u>$_2$—C<u>H</u>—C<u>H</u>—C<u>H</u>$_2$), 0·17–0·0 ppm (m, 2, cyclopropane C<u>H</u>$_2$); ms, *m/e* (rel intensity) 235(3), 234(30), 127(21), 107(84), 105(11), 92(12), 91(53), 79(100), 78(16), 77(32), 67(26), 66(30), 65(24), 54(15), 53(67), 52(16), 51(30), 50(19). (Found: C,41·23; H, 4·58; I, 54·12. $C_8H_{11}I$ requires: C, 41·05; H, 4·74; I, 54·21%). Also obtained were 0·87 g (12%) bicyclo[5.1.0]oct-3-ene, b.p. 66–67°, identical with an authentic sample,[11] and 1·3 g (13%) of recovered **7a**, b.p. 75–79° (12 mm).

Reactions of halocycloheptenes with KO-t-Bu

(A) *In THF*. The following is representative. To a stirred soln of 18·9 g (0·168 mole) KO-t-Bu in 100 ml THF at 65° under N_2 was added dropwise 10·0 g (0·0766 mole) 1-chlorocycloheptene. After 2 hr, the mixture was cooled and quenched with 30 ml sat K_2CO_3 aq. The mixture was poured into 200 ml water and extracted with ether (3 × 100 ml). The ether extract was washed with K_2CO_3 aq (2 × 100 ml), dried (K_2CO_3), and distilled to give two fractions. The first fraction was 0·35 g (2·7%) of 1-t-butoxycycloheptene: b.p. 80–84° (14 mm); $n^{25}D$ 1·4684; IR 1650 (C=C) and 1140–1170 cm^{-1} (C—O—C); NMR δ 5·0 (t, 1, J = 7 Hz, C<u>H</u>=COR), 2·45–1·85 (m, 4, —C<u>H</u>$_2$C=CC<u>H</u>$_2$), 1·8–1·45 (m, 6, —CH$_2$[C<u>H</u>$_2$]$_3$CH$_2$—) and 1·22 ppm (s, 9, —C[C<u>H</u>$_3$]$_3$); ms, *m/e* (rel intensity) 168(2·5), 113(8), 112(94), 111(8), 97(50), 95(20), 94(19), 84(64), 83(54), 81(8), 79(11), 77(6), 70(28), 69(21), 68(31), 67(14), 59(20), 58(27), 57(65), 56(30), 55(81), 54(10), 53(20), 51(9), 43(28), 42(22), 41(100), 40(11), 39(56). (Found: C, 78·68; H, 11·88. $C_{11}H_{20}O$ requires: C, 78·51; H, 11·98%). The second fraction was 3·89 g (54%) **4**: b.p. 123–137° (4 mm) [lit.[2,3] b.p. 95° (0·5 mm)]; m.p. *ca* −20°, UV (2,2,4-trimethylpentane), λ 269(sh), λ_{max} 259 (ε = 10,500), and λ 251 nm (sh); IR 1630 cm^{-1} (C=C); NMR, δ 5·63 (t, m, 1, J = 5 Hz, RC<u>H</u>=CR'R"), 2·55–1·05 ppm (m, 9, other <u>H</u>); ms (in part), *m/e* (rel intensity) 189(11), 188(68), 92(28), 91(100). Yields of products from this and other reactions are summarized in Table 1.

(B) *In DMSO*. The following is representative. To a stirred soln of 9·49 g (0·0845 mole) of KO-t-Bu and 6·25 g (0·0845 mole) of t-BuOH in 100 ml of DMSO at 65° under N_2 was added dropwise 10·0 g (0·0768 mole) 1-chlorocycloheptene. After 1 hr, when VPC analysis (5 ft SE 30, 150°) of an aliquot indicated that the reaction was complete, the mixture was cooled and poured into 400 ml water, and the mixture that resulted was extracted continuously overnight with 200 ml of ether. The ether extract was washed with saturated potassium carbonate solution (2 × 100 ml), dried (K_2CO_3), and distilled to give two fractions. The first fraction, b.p. 77–84° (9 mm), weighed 0·21 g and consisted of 46% t-BuOH, 14% 1-t-butoxycycloheptene, and 40% dimeric material as determined by VPC and NMR analysis. The second fraction, b.p. 118–123° (4 mm), weighed 4·79 g. VPC analysis (5 ft SE 20, 125°) indicated that the fraction was 70% **4** and 30% of two other products in a ratio of 2:1. The NMR consisted of δ 6·0–5·4 (m, 1, vinyl <u>H</u>) and 2·8–1·0 ppm (m, 7·9, other <u>H</u>), which, together with the other data, indicated that the by-products were isomers of the diene and contained 3 vinyl hydrogens per molecule. Yields from this and other reactions are summarized in Table 1.

