Bridged Polycyclic Compounds. 85. Cationic Rearrangements Accompanying Heterolysis of 7-Dibenzobicyclo[2.2.2]octadienylcarbinyl Derivatives[1]

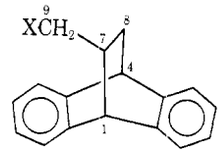
Stanley J. Cristol,* Gwendolyn O. Mayo, and Jan P. Kochansky

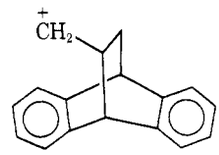
Department of Chemistry, University of Colorado, Boulder, Colorado 80309

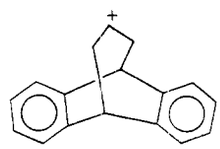
Received September 13, 1976

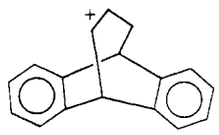
7-Dibenzobicyclo[2.2.2]octadienylcarbinyl trifluoromethanesulfonate (1-OTf) has been acetolyzed and the corresponding amine has been deaminated. The product mixtures, which contain a variety of rearrangement products, have been analyzed. Paths leading to the products have been considered, and the results are discussed briefly.

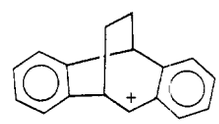
The reaction of 7-dibenzobicyclo[2.2.2]octadienylcarbinyl derivatives 1 under conditions which lead to carbenium ions offers a variety of reaction paths for rearrangements. Thus processes aimed at the formal generation of the primary cation 2 might be accompanied (or followed) by migration of the 1,7 bond to C-9 to give 3, by migration of the 8,7 bond to give 4, which is known[1,2] to equilibrate rapidly with 5, and by migration of the C-7 hydrogen to give 6, which would equilibrate[3] with 7. Products from these rearrangements, as well as from that to give 8, might therefore be anticipated. Our interest in the variances in fates of the "same" ion from different sources,[4] as well as the prospect of forming products from ion 3, which we wished for other studies, prompted our studies of the solvolysis of 1 derivatives, and of the nitrous acid deamination of 1-NH_2.

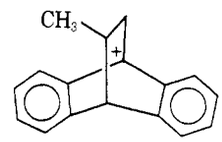

1

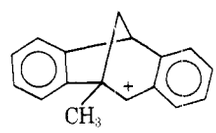

2

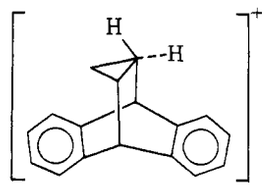

3


4


5

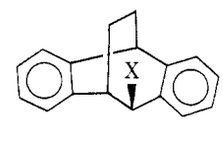

6

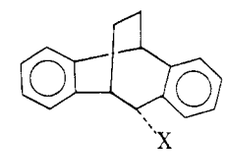

7

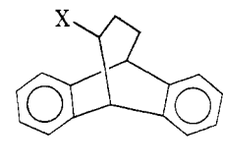

8

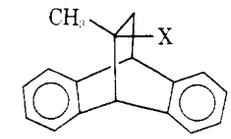
Compounds 1 were, as might be expected for primary carbinyl derivatives, quite unreactive toward solvolysis. 1-Cl was stable toward silver acetate in refluxing acetic acid for 8 days, and the *p*-toluenesulfonate ester 1-OTs and methanesulfonate ester 1-OMs were found to acetolyze at rates about 1/20 those of the corresponding ethyl or isobutyl derivatives. Thus formation of acetolysis products of these compounds required long periods of time at elevated temperatures, for example, 1 month at 121 °C for approximately 9 half-lives of 1-OTs. The prospect of isolation of kinetically controlled products therefore appeared dim. However, the trifluoromethanesulfonate ester 1-OTf acetolyzed in acetic acid containing 0.5 M sodium acetate at 81 °C with a half-life of 10 min, and these conditions represented ones where most of the anticipated products might be expected[1] to survive, or at least give readily recognizable descendants.

