Tetrahedron Vol 31, pp 1131 to 1134 Pergamon Press 1975 Printed in Great Britain

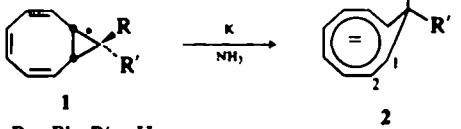
ON THE MECHANISM OF THE REDUCTIVE CLEAVAGE OF *anti*-9-PHENYL-*cis*-BICYCLO[6.1.0]NONA-2,4,6-TRIENE

S. W. STALEY,* G. E. LINKOWSKI and A. S. HEYN
Department of Chemistry, University of Maryland, College Park, Maryland 20742

(*Received in the USA 6 August 1974; received in the UK for publication 30 September 1974*)

Abstract—Treatment of the title compound (**1a**) with potassium in liquid ammonia at *ca* −33° immediately afforded the benzylcyclooctatetraene dianion (**4a**) which, upon quenching with iodine-pentane, gave benzylcyclooctatetraene (**5**) as the only isolable product. In contrast, treatment of **1a** with potassium amide in liquid ammonia at −69° initially afforded the 9-phenylmethylenecyclooctatrienyl anion (**6a**) as a short-lived intermediate which was then converted to the α-aminobenzylcyclooctatetraene dianion (**7a**). These results, coupled with the observation that *cis*-bicyclo[6.1.0]nona-2,4-diene (**12**) in potassium amide-liquid ammonia affords the *cis*-bicyclo[6.1.0]nonadienyl anion (**8b**) which then slowly opens to the methylcyclooctatetraene dianion (**4b**) at 12°, lead to the conclusion that **4a** is produced by a reductive cleavage of **1a** *via* a radical anion or dianion.

The reduction of *cis*-bicyclo[6.1.0]nona-2,4,6-triene and its 9-alkyl derivatives (**1b–e**)[1,2] with potassium in liquid ammonia at −65° or higher affords cyclononatrienyl anions[2,3]† (**3b–e**) *via* the corresponding monohomocyclooctatetraene dianions (**2b–e**).[2] In contrast, treatment of the title compound (**1a**) under essentially the same

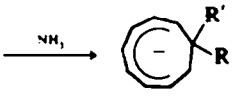


1

a: R = Ph, R′ = H
b: R = R′ = H
c: R = H, R′ = Me

2

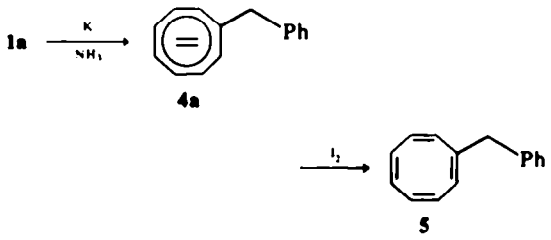
d: R = Me, R′ = H
e: R = R′ = Me

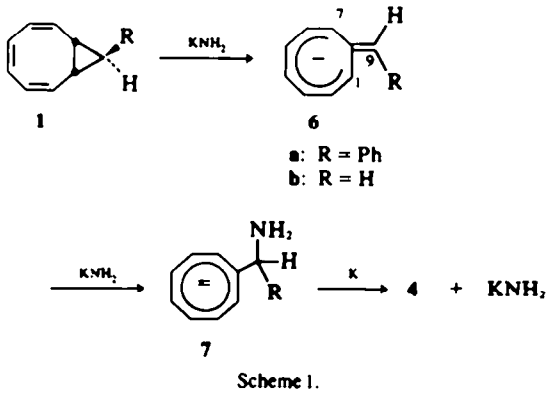


3

conditions immediately produces a deep-red solution of dianion **4a**, the NMR spectrum of which (at −65°) displays a complex multiplet at δ 6·98–7·83 (5H, phenyl), a broad (width at half-height ≈ 10 Hz) singlet at 5·66 (7H), and a two proton singlet at 4·17. This dianion, which was stable at room temperature, was quenched into iodine-pentane to afford benzylcyclooctatetraene (**5**), which displayed i.r. and NMR spectra identical in all respects with those from material prepared by the treatment of cyclooctatetraene with benzyllithium.[3,4]

