

Identification of Minor Products from Oxymercuration-Demercuration of Bullvalene: Substituent Effects on Mechanisms of Free-Radical Rearrangements

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Minor products from oxymercuration-demercuration of tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene (bullvalene) were separated and identified as *cis*-bicyclo[4.1.0]decatrienols. Information from product stereochemistry and mechanisms of similar free-radical reactions seems to indicate that one of the intermediates may be a hydroxy radical analogue of a homoallylic (or even homoaromatic) cation.

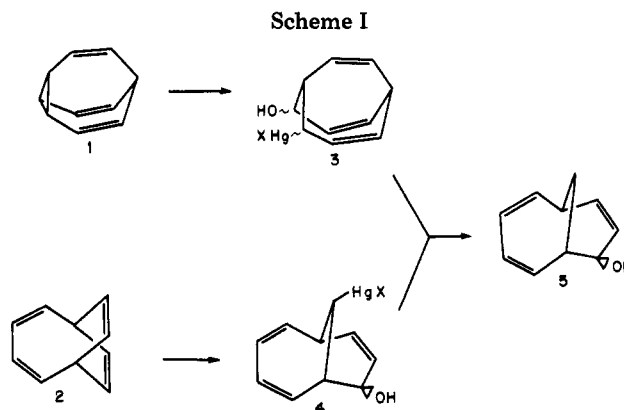
In our search for precursors that could be used for the generation of relatively stable bishomotropylium cations,¹ an obvious choice was the preparation of [4.3.1]deca-2,4,8-trienyl derivatives. Here the geometry should be favorable for homoconjugative backside participation of π bonds with the vacant p lobe on the site where the ion is generated. Comparison with data for cations generated from allylic systems in which different types of electronic or geometric effects could play a role should provide further insight into their relative importance in the generation of ions under conditions of long or short life.²

An attractive route for the preparation of this type of compound was suggested by a report³ on methoxymercuration-demercuration of both tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene (1), commonly referred to as bullvalene, and bicyclo[4.2.2]decatetraene (2) (Scheme I). Either one leads to the desired *exo*-7 derivative along with minor unidentified products. Substitution of methoxy for oxy groups provided us with materials necessary for our solvolytic investigations.

However, as demercuration proceeds through free-radical pathways⁴ and does not normally result in rearrangements, we decided to also investigate the nature of minor products formed in this reaction. The structure of these products should throw light on the mechanism for rearrangements involving radical species with a [4.3.1] skeleton, the cation analogue of which had been found to be unusually stable.^{1,2}

Results and Discussion

Oxymercuration 3, obtained from the reaction of bullvalene^{5,6} with mercuric acetate in aqueous tetrahydrofuran, was treated *in situ* with a solution of sodium borohydride in dilute sodium hydroxide. Reaction products were extracted and immediately placed on a silica gel column. Elution with fractions of hexane-ether solutions, gradually increasing in ether concentration, separated 5 and a mixture of isomer alcohols. Successive runs on the column and enrichment of fractions afforded the separation of two compounds, henceforth referred to as A and B. Spectral data shows that they are structurally similar C₁₀H₁₂O alcohols containing three double bonds, two of which are conjugated. Although both compounds decompose rapidly



at room temperature, storage under nitrogen in a dry ice bath enabled us to obtain their NMR spectra in the presence of lanthanide shift reagents.⁷

Further interpretation is based on the consideration of possible structures for A and B. On elimination of compounds with a [7.1.0] skeleton, on the basis of NMR spectra (absence of any absorption below 1.5 ppm), [6.2.0], [5.3.0], [4.4.0], [5.2.1], [4.3.1], and [4.2.2] structures with various combinations of positions for hydroxyl and olefinic groups as well as stereochemistry can be analyzed.

NMR spectra of A and B in the presence of increasing amounts of Pr(fod)₃ afforded separation of individual absorptions and furnished the data in Tables I and II, respectively. Although complexation may occur in both 1:1 and 2:1 ratios to an organic substrate, lanthanide-induced shifts (LIS) can be treated qualitatively. Molecular models of possible structures were constructed and their LIS estimated⁷ for positions corresponding to intervals of 45° around the oxygen atom. These were later reassessed in view of steric hindrance to complexation of the lanthanide. Assignments that could be made this way were compared to shift data and coupling constants and evaluated for different structures that could be ascribed to A and B. The same procedure applied to known compound 5 leads to highly satisfactory results.