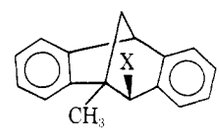
When the triflate 1-OTf was heated in acetic acid containing excess sodium acetate at 81 °C for 2.2 h, six products were formed in measurable amounts (>2%). The principal products were 3,6-dibenzobicyclo[3.2.2]nonadienyl acetates, 9-OAc and 10-OAc, formed as 63% of the product mixture, and the 6,8 isomer 11-OAc, formed in 15% yield. These are related to the 4 ⇄ 5 equilibrating[1] cations, and indicate that migration of the 8,7 bond to give 4 accompanies about 80% of the acetolysis of 1-OTf.[5] Formed in 9% yield each were 12-OAc and 13-OAc, which, with 2.5% of 14, indicate that about 20% of the 1-OTf undergoes solvolysis with accompanying hydride migration to give ion 6. The only other product seen was 16-OAc (3%), which is known[1] not to involve itself in equilibria with the 9, 10, and 11 system, or the 12–13 system, but which probably

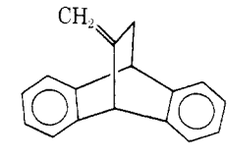

9

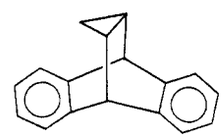

10

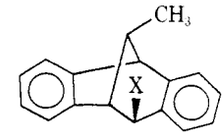

11

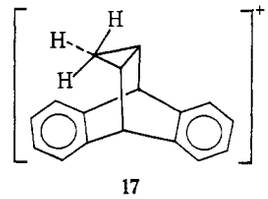

12

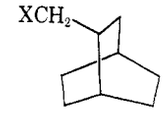

13

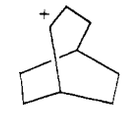

14


15


16


17


18


19

arises from the isomerization of 8 to 17.[6] This latter ion has been shown[1] to be the precursor of 16-OAc in the acid-catalyzed addition of acetic acid to the cyclopropane 15. It is of interest that no 1-OAc is formed in the acetolysis, indicating that the triflate 1-OTf does not suffer direct displacement by acetate, and that the primary cation 2 is also probably not involved. 1-OAc is stable to the reaction conditions.

When the amine 1-NH_2 (as the hydrochloride) was dissolved in acetic acid and treated with sodium nitrite, the product mixture was significantly different from that of the triflate acetolysis. No 11-OAc was found, but 37% of 9-OAc and 10-OAc reflected the 8,7-bond migration to the cation 4.[8] Twenty-six percent of the product, divided as 12% of 12, 6% of 13, and 8% of 14, may be conceived as derived from hydride migration to give 6, which equilibrates rapidly to give 7, and 13% was 16. In addition to these products, which were also found in acetolysis, although in different ratios, 8% of the cyclopropane 15 and 14% of the unrearranged acetate 1-OAc were obtained. The latter product may be ascribed to a direct displacement on the intermediate diazonium ion,[9] and the former is another example of the common observation[11] that cyclopropanes are formed in substantial amounts in the deamination of amines of primary alkyl radicals.

We ascribe the product differences to conformational requirements in solvolysis vs. those in deamination. In the solvolysis, the loss of nucleofuge to give a cation–anion pair is a highly endothermic process, while, in the deamination, loss of nitrogen nucleofuge should be considerably less endothermic, even though in both cases a primary cation would be generated if rearrangement did not occur.

The results can thus be rationalized on the assumption that the need for anchimeric assistance attendant upon the concomitant anti group migrations differ for the two cases. Thus the conformational restrictions (i.e., appropriate geometric alignments) on nucleofuge loss in the deamination are less severe than are those in the solvolysis, and rearrangement to ion 4 is diverted in part to insertion to give ion 8 and solvent participation to give 1-OAc.

It is of interest that no product from migration of the 1,7 bond to give ion 3 was observed in either case. (We have studied[12] acetolyses involving 3, and they proceed normally without rearrangement.) This seems unusual, as the corresponding rearrangement has been noted[13,14] in the system without the benzo substituents, that is, deamination of 18 gives the alcohol derived from 19. Inspection of models does not give us any insight into conformational problems for the 1 system that would prevent such a rearrangement to 3 from occurring.