A priori, there are several pathways which could account for the formation of **4a**. In the pathway outlined in Scheme 1, a small amount of adventitious potassium amide effects ring cleavage to afford methylenecyclooctatrienyl anion **6a** which then suffers amide attack and reductive cleavage of the resultant amine derivative (**7a**). The first two steps find close analogy in the rapid formation of **6b** and **7b** at −65°[7] while the last step is analogous to the putative reductive cleavage of triphenylmethylamine to triphenylmethylsodium in liquid ammonia at −33°.[8] Note that only a catalytic amount of potassium amide is required.



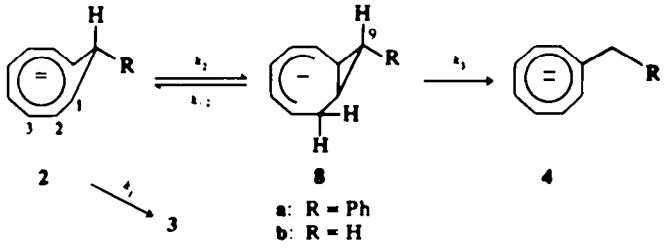


Scheme 1.

†The methylcyclooctatetraene radical anion has been observed during electrolytic[4a] or alkali metal reduction[4b] of **1b** but this presumably represents a relatively minor pathway.

This mechanism was tested by treating **1a** with an excess of potassium amide in liquid ammonia.[9] Anion **6a** was formed immediately at −69°, and its NMR spectrum displayed a pattern of signals (see Experimental section) which, although weak, was essentially identical to that of the lithium salt of **6a**.[10] The latter was obtained by the treatment of **1a** with lithium amide in liquid ammonia and is stable at room temperature. The potassium salt of **6a** is converted to dianion **7a** (δ 6·98–7·77 (m, 5H), 5·73 (s, width at half height = 5 Hz, 7H), and 5·28 (s, 1H)),* but the former anion is stable for over 1 h at −65°. Since **1a** is completely converted to **4a** within 10 min at −65°, this eliminates the mechanism in Scheme 1 as the pathway leading to **4a**.

A second possibility (Scheme 2) involves protonation of **2a** at C_2 followed by cyclopropyl ring cleavage and deprotonation. This mechanism receives some support



Scheme 2.

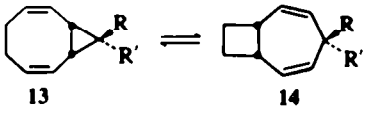
from the observation that **2b** in tetrahydrofuran is deuterated by CH_3OD at C_2 and C_3 to afford **9**.[11] In contrast, **2e** is deuterated in ammonia-d_3 at C_1 to afford **3e** which is stable under the reaction conditions.[2] The latter result suggests that $k_1 > k_2$ (Scheme 2). While this might at first seem to rule out the formation of **4a** *via* Scheme 2, this pathway might still obtain if (1) $k_{-2} > k_2 > k_1$ and $k_{-2} \gg k_3$ for R = H, (2) $k_{-2} > k_2 > k_1$ but $k_3 > k_{-2}$ for R = Ph, and (3) the protonation and deprotonation steps (k_2 and k_{-2}, respectively) are stereospecific. The latter point is required in order to account for the fact that **3b** and **3e** did not show deuterium uptake at C_2 as well as at C_1 in ammonia-d_3,[2] and finds ample precedent in several previous studies of deuterium transfer in nonplanar cyclic homoconjugated anions (**10**[12] and **11**[13]). Furthermore, the

9 **10** **11** **12**

reversal of the relative magnitudes of k_{-2} and k_3 could be rationalized on the basis of a much greater anion-stabilizing ability of R = Ph relative to R = H during the cyclopropyl ring-cleavage step.