The data in Tables I and II compared to values of LIS obtained this way and of coupling constants from either the Karplus equation⁸ or similar compounds⁸⁻¹² permit the

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Table I. Induced Shifts and Coupling Constants for A^{d,a}

| | | | | | | | | | | | |
|------|-----|------|------|------|------|-----------------|------|------|-----------------|------|------|
| H-1 | | | | | | | | | | | |
| H-2 | 6 | -318 | | | | | | | | | |
| H-3 | 7 | X | -333 | | | | | | | | |
| H-4 | 4 | 17 | X | -255 | | | | | | | |
| H-5 | X | X | 8.5 | X | -243 | | | | | | |
| H-6 | X | X | 4 | X | X | -186 | | | | | |
| H-7 | X | c | X | 2 | X | X | -126 | | | | |
| H-8 | X | c | X | c | 3 | X | 10 | -126 | | | |
| H-9 | X | X | X | X | 4 | c | X | X | -82 | | |
| H-10 | X | X | X | X | X | 10 ^a | X | X | 10 ^b | -63 | |
| H-11 | X | X | X | X | X | 10 ^a | X | X | 10 ^b | X | -63 |
| | H-1 | H-2 | H-3 | H-4 | H-5 | H-6 | H-7 | H-8 | H-9 | H-10 | H-11 |

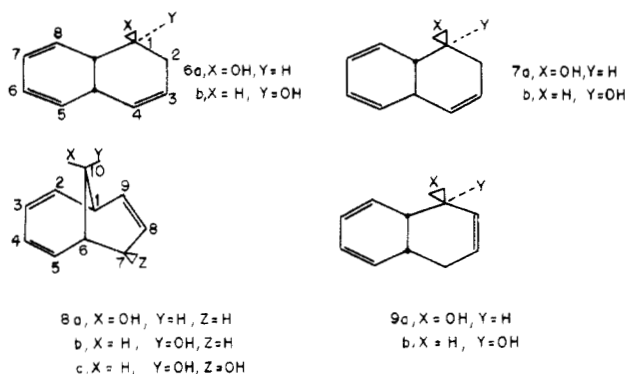
^a Coupling of H-6 to H-10 or H-11. ^b Coupling of H-9 to H-10 or H-11. ^c Coupling observed, value undetermined. ^d X indicates that no coupling is observed. ^e LIS in the presence of shift reagent are on the diagonal ($\Delta\delta_i$, Hz). The coupling constants are in hertz.

Table II. Induced Shifts and Coupling Constants for B^{e,f}

| | | | | | | | | | | | |
|------|-----|------|------|------|-----------------|----------------|------|------|-----------------|------|------|
| H-1 | | | | | | | | | | | |
| H-2 | 4 | -432 | | | | | | | | | |
| H-3 | 2 | X | -375 | | | | | | | | |
| H-4 | X | 6 | X | -301 | | | | | | | |
| H-5 | X | 3 | X | X | -177 | | | | | | |
| H-6 | X | X | 10 | X | X | -147 | | | | | |
| H-7 | X | X | d | d | X | 6 ^b | -138 | | | | |
| H-8 | X | X | d | d | X | 6 ^b | X | -138 | | | |
| H-9 | X | X | X | 5 | d | X | X | X | -96 | | |
| H-10 | X | X | X | X | 10 ^a | X | X | X | 10 ^c | -60 | |
| H-11 | X | X | X | X | 10 ^a | X | X | X | 10 ^c | X | -60 |
| | H-1 | H-3 | H-3 | H-4 | H-5 | H-6 | H-7 | H-8 | H-9 | H-10 | H-11 |

^a Coupling of H-5 to H-10 or H-11. ^b Coupling of H-6 to H-7 or H-8. ^c Coupling of H-9 to H-10 or H-11. ^d Coupling observed, value undetermined. ^e X indicates that no coupling is observed. ^f LIS in the presence of shift reagent are on the diagonal ($\Delta\delta_i$, Hz). The coupling constants are in hertz.

choice to be narrowed down to structures 6–8 for A and 9 for B.