Experimental Section

Preparation of Compounds. 7-Dibenzobicyclo[2.2.2]octadienylcarbinol (1-OH) was prepared by the method of Alder and Windemuth[15] and converted to its **acetate** (1-OAc) with acetyl chloride in pyridine, mp 120.5–121.5 °C (lit.[15] 122 °C, lit.[16] 119–119.8 °C).

The **methanesulfonate ester** (1-OMs) was prepared from methanesulfonyl chloride in pyridine, mp 114–116.5 °C.

Anal.[17] Calcd for $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77. Found: C, 69.06; H, 5.67.

The ***p*-toluenesulfonate ester** (1-OTs) was prepared from *p*-toluenesulfonyl chloride in pyridine, mp 141.5–142.5 °C (lit.[18] 140–141.5 °C, lit.[19] 143–144 °C).

The **trifluoromethanesulfonate ester** (1-OTf) was prepared by mixing a solution of 3.1 g (11 mmol) of trifluoromethanesulfonic anhydride[20] in 75 ml of benzene and a solution of 2.58 g (11 mmol) of 1-OH and 1.36 g (11 mmol) of *N,N*-dimethylaniline in 25 ml of benzene. Both solutions were cooled to 5 °C before mixing and the mixture was held at 5 °C for 30 min. The precipitate was filtered and the filtrate washed rapidly with ice-cold 5% aqueous hydrochloric acid, followed by saturated aqueous sodium bicarbonate. The organic layer was dried and the benzene removed by reduced pressure distillation at 25 °C. The resulting oil was dissolved in 10 ml of pentane and placed in a refrigerator. White platelets precipitated (2.25 g, 53%, mp 89–91 °C) which upon recrystallization from pentane had mp 90.5–92 °C dec. The compound decomposed upon standing at room temperature, so that a satisfactory analysis could not be obtained, but it could be stored for several months in a refrigerator.

Mass spectrum. Calcd for $C_{18}H_{15}F_3O_3S$: *m/e* (rel intensity, corrected for $M^+ + 1$ peaks) 368 (100), 369 (20.6), 370 (6.9). Found: 368 (100), 369 (20.6), 370 (6.9).

3,6-Dibenzobicyclo[3.2.2]nonadien-*exo*-2-yl acetate (9-OAc) and the endo isomer **10-OAc** have been described previously,[1,2] as has the 6,8 isomer (11-OAc). *syn*-8-Methyl-*exo*-2-dibenzobicyclo[3.2.1]-octadienyl acetate (16-OAc) has also been described.[1] **7-Methyl-7-dibenzobicyclo[2.2.2]octadienol** was prepared by the method of Shiner and Humphrey.[21] Its acetate, 12-OAc, the isomeric 1-methyl-2-dibenzobicyclo[3.2.1]octadienyl acetate (13-OAc), and the olefin 14 have been found[3] to equilibrate rapidly in acetic acid when traces of mineral acid are present. Olefin 14[19] was prepared as described earlier.[22] **Dibenzotricyclo[3.2.2.$0^{2,4}$]nonadiene (15)**, mp 178–179.5 °C, was prepared by reduction of 3,3-dichlorodibenzotricyclo[3.2.2.$0^{2,4}$]nonadiene[23] with excess sodium metal in *tert*-butyl alcohol. It was identical with the compound isolated in the deamination and with that prepared by an alternative and more convenient method.[1]

Anal. Calcd for $C_{17}H_{14}$: C, 93.53: H, 6.47. Found: C, 93.59; H, 6.62.