Reaction of tricyclo[7.5.0.0^{2,6}]*tetradeca-2,14-diene*(**4**) *with* KO-t-Bu *in DMSO*. To a stirred soln of 0·116 g (1·04 mmoles) KO-t-Bu in 20 ml DMSO at 65° under N_2 was added dropwise 1·0 g (5·32 mmoles) of **4**. The mixture darkened immediately, and VPC analysis (5 ft SE 30, 125°) after 1·25 hr and 2·5 hr showed two new products in the ratio of *ca* 2:1; only a small amount of the starting diene remained. Approximately 0·5 g of KO-t-Bu in 2 ml of DMSO was added after 3 hr. This caused no further change in the product mix. The reaction was cooled, poured into 75 ml water, and the mixture that resulted was extracted continuously with ether overnight. The ether

extract was washed with water (2 × 50 ml), dried ($MgSO_4$), and distilled to give a 0·30-g fraction (30%): b.p. 118–120° (3 mm); IR 1670 cm^{-1} (C=C); NMR δ 5·63 (m, 3, vinyl H) and 2·9–1·0 (m, 17, other H); ms (in part), *m/e* (rel intensity) 189(7·2), 188(47), 92(46), 91(100). The residue weighed 0·4 g.

Reactions of 1-*halocycloheptenes with* $NaNC_4H_8$. The following is representative. To a slurry of sodamide prepared from 4·40 g (0·192 mole) Na and 100 ml liquid ammonia under N_2 was added 12·0 g (0·168 mole) of pyrrolidine (freshly distilled from NaOH). THF (100 ml) was added, and the mixture was allowed to warm to room temp, then heated under reflux for 1 hr. To the stirred mixture at reflux was added dropwise 10·0 g (0·0766 mole) 1-chlorocycloheptene. The reaction was very exothermic. After 1 hr, the mixture was cooled and filtered under N_2 in a dry box. The ppt was washed with ether, and the organic solns were combined and distilled to give two fractions. The first fraction weighed 3·53 g (28%) and was **1e**: b.p. 105–108° (7 mm), $n^{25}D$ 1·5226 [lit.[13] b.p. 100–102° (5 mm), $n^{25}D$ 1·5195]; IR 1630 cm^{-1} (C=C); NMR (C_6H_6) δ 4·68 (t, 1, $J = 7$ Hz, $CH{=}CNR_2$), 2·9 (m, 4 $-CH_2-N(R)CH_2$), 2·33 (m, 4 $CH_2C{=}CCH_2$), and 1·9–1·4 (m, 10, other H); ms, *m/e* (rel intensity) 165(49), 150(57), 136(100), 95(24), 70(36). The second fraction, b.p. 87–94° (0·5 mm), weighed 0·61 g (11%), and NMR and VPC analysis indicated that it consisted of 70% **4** and 30% of the isomeric 2,13-dienes. The residue weighed 1·43 g (22% based on complete dehydrohalogenation). Yields of products from reactions of 1-chloro- and 1-iodocycloheptene with $NaNC_4H_8$ are given in Table 2.

Treatment of 7·85 g (0·055 mole) of **7a** and 3·3 g (0·014 mole) of **7b** with $NaNC_4H_8$ in THF gave, respectively, 0·91 g (10%) and 0·25 g (12%) of mixed 3- and 4-(1-pyrrolidino)bicyclo[5.1.0]oct-3-enes: b.p. 56–68° (0·15 mm); IR 1618 cm^{-1} (C=C); NMR (C_6H_6) (in part), δ 4·0 (m, C=CH of 4-isomer), 3·8 ppm (broad s, C=CH of 3-isomer). The mixtures, which were contaminated with the corresponding bicyclo[5.1.0]octanones, were analyzed as described below.