Structures 7 would correspond to *trans*-1,2,4a,8a-tetrahydronaphthalene with a hydroxyl group in the 1-position. In this case, a large (~ 18 Hz) coupling constant between methine protons on the 4a,8a-bond should be observed around 2.7 ppm.¹² There is no corresponding absorption in the NMR spectrum of A.

The NMR spectrum of *exo-anti*-bicyclo[4.3.1]deca-2,4,8-triene-7,10-diol (8c) reveals¹³ absorptions for protons 1 and 6 at 3.12 ppm and for proton 10 at 4.18 ppm. Since the absorption at 3.15 ppm in the spectrum of A integrates for one proton and no large coupling constant for geminal protons on carbon 10 to the α -proton should be observed for 8, these structures can be eliminated.

Spectral data for *cis*-1,2,4a,8a-tetrahydronaphthalene¹⁴ (6), with proper allowances for the introduction of a hydroxyl group in position 1, are very similar to those for A.

LIS for an equilibrium between the hydroxyl group in equatorial and axial positions (80:20 and 90:10)¹⁵ in 6a led to the following sequence of absorptions: $H_1 > H_{8a} > H_2' > H_2 > H_{4a} > H_8 > H_3 > H_4 > H_5 > H_6 > H_7$, whereas from table I the sequence $H_1 > H_2' > H_{8a} > H_2 > H_{4a} > H_8 > H_3, H_4 > H_5 > H_6 > H_7$ can be predicted. The inversion between protons H_{8a} and H_2' is relatively small, the shifts corresponding to 7.3 and 6.9 ppm, respectively.

For 6b, similar considerations led to the sequence $H_1 > H_8 > H_2 > H_{8a} > H_2' > H_{4a} > H_4 > H_3 > H_5 > H_6 > H_7$, as compared to $H_1 > H_2 > H_{8a} > H_2' > H_4 > H_8 > H_3 > H_4 > H_5 > H_6, H_7$ which was expected for the structure. The difference in LIS between H_8 and H_{4a} , which appear inverted in the order of induced upfield shift is verified for all situations in which complexations with the lanthanide ion could occur, although the LIS for H_8 is estimated at three times that of H_{4a} .

In the investigation of possible structures for the second minor product, *cis*-1,4,4a,8a-tetrahydronaphthalene¹⁶ (9) provides UV and NMR data which are similar to those found for B. Thus, the question now lies in the stereochemistry of the hydroxyl group.

Peak widths¹⁷ and vicinal coupling constants¹⁸ for the α -proton indicate that a pseudoaxial position for the hydroxyl group is preferred. Recourse to a molecular model of 9a reveals that this situation presents the smallest degree of interaction possible between the hydroxyl group and neighboring protons. The sum of the coupling con-

(15) (a) An equatorial-axial equilibrium was considered since *cis*-/*trans*-1-decalol is found in a 65:35 ratio and the width of the α -proton signal is 16 Hz.^{15b} In the present case, the width of the corresponding proton absorption is 21 Hz at half-height. (b) Grob, C. A.; Tam, S. W. *Helv. Chem. Acta* 1965, 48, 1317–1321.