7-Aminomethyldibenzobicyclo[2.2.2]octadiene (1-NH_2). A mixture of 40 g (0.22 mol) of anthracene and 125 ml (1.7 mol) of allylamine was heated in a sealed glass tube at 220 °C for 24 h. The tube was cooled and opened and the liquid decanted. Methanol was added and the solution was treated with an excess of 3% aqueous hydrochloric acid. The precipitate (amine hydrochloride) was filtered, washed with benzene, and recrystallized from water, with activated charcoal clarification. The product, an off-color salt, weighed 46 g (78%). The amine hydrochloride was dissolved in boiling water, and the resulting solution was made basic with dilute aqueous sodium hydroxide. The oil was dissolved in ether, and the ethereal solution washed with water and dried ($MgSO_4$). The ether was removed by rotary evaporation and recrystallization from benzene–hexane gave 1-NH_2, mp 116–117 °C (lit.[24] 116–117 °C).

Analysis of Solvolysis and Deamination Products. The product mixtures were analyzed by a combination of gas chromatography and ^1H NMR methods. For the latter, the hydrocarbon and acetate mixtures were used directly; for the former, the mixtures were treated with lithium aluminum hydride to convert the acetates to alcohols. The chromatograms were obtained on an Aerograph A-90 instrument (thermal conductivity detector) at a column temperature of 185 °C with a helium flow rate of 50 ml/min with 5 ft × 0.25 in. columns. The column packings were (A) 3% SE-52 or (B) 3% QF-1 on 100–120 mesh Aeropak 30. Retention times (min) were as follows: 1-OH, (A) 14.5, (B) 24.8; 9-OH, (A) 22.0, (B) 27.1; 10-OH, (A) 19.5, (B) 17.3; 12-OH, (A) 9.8, (B) 8.2; 13-OH, (A) ~13.5, (B) ~14.0; 14, (A) 7.7, (B) 4.8; 15, (A) 9.2, (B) 5.2; 16-OH, (A) ~13.5, (B) ~14.0.

^1H NMR analysis was done on a Varian A-60A instrument, using the following peaks (ppm from Me_4Si), and comparing peak areas with total aromatic peaks: 1-OAc, multiplets at δ 3.43 or 3.71; 9-OAc, doublet at δ 6.17; 10-OAc, doublet at δ 6.07; 11-OAc, doublet at δ 4.25; 12-OAc, singlet at δ 1.57 (3 H); 13-OAc, singlet at δ 5.93; 14, multiplet at δ 6.6–6.7 (2 H); 16-OAc, singlet at δ 1.10 (3 H).

Acetolysis of 1-OTf. A sample of 1-OTf (467 mg, 1.27 mmol) was dissolved in 5 ml of 0.5 M sodium acetate in acetic acid, placed in a tube, and heated at 81 °C for 2.2 h. The tube was opened, cooled, poured into 10 ml of CCl_4, and washed with 30 ml of water. The organic layer was drawn off and the aqueous layer washed with two 10-ml portions of CCl_4. The combined CCl_4 layers were treated with a small amount of sodium bicarbonate, then dried ($MgSO_4$). The solvent was removed in vacuo and the ^1H NMR spectrum run in deuteriochloroform.

Deamination of 1-NH_2. To 2.86 g (10.5 mmol) of 1-NH_3Cl in 50 ml of glacial acetic acid in a flask with a magnetic stirrer, cooled in a water bath, was added 770 mg (11 mmol) of solid sodium nitrite, in small portions, over a 2-h period. The reaction mixture was poured into water, and sodium hydroxide was added to neutralize the excess acid. The mixture was extracted with ether, and the ethereal solution was washed with water and dried ($MgSO_4$). Removal of the solvent left a product which was subjected to analysis as above; however, the major portion was treated by chromatography on alumina. Elution with hexane gave first a mixture of 14 and 15, then further elution with petroleum ether or with carbon tetrachloride gave acetate products. Analysis of the partially separated fractions confirmed the other analysis.

Rough acetolysis rates were measured on 1-OTs and 1-OMs in sealed ampules containing 0.1 M 1 and 0.2 M NaOAc in 2% acetic anhydride in glacial acetic acid at 121.4 ± 0.3 °C, using the procedure of Young, Winstein, and Goering.[25] 1-OTs had a rate constant of 2.1×10^{-6} l./s mol and 1-OMs of 2.8×10^{-6} l./s mol.