1-*Chorocycloheptene*-1-^{14}C. By use of the procedure of Gilman and Blatt[14] for the preparation of α,ω-dicyano compounds, 61·2 g (0·942 mole) KCN -^{14}C (0·5 mc/mole, obtained from New England Nuclear Corp.) was converted to 36·8 g (69%) of ^{14}C-labelled 1,6-*dicyanohexane*: b.p. 116–120° (0·5 mm), $n^{25}D$ 1·4416 [lit.[15] b.p. 128° (0·8 mm), $n^{25}D$ 1·4437]. The procedure used by Allinger *et al*[16] for the preparation of *cis*-bicyclo[5.2.0]nonan-4-one was modified appropriately to convert 7·0 g (0·051 mole) of the labelled dicyanide to 4·81 g (84%) of *cycloheptanone*-1-^{14}C, and the procedure of Mousseron and Jacquier[1,17] was used to prepare 23·37 g 1-chlorocycloheptene-1-^{14}C (sp act 0·08 mc/mole) in 67% yield from 29·85 g cycloheptanone-1-^{14}C. The final product had b.p. 68–70° (30 mm), $n^{25}D$ 1·4852 [lit.[1] b.p. 52–53° (11 mm)].

Degradation of 1-(1-*pyrrolidino*)*cycloheptene*-X-^{14}C. A soln prepared from 2·8 g (0·0170 mole) 1-(1-pyrrolidino)-cycloheptene-x-^{14}C, b.p. 105–107° (5 mm), $n^{25}D$ 1·5226, and 20 ml of ether was shaken vigorously with three 10-ml portions 0·2 N HCl, dried ($MgSO_4$), and distilled to give 1·48 g (78%) cycloheptanone-x-^{14}C, b.p. 82–84° (30 mm); $n^{25}D$ 1·4590 (lit.[18] b.p. 180°, $n^{21}D$ 1·4604); semicarbazone, m.p. 163–164° (lit.[18] m.p. 163°). Cycloheptanone-x-^{14}C was degraded using the method described by Roberts *et al*[10] for the degradation of cyclohexanone to 1,5-diaminohexane and carbon dioxide; details are given by Frost.[19] From 1·0 g labelled ketone was obtained 50·5 mg (9%) of barium carbonate and 75 mg (7%) 1,6-diaminohexane dibenzenesulfonamide-x-^{14}C: m.p. 151–153° (ethanol–water) (lit.[20] m.p. 154°). ^{14}C-Assays of cycloheptanone-x-^{14}C (as the semicarbazone) and its degradation products were made by the method of Neville.[21] The results are summarized in Table 3.

Table 3. ^{14}C distribution data for 1-(1-Pyrrolidino)cycloheptene-X-^{14}C from 1-chlorocycloheptene-1-^{14}C[a]

Compound	Wt, mg	Activity, mv sec^{-1}	Specific Activity, × 10^4 mv $sec^{-1}mole^{-1}$
Cycloheptanone	5·970	1·343	3·80
semicarbazone	5·663	1·296	3·87
	5·402	1·215	3·80
	average (10%)		3·82 ± 0·03
1,6-Diaminohexane	4·708	0·1583	1·34
dibenzenesulfonamide	4·630	0·1560	1·37
	4·753	0·1600	1·34
	average (35 ± 2%)		1·35 ± 0·01

[a]All barium carbonate determinations were between 5 and 10%.

Analysis of mixtures of 3- *and* 4-*bicyclo*[5.1.0]*octanones*. Mixtures containing 24–49% 3-bicyclo[5.1.0]-octanone[11] and 51–76% 4-bicyclo[5.1.0]octanone were prepared, taken up in ether, and analyzed by VPC using a 500-ft × 0·03 in. stainless steel column (Carbowax 20 M). A 100-μl aliquot of the product mixture from the reaction of **7a** with $NaNC_4H_8$ was taken up in a small amount of ether and treated with 1·5 N HCl. Comparison of the chromatograms with those of the standards showed that the ketone mixture was 35% 3-bicyclo[5.1.0]octanone and 65% 4-bicyclo[5.1.0]octanone. The product mixture from **7b** and $NaNC_4H_8$ was treated and analyzed in the same way; the hydrolyzate was a 34:66 mixture of 3- and 4-bicyclo[5.1.0]octanone.

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