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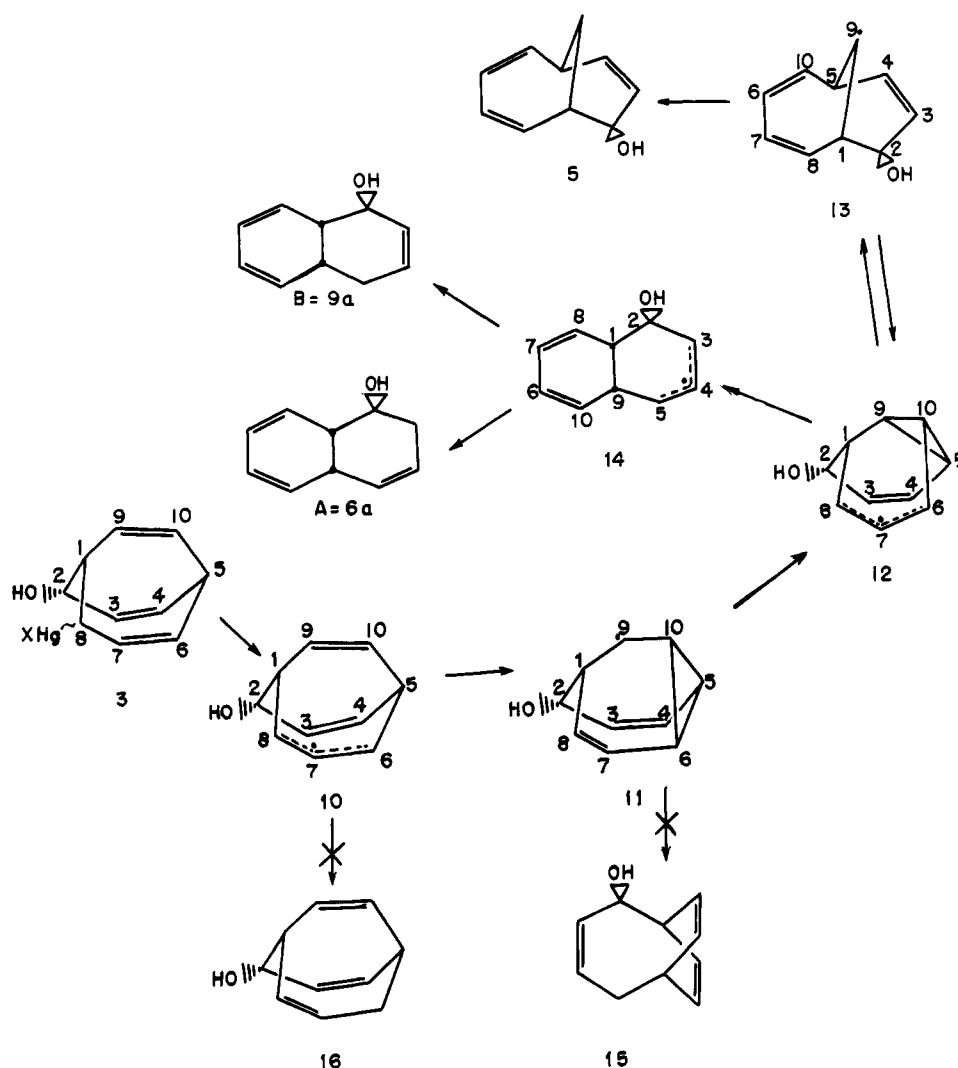
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Scheme II



stants of the α -proton is also in accordance with the 8-Hz total observed for B.

LIS for **9a**, on consideration of the hydroxyl group in a pseudoaxial position and the different conformations which would favor complexation with the lanthanide, led to the sequence $H_1 > H_{8a} > H_2 > H_{4a} > H_8 > H_3 > H_4 > H_4' > H_5 > H_6$ for the induced shifts, which is the same as that estimated from the data in Table II.

In the case of **9b**, in which the α -proton coupling constants predict¹⁸ that the hydroxyl group is in an equatorial position, LIS estimated in the same fashion as above led to the sequence $H_1 > H_8 > H_{8a} > H_2 > H_3 > H_{4a} > H_7 > H_4', H_4 > H_5 > H_6$. As in the discussion of possible structures for A, an inversion in the order of the induced shifts of H_8 and H_{4a} occurs, and the upfield induced shift of H_8 is estimated at three times that of H_{4a} .

On addition of shift reagent, both **6b** and **9b** should exhibit a large induced shift for an olefinic proton. These are relatively modest, and in B the largest induced shift for an olefinic proton corresponds to an isolated double bond, i.e., not part of the conjugated system, as would be expected.