The acetolysis of 1-OTf was followed by NMR analysis, using 0.44 M 1-OTf and 0.87 M NaOAc. The ester in acetic acid has a sharp singlet (^{19}F NMR) at 7116 Hz above $CFCl_3$ while trifluoromethanesulfonate ion has one at 6787 Hz. Rate constants for acetolysis follow: at 60.0 ± 0.3 °C, 1.0×10^{-4} l./s mol; at 70.0 ± 0.3 °C, 4.1×10^{-4} l./s mol.

Acknowledgment. The authors are indebted to the National Science Foundation for generous support of this research under Grant GP 8913X.

Registry No.—1-OMs, 61436-65-5; 1-OTf, 61436-66-6; 1-OH, 6624-25-5; 1-OAc, 61394-44-3; 1-NH_2, 4053-27-4; 1-NH_3Cl, 6275-73-6; 1-OTs, 4427-38-7; 9-OH, 23445-14-9; 9-OAc, 24332-09-0; 10-OH, 23445-15-0; 10-OAc, 24332-08-9; 11-OAc, 24330-16-3; 12-OH, 61394-45-4; 12-OAc, 61394-46-5; 13-OH, 61394-47-6; 13-OAc, 61394-48-7; 14, 19978-14-4; 15, 30122-20-4; 16-OH, 59938-58-8; 16-OAc, 59938-57-7; methanesulfonyl chloride, 124-60-3; trifluoromethanesulfonic anhydride, 358-23-6; 3,3-dichlorodibenzotricyclo[3.2.2.0^{2,4}]nonadiene, 6531-28-8.

References and Notes

(1) Part 84: S. J. Cristol and A. L. Noreen, *J. Org. Chem.*, **41**, 4016 (1976).
(2) (a) E. Ciorănescu, M. Banciu, R. Jelescu, M. Rentzer, M. Elian, and C. D. Nenitzescu, *Tetrahedron Lett.*, 1871 (1969); (b) *Rev. Roum. Chim.*, **14**, 911 (1969).
(3) R. S. Beckley, Ph.D. Thesis, University of Colorado, 1970.
(4) See, for example, S. J. Cristol, G. C. Schloemer, D. R. James, and L. A. Paquette, *J. Org. Chem.*, **37**, 3852 (1972).
(5) The possibility that some of these products arise from the sequence **1** → **8** → **4** relates to the question of whether **8** is an intermediate rather than a transition state on the reaction coordinate. Our experience[1] on ring-opening electrophilic addition to **15** suggests the former.
(6) Hydrogen migrations in protonated cyclopropanes are well documented.[7]
(7) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964).
(8) It has previously been shown[1,2] that kinetic control in the **4** ⇄ **5** cationic system leads to **9** and to **10**, with slower rearrangement to **11** species.
(9) A number of investigators[4,10] have suggested direct displacement by nucleophiles upon diazonium ions, and this was first demonstrated by Collins and Benjamin.[10h]
(10) (a) J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4094 (1959); (b) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964); (c) J. G. Traynham and M. T. Yang, *ibid.*, **87**, 2394 (1965); (d) R. D. Guthrie, *ibid.*, **89**, 6718 (1967); (e) J. H. Bayless, A. T. Jurewicz, and L. Friedman, *ibid.*, **90**, 4466 (1968); (f) V. T. Albry, J. E. C. Hutchins, R. M. Hyde, and R. H. Johnson, *J. Chem. Soc. B*, 219 (1968); (g) L. Friedman in G. A. Olah and P. v. R. Schleyer, "Carbonium Ions", Vol. II, Wiley-Interscience, New York, N.Y., 1970, p 655 ff; (h) C. J. Collins and B. M. Benjamin, *J. Am. Chem. Soc.*, **92**, 3182 (1970).
(11) For examples and discussions of cyclopropane formation in diazonium ion reactions see ref 10g and J. T. Keating and P. S. Skell in G. A. Olah and P. v. R. Schleyer, "Carbonium Ions", Vol. II, Wiley-Interscience, New York, N.Y., 1970, p 573 ff.
(12) J. P. Kochansky, Ph.D. Thesis, University of Colorado, 1971.
(13) K. Alder and R. Reubke, *Chem. Ber.*, **91**, 1525 (1958).
(14) (a) J. P. Schaefer, L. S. Endres, and M. D. Moran, *J. Org. Chem.*, **32**, 3963 (1967); (b) J. A. Berson, R. T. Luibrand, N. G. Kundu, and D. G. Morris, *J. Am. Chem. Soc.*, **93**, 3075 (1971).
(15) K. Alder and E. Windemuth, *Chem. Ber.*, **71**, 1939 (1938).
(16) E. I. Snyder and R. A. Clement, *J. Am. Chem. Soc.*, **82**, 1424 (1960).
(17) Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.
(18) P. K. Shenoy, Ph.D. Thesis, University of Arizona, 1966.
(19) J. R. Geigy AG, Netherlands Patent Application 6 412 205 (April 22, 1965); *Chem. Abstr.*, **63**, 14788a (1965).
(20) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957).
(21) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **85**, 2416 (1963).
(22) S. J. Cristol and G. O. Mayo, *J. Org. Chem.*, **34**, 2363 (1969).
(23) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *J. Am. Chem. Soc.*, **90**, 5564 (1968).
(24) N. V. de Bataafsche Petroleum Maatschappij, British Patent 749 723 (1956); *Chem. Abstr.*, **51**, 11371e (1957).
(25) W. G. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951).