Accordingly, we have prepared **8b** cleanly by the treatment of **12** with excess potassium amide in liquid ammonia and have characterized this anion by its NMR spectrum at −48° (Experimental) and by quenching it with water to afford a mixture of **12** and *cis*-bicyclo[6.1.0]nona-2,5-diene. Interestingly, **8b** is converted to **4b** as shown by the NMR spectrum of the latter species at 37° (δ 5·60 (s, 7H), δ 2·87 (s, 3H)), and by its oxidative quenching with iodine to afford methylcyclooctatetraene. However, the rate of conversion is relatively slow ($t_{1/2}$ (−12°) ≈ 2·5 h). Thus if **8b** were formed in the reduction of **1b** at −65° (i.e. if $k_2 > k_1$), then the former species would have accumulated and would have been detected by NMR spectroscopy. The foregoing experiment therefore provides the final proof that **2b** is protonated more rapidly at C_1 than at C_2 in liquid ammonia (i.e. that $k_1 > k_2$).

Since the transition state leading to **8** (in which the exocyclic orbitals on C_9 are sp^2) will be stabilized more by R = Ph relative to R = H than will that leading to **3** (in which the corresponding orbitals are sp^3), it is not unreasonable to expect that k_2 will increase relative to k_1 on going from R = H to R = Ph. However, it has been found that geminate methyl groups stabilize **13b** relative to **14b** (K_{eq} (200°) = 0·7)[14] to about the same extent that an *anti*-phenyl group stabilizes **13a** relative to **14a** (K_{eq} (150°) = 0·6).[15] Since **2e** also undergoes deuteration at C_1



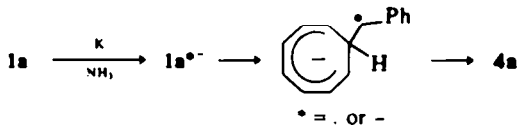
13 **14**

a: R = Ph, R' = H
b: R = R' = Me

(although at a slower rate than for **2b**),[2] it is probable that $k_1 > k_2$ for **2e** and **2a** also. This assumes, of course, that the phenyl group in **2a** does not sterically inhibit protonation at C_1 to a significantly greater extent than do the methyl groups in **2e**. This reasonable, although unproven, assumption permits the tentative conclusion that Scheme 2 can be excluded as a major pathway in the formation of **4a**.

In our view, the formation of **4a** is best explained by a cleavage of bond a in **1a** *via* an intermediate radical anion or dianion prior to protonation (Scheme 3). The complete reversal of the regioselectivity in the cleavage of **1a** relative to **1b** can be reasonably attributed to stabilization of the transition state for cleavage of bond a in the former compound by the phenyl group.[16]

*Recorded at 37°; the amino proton signal was obscured by the solvent absorption at δ 0·2–1·4.



Scheme 3.

EXPERIMENTAL

General. I.R. spectra were recorded on a Perkin-Elmer model 337 grating spectrometer and were obtained on solutions in 0·1 mm NaCl cells or on neat samples in a 0·025 mm KBr cell. Only the major bands are given. NMR spectra were obtained on a Varian A-60A instrument with TMS as an internal standard in CCl_4 or with trimethylamine (δ_{TMS} = 2·135) as an internal standard in liquid ammonia. Preparative glpc separations were performed on a Varian-Aerograph A-90P3 thermal conductivity instrument equipped with 0·25 in copper columns. M.ps are uncorrected. Microanalyses were performed by Dr. Franz Kasler of the University of Maryland Department of Chemistry.