Further information on the stereochemistry of A is afforded by *cis,cis*-1-decalinol, which would correspond to the saturation of **6b** and adopts a conformation in which the hydroxyl group is equatorial due to interaction with protons on carbons 3, 5, and 7.^{15b} In **6b** this interaction is not as significant, and a larger contribution from an axial conformation is to be expected, resulting in a narrowing

of the α -proton peak. From molecular models, the sum of the coupling constants for the molecule in a totally equatorial situation, or its upper limit, is estimated at 18 Hz.

For **6a**, this sum should be larger than the observed 21 Hz for an equatorial hydroxyl group. An estimate from peak widths¹⁹ places the equatorial-axial equilibrium of **6a** between 80:20 and 90:10.

Hydrogenation products of A and B exhibit essentially the same mass spectrum, and the IR spectrum of A is similar to that of *cis,trans*-1-decalinol,²⁰ the saturated analogue of **6a**. The same pattern appears in the IR spectrum of hydrogenated B along with some new absorptions, the principal one being at 1710 cm^{-1} . This is ascribed to the formation of a ketone, as is observed on hydrogenation of allylic alcohols over platinum(IV) oxide.²¹

Establishment of structures **6a** and **9a** for A and B, respectively, allows an inference of the mechanism of the free radical rearrangements that follow oxymercuration-demercuration of both bullvalene and bicyclo[4.2.2]deca-3,4,7,9-tetraene.

Thus free radical **10**, initially formed, undergoes a homoallyl-cyclopropylcarbinyl rearrangement^{22,23} to **11**

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(Scheme II). Here the hydroxyl group is pseudoaxial and the half-occupied p orbital assumes a bisected position relative to the cyclopropyl ring.²⁴ Similar intermediates are proposed for the reduction of products resulting from the bromination of bullvalene.^{25a,b} Further rearrangement leads to 12, which furnishes a route into 13 and 14 and the observed products by hydrogen abstraction. Rearrangement of 12 to 13 must be reversible, since similar products are observed from both 3 and 4.³

It is interesting to compare the behavior of these bicyclic radicals with their cation analogues^{25c,d} in which a [4.3.1]bishomotropylium ion is found to be the lowest energy intermediate.^{1,2,26,27} Comparison of organic cations and radicals has shown that, in certain systems, free-radical rearrangements, proceed with lower activation energies than their carbocation analogues,^{23,28} whereas in other reactions^{29b,30} no evidence is found for the intervention of free-radical analogues of carbocation intermediates. Yet, curiously enough, radical 10, initially formed, goes on to 14 instead of yielding mainly [3.3.2] and [4.2.2] products as has been observed on treatment of brominated bullvalene with tri-*n*-butyltin hydride.^{25a}

This could well be the result of trapping by a better hydrogen donor before rearrangement 12 → 14 could occur. Nonetheless, it is also well-known^{4b} that the position of equilibria between free radicals is influenced by substituents. In intermediates 10 and 11 it is hard to imagine any type of contribution to the stability of radical intermediates that could be ascribed to the presence of a hydroxyl group, and these radicals must be similar to the ones derived from brominated bullvalene (i.e., 10 and 11 minus the substituent). This is apparently not the case with 12.

It has been shown¹⁷ that in methylene cyclohexanes and cyclohexenes the double bond stabilizes the conformer with an axial electronegative group in the allylic position. In 12, placing a hydroxyl group in an axial position lines up p orbitals on C₂-C₃-C₄ as well as on C₆-C₇-C₈, thus flattening out both halves of this intermediate and forcing the rupture of either the C₅-C₁₀ bond (to form 14) or the C₉-C₁₀ bond (to form 13).

This preference for further rearrangements to highly strained species like 11 to 12 over hydrogen abstraction to form species 15 to 16 (which comprise 80% of products observed in rearrangements of the corresponding unsubstituted radicals)^{25a,b} also lends itself to other interpreta-

tions. One of these would involve an added stability of 12 over 10 and 11.

This "flattening" effect could also lead to a better alignment of orbitals on the allyl radical with those on either the olefinic or cyclopropyl (or both) groups, thus providing the distortion necessary for further charge delocalization.³¹ Although there is no necessity to account for such geometry by solely invoking electronic requirements of radical intermediates, one cannot rule out the possibility that, once it is achieved largely due to other effects, electron density is delocalized in a fashion similar to but probably of much lesser magnitude than that for a homoallylic (or even homoaromatic) cation.