Mode of Formation of Deoxybenzoin in the Reaction of *N*-Benzyl-α-phenylnitrone with Potassium Hydroxide–*tert*-Butyl Alcohol

J. Herbert Hall* and Matthias R. Gisler

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

Received February 13, 1976

Treatment of *N*-benzyl-α-phenylnitrone with potassium hydroxide–*tert*-butyl alcohol was found to give deoxybenzoin. The formation of the deoxybenzoin was found to be the result of base attack on an aldol type condensation product (**7**) of the nitrone. The latter compound could be formed in moderate yield, by treatment of the nitrone with lithium dimsylate. Treatment of the condensation product with potassium hydroxide–*tert*-butyl alcohol gave deoxybenzoin, benzoic acid, benzamide, benzyl alcohol, tetraphenylpyrazine, and a trace of benzaldehyde. A scheme is proposed to account for these products.

In connection with an entirely different investigation, we had occasion to treat tribenzylamine *N*-oxide with potassium hydroxide in *tert*-butyl alcohol, and obtained, among other products, the ketone, deoxybenzoin (**6**).[1] Since we obviously had chanced on to some type of rearrangement reaction, we undertook to determine the mode of formation of the deoxybenzoin.

The first clue to the deoxybenzoin formation was the isolation of a small amount of *N*-benzyl-α-phenylnitrone (**1**) from the above reaction mixture. With the thought that this nitrone might possibly be the precursor of the deoxybenzoin, we synthesized the nitrone in quantity, using a modification of the procedure reported by De La Mare and Coppinger.[2] Treatment of the *N*-benzyl-α-phenylnitrone with potassium hydroxide in refluxing *tert*-butyl alcohol did indeed give deoxybenzoin, along with a number of other products.

One of the possible mechanistic pathways for the formation of the deoxybenzoin from the nitrone is given in Scheme I. According to this scheme the anion of the nitrone undergoes ring closure to the anion of an *N*-hydroxyaziridine (**3**), which subsequently could undergo C–N bond cleavage to ultimately give deoxybenzoin oxime (**5**). The observed deoxybenzoin could then be formed on workup in aqueous solution. However, examination of the reaction products failed to reveal the presence of any of the oxime (**5**). Further, refluxing of an authentic sample of deoxybenzoin oxime with potassium hydroxide–*tert*-butyl alcohol, followed by the same workup of the reaction as used with the nitrone, gave only recovered oxime and no deoxybenzoin. This result apparently eliminates Scheme I.

A second clue to the deoxybenzoin formation was found when we succeeded in isolating from the nitrone (**1**), KOH,