anti-9-*Phenyl*-cis-*bicyclo*[6.1.0]*nona*-2,4,6-*triene* (**1a**). Freshly distilled cyclooctatetraene (10·0 g, 0·096 mol) was cautiously added to a soln of 1·35 g (0·195 g at) Li in 250 ml ammonia at *ca* −30° to produce a tan-colored suspension. A soln of 10·5 g (0·061 mol) α,α-dichlorotoluene in 10 ml ether was then added with stirring over about 30 min. After stirring for an additional hour, 5 ml sat NH_4Cl aq was added, followed by 50 ml of ether and 200 ml water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether layers were then washed with water, dried ($MgSO_4$), the ether was removed by rotary evaporation, and the cyclooctatetraene was distilled *in vacuo*. The residue was chromatographed with pentane on neutral alumina and recrystallized from pentane to afford 2·95 g (25%) of **1a**, m.p. 61·5–62°; i.r. (CCl_4): 3015, 1600, 1500, 1216, 1081, 1048, 732 and 695 cm^{-1}; NMR (CCl_4): δ 6·9–7·2 (m, 5H, aromatic), 5·7–6·1 (m, 6H, olefinic), AB_2 pattern at 1·80 (2H, bridgehead) and 1·47 (1H, H_9, $J_{1,9} = J_{6,9}$ = 5·8 Hz). (Found: C, 92·91; H, 7·40. $C_{15}H_{14}$ requires: C, 92·74; H, 7·26%).

Cleavage of anti-9-*phenyl*-cis-*bicyclo*[6.1.0]*nona*-2,4,6-*triene* (**1a**). A soln of 1·0 g (0·005 mol) **1a** in 10 ml anhyd. ether was added dropwise to a soln of 1·0 g (0·026 g at) K in 125 ml liquid ammonia at *ca* −30°. The reddish-brown soln was stirred for 30 min after which time the contents of the flask were *cautiously* added to a vigorously stirred suspension of 6·5 g (0·026 mol) I_2 in 200 ml pentane. The organic layer was washed several times with sat sodium thiosulfate aq and dried over Na_2SO_4. (*Caution is strongly recommended since it is possible that an explosive substance, nitrogen triiodide, may be formed in this procedure.* However, we have never experienced any problems.) The solvent was removed by rotary evaporation and the residue was chromatographed on neutral alumina with pentane. Final purification was effected by bulb-to-bulb distillation at 0·1 mm to afford 0·2 g (20%) **5**; IR (CCl_4): 3020, 3000, 1072, 1028, 862, 732, 696, 662, 642 cm^{-1}; NMR (CCl_4): δ 7·13 (s, 5H), 5·66 (broadened s, 7H), and 3·30 (s, 2H). (Found: C, 92·88; H, 7·16. $C_{15}H_{14}$ requires: C, 92·74; H, 7·26%).

Benzylcyclooctatetraene (**5**)[3]. Freshly distilled cyclooctatetraene (5·0 g, 0·005 mol) was added dropwise to a stirred soln of benzyllithium[18] (from 12·0 g (0·0066 mol) of benzyl ether and 4·0 g (0·58 g at) Li in 125 ml anhyd. ether. The mixture was stirred for 24 h and then added to an ice-cooled soln of 4·0 g (0·016 mol) I_2 in 200 ml pentane. After extraction of the aqueous layer with pentane the organic layers were washed with $Na_2S_2O_3$ aq and dried ($MgSO_4$). The solvent was removed by rotary evaporation and 3·0 g unchanged cyclooctatetraene was recovered by distillation *in vacuo*. The residue was then extracted with 10 × 20 ml 20% $AgNO_3$ aq and the extracts were extracted with ether, treated with aqueous ammonia, and extracted with ether a second time. The latter extracts were dried ($MgSO_4$), the solvent was removed *in vacuo*, and the residue was chromatographed on neutral alumina with pentane to afford 0·5 g (13% based on unrecovered cyclooctatetraene) benzylcyclooctatetraene. NMR and i.r. spectral data for this material were identical to data recorded for **5** which was obtained by the reductive cleavage of **1a**.