Experimental Section

The NMR spectra were recorded on a Hitachi Perkin-Elmer R-20B spectrometer operating at 60 MHz. A Hitachi R-201 SD decoupler and a Takeda-Riken 8324X frequency counter were used for double-resonance experiments. Deuterated chloroform (spectral grade) with 1% Me₄Si was used as a solvent. Absorptions were separated by addition of small quantities of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-praseodymium(III) octadionate (Pr(fod)₃). IR and UV spectra were run on Perkin-Elmer 180 and 356 spectrometers, respectively. Mass spectral data were obtained from a Varian CH5 spectrometer. Perkin-Elmer 900 and Varian 1400 gas chromatographs were used to analyze compounds on Dega, Ucon-polar, SE-30, SE-52, and Carbowax 20M 1/8 in. columns supported on Chromosorb W-AW (80-100 mesh).

Pentacyclo[9.3.2.0^{2,9}.0^{3,8}.0^{10,12}]hexadeca-4,6,13,15-tetraene was prepared⁶ from 62 g (0.6 mol) of freshly distilled cyclooctatetraene. Recrystallization from ether gave 4 g (0.019 mol) of the desired product: mp 74-78 °C (lit.⁶ mp 75-76 °C) in 30% yield (based on starting material consumed).

Bullvalene (1) was obtained⁶ by irradiation of 2.1 g (0.010 mol) of the hexadecatetraene above with a low-pressure mercury lamp (Ultra Violet Products, Inc., Model PCQ XI). The resulting product was sublimed twice under reduced pressure, yielding 0.68 g (0.005 mol) of bullvalene, mp 93-95 °C (lit.⁶ mp 95-96 °C).

Oxymercuration-demercuration of bullvalene was effected in a stirred suspension of 6.38 g (0.02 mol) of mercuric acetate in 40 mL of 1:1 distilled water/THF. The 2.6 g (0.02 mol) of bullvalene was added, and the mixture was allowed to react for 10 min and then treated with 20 mL of a 3 M NaOH solution, followed by another 20 mL of 0.5 M sodium borohydride in 3 M NaOH. The solution darkened immediately, metallic mercury beginning to precipitate. This solution was saturated with NaCl and allowed to settle. The organic layer was separated and washed with ammonium chloride, the aqueous layer being extracted twice with ether. The organic solutions were combined, dried, and evaporated to 1.6 g of a brown pasty residue.

Separation of the reaction mixture was achieved by placing 1.6 g of the mixture obtained from the reaction on a column prepared with 100 g of silica gel (70-230 mesh) in 19:1 hexane-ether. The column was eluted successively with 1, 1, and 0.5 L portions of 19:1, 9:1, and 17:3 of hexane-ether, respectively.

The initial fractions contained small amounts of bullvalene and another hydrocarbon. Elution with 2.5 L of hexane-ether separated mixtures of A, B, and 5. A and B begin to decompose at room temperature, but fractions containing combinations of A, B, and 5 could be rechromatographed, affording about 100 mg of over 95% pure compounds.

Spectral Data for A: UV (EtOH) λ_{max} 258 (ε_{max} 3370); IR 3350, 3030, 2910, 1660, 1585, 1045, 1005, 904, 715, 685 cm⁻¹; NMR 6.10-5.30 (m, 6 H), 3.95 (m, 1 H) 3.15 (d, 1 H) 2.50-1.80 (m, 4 H) ppm; mass spectrum, *m/e* 148 (M⁺), 130, 129, 128, 117, 115, 104, 91, 79, 70, 51.

For B: UV (EtOH) λ_{max} 261 nm (ε_{max} 3370); IR 3350, 3030, 2920, 1660, 1570, 1040, 950, 712, 686 cm⁻¹; NMR 6.60-5.50 (m, 6 H), 4.15 (m, 1 H), 2.70-2.20 (m, 2 H), 2.20-1.90 (m, 3 H) ppm; mass spectrum, *m/e* 148 (M⁺), 130, 129, 117, 115, 104, 91, 78, 70, 51.