cis-*Bicyclo*[6.1.0]*nona*-2,4-*diene* (**12**). A mixture of 60% 1,3,5- and 40% 1,3,6-cyclooctatriene[19] (9·0 g, 0·085 mol) was added to a suspension of diethylzinc[20] (from 22·9 g (0·35 mol) of Zn–Cu couple,[21] 42·0 g (0·27 mol) EtI, and 28·0 (0·27 mol) EtBr in 25 ml ether, followed by 45·0 g (0·168 mol) diiodomethane. At this point the mixture became exothermic and was cooled by a water bath and then stirred at *ca* 50° overnight. Pentane (25 ml) and 100 ml of 5% HCl were added, and the contents of the flask were filtered. The aqueous layer was extracted with pentane and the organic layers were washed 3 times each with 5% HCl, 5% $NaHCO_3$ aq, and water, dried ($MgSO_4$), concentrated by rotary evaporation, and distilled to afford 4·7 g of colorless liquid at 25–30° (0·2 mm). Analysis by glpc (5% Igepal-C0880 on 80/100 Chromosorb P at 60°) showed the mixture to contain 2% 1,3,6- and 18% 1,3,5-cyclooctatriene, 36% **12**, and 36% of four longer retention time products which, taken together, had an NMR spectrum which showed strong cyclopropyl absorption. The relative retention times were 1·0, 2·0, 3·5, 5·2, 6·2, 7·0 and 7·2, respectively. Compound **12** was isolated by glpc and identified by comparison of its i.r. spectrum with a published spectrum.[22]

Cleavage of cis-*bicyclo*[6.1.0]*nona*-2,4-*diene* (**12**) *to methylcyclooctatetraene.* Ammonia (3 ml) was condensed (at −78°) into a heavy-walled 1·3 × 18 mm Pyrex tube which was narrowed to 0·6 × 5 cm at one end and could be sealed by a Teflon septum-type Swagelok fitting. A small crystal of ferric chloride and 59 mg (1·5 mg at) K were added and the tube was sealed and allowed to warm to room temp. After the blue potassium soln was converted to a yellowish-gray color the tube was again cooled to −78° and 80 μl of a 58:42 mixture of **12** and undecane was injected. The contents of the tube were warmed to room temp. and shaken thoroughly. After 2 h the tube was again cooled to −78°, opened, and the contents were inverted *cautiously* into an Erlenmeyer flask containing a stirred soln of 1·0 g (4·2 mmol) I_2 in 30 ml pentane. (*See cautionary note in the description of the reductive cleavage of* **1a**.) The organic layer was washed with 50 ml of 5% $K_2S_2O_3$ soln, dried ($MgSO_4$), and concentrated. Analysis by glpc (5% Igepal-C0880 on 80/100 Chromosorb P at 80°) showed a 17:83 ratio of methylcyclooctatetraene (29% yield) and undecane and no unchanged **12**. The methylcyclooctatetraene was isolated by glpc and identified by comparison of its neat i.r. spectrum with a published spectrum.[23] The latter shows an extra band at *ca* 760 cm^{-1} which is not present in our spectrum.

NMR spectra of samples in liquid ammonia. Our previously published general technique for obtaining NMR spectra of samples in liquid ammonia (4–5 molar excess of base) was employed.[17] The spectra of anions **4a**, **4b**, and **7a** are given in the text. Anion **6a** (in ammonia at −69°) showed a sharp multiplet at δ 7·31 (phenyl), a singlet at 6·17 (H_9), an 11 Hz triplet at 4·95 (H_6), two 13 Hz doublets at 4·47 and 4·13 (H_1 and H_7), and two apparent 10–11 Hz triplets at 3·60 and 3·50 (H_2 and H_5). The signals for H_3 and H_4 were partially obscured by the δ 5·22 singlet for $CHNH_2$ in dianion **7a**. Anion **8b** (in ammonia-*d*, at −48°) displayed a downfield pattern of at least five lines which is consistent with doublets of doublets for H_1 and H_7 at δ 5·48 and 5·62, respectively, an apparent 8 Hz quartet for H_6 at 3·65, a four line pattern interpretable as an 11 Hz doublet for H_2 at 3·16 and an apparent 8·5 Hz triplet for H_4 at 2·83, a 7·4 Hz triplet at 2·02 (2H, H_3), several lines in the region 1·25–1·6, and a broadened 4·6 Hz triplet for H_9 (endo) at −0·89. These assignments have been

confirmed by 100 MHz spectra and by spin decoupling experiments.

Protonation of anion **8b**. *cis*- **12** (75 mg, 0·63 mmol) was added to a soln of potassium amide (from 70 mg (1·8 mmol) K) in 20 ml of liquid ammonia at *ca* −30° to produce an intense orange-red color. This soln was quenched after 10 min with sat NH_4Cl aq and extracted with pentane. Glpc analysis (8% TCEP on 100/120 Chromosorb P at 70°) indicated two products with relative retention times (and relative yields) of 1·0 (59%) and 1·2 (41%). These were purified by glpc and identified as *cis*-bicyclo[6.1.0] nona-2,5-diene and **12**, respectively, by comparison of their i.r. and NMR spectra with published data.[22]

Acknowledgement—We are pleased to acknowledge the National Science Foundation for support of this work.

REFERENCES

[1]W. H. Okamura, T. I. Ito and P. M. Kellett, *Chem. Commun.* 1317 (1971)
[2]S. V. Ley and L. A. Paquette, *J. Amer. Chem. Soc.* **96**, 6670 (1974)
[3]S. W. Staley and N. J. Pearl, *Ibid.* **95**, 3437 (1973)
[4a]T. J. Katz and C. Talcott, *Ibid.* **88**, 4732 (1966); [b]R. M. Owens, cited by F. J. Smentowski, R. M. Owens and B. D. Faubion, *Ibid.* **90**, 1537 (1968).
[5]This is an extension of the method of A. C. Cope and M. R. Kinter, *Ibid.* **73**, 3424 (1951)
[6]Initial attempts to employ the procedure of C. A. Harmon and A. Streitwieser, Jr., (*J. Org. Chem.* **38**, 549 (1973)) were unsuccessful.
[7]S. W. Staley, G. M. Cramer and G. E. Linkowski, unpublished results
[8]C. A. Kraus and R. Rosen, *J. Am. Chem. Soc.* **47**, 2745 (1925)
[9]The initial spectra were obtained by G. M. Cramer
[10]S. W. Staley, G. E. Linkowski and G. M. Cramer, *Abstracts*, 166th National A.C.S. Meeting, ORGN 137, Chicago, Ill., August (1973)
[11]M. Ogliaruso and S. Winstein, *J. Am. Chem. Soc.* **89**, 5290 (1967)
[12]P. Radlick and W. Rosen, *Ibid.* **89**, 5308 (1967)
[13]J. M. Brown and E. N. Cain, *Ibid.* **92**, 3821 (1970)
[14]W. Grimme, *Ibid.* **95**, 2381 (1973)
[15]W. Grimme and K. Seel, personal communication
[16]For other examples of reductive cleavages in which the regioselectivity is controlled by phenyl groups, see S. W. Staley, *Selective Organic Transformations* (Edited by B. S. Thyagarajan) Vol. 2, p. 309. Wiley, New York, N.Y. (1972)
[17]S. W. Staley, G. M. Cramer and A. W. Orvedal, *J. Am. Chem. Soc.* **96**, 7433 (1974)
[18]L. H. Sommer, W. D. Korte and P. G. Rodewald, *Ibid.* **89**, 862 (1967)
[19]A. C. Cope and F. A. Hochstein, *Ibid.* **72**, 2515 (1950)
[20]J. Furkawa, N. Kawabata and J. Nishimura, *Tetrahedron* **24**, 53 (1968)
[21]E. LeGoff, *J. Org. Chem.* **29**, 2048 (1964)
[22]W. R. Roth, *Liebigs Ann.* **671**, 10 (1964)
[23]A. C. Cope and H. C. Campbell, *J. Am. Chem. Soc.* **74**, 179 (1952)