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(25) (a) Löffler, H. P. *Chem. Ber.* **1971**, *104*, 1981-1986. (b) No presence of minor products (less than 8%) is reported,^{25a} although they would probably be more stable than the ones identified in the present work. (c) Acetolysis of [3.3.2] precursors yields [3.3.2], [4.2.2], and [4.3.1] acetates along with that which would correspond to a product from the cation analogue of 11.^{25d} No [4.4.0] products are observed, as is expected.^{1,5} (d) Löffler, H. P. *Tetrahedron Lett.* **1971**, 4893-4896.

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(29) (a) Recent investigation^{29b} of the bicyclo[3.2.2]nonatrienyl radical suggests that it is more stable than the barbaralyl radical, the exact opposite of what is observed in the case of the corresponding cations. However, the barbaralyl cation and other intermediates in the rearrangements they undergo^{29c} are hardly as stable as cations with a [4.3.1] skeleton.^{1,2} (b) Washburn, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6235-6236. (c) Ahlberg, P.; Harris, D. L.; Winstein, S. *Ibid.* **1970**, *92*, 2146-2147, 4452-4456.

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Hydrogenation of A and B was run over 10 mg of platinum(IV) oxide in 3 mL of ethanol. After hydrogen was bubbled through the solution for 1 h, approximately 10 mg (0.07 mmol) of the alcohol in 1.0 mL of ethanol was added. After another hour of hydrogen addition under stirring, the reaction mixture was filtered and ethanol evaporated under reduced pressure. The yield of hydrogenated product was 6 mg. Mass spectra for both compounds are the same with peaks at m/e 136, 121, 107, 94, 81, 67, 55: IR (A) 3350, 2920, 2855, 1445, 1040, 975, 965, 930 cm^{-1} ; IR (B) 3360, 2920, 2855, 1710, 1460, 1445, 1040, 975, 965, 930 cm^{-1} .

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Registry No. 1, 1005-51-2; 5, 33626-20-9; 6a, 79568-63-1; 9a, 79568-64-2; pentacyclo[9.3.2.0^{2,9}.0^{3,8}.0^{10,12}]hexadeca-4,6,13,15-tetraene, 1082-45-7; cyclooctatetraene, 629-20-9.

Photostimulated Reaction of Diphenylarsenide and Diphenylstibide Ions with Haloaromatic Compounds by the $S_{RN}1$ Mechanism. Electron Transfer vs. Bond Breaking of the Radical Anion Intermediate¹

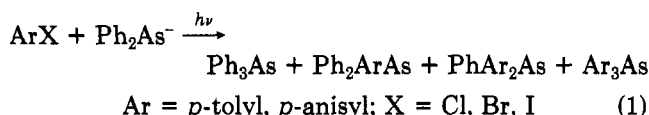
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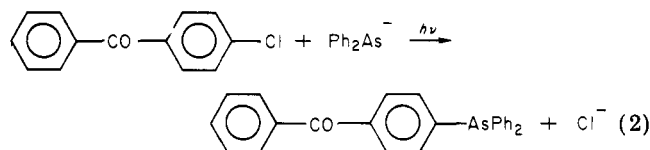
Photostimulated reactions of haloaromatic compounds with potassium diphenylarsenide and potassium diphenylstibide were studied in liquid ammonia. 1-Bromonaphthalene and 9-bromophenanthrene reacted with diphenylarsenide ion to give four products: triphenylarsine, diphenylarylsarsine, phenyldiarylsarsine, and triarylsarsine (aryl = 1-naphthyl and 9-phenanthryl); with 2-chloroquinoline as substrate only the straightforward substitution product 2-quinolyldiphenylarsine was formed. *p*-Bromoanisole and 4-chlorobenzophenone reacted with potassium diphenylstibide to give four stibines: triphenylstibine, diphenylarylstibine, phenyldiarylstibine, and triarylstibine (aryl = *p*-anisyl and 4-benzoylphenyl). These reactions are believed to occur by the $S_{RN}1$ mechanism with an extra feature of reversible coupling of aryl radicals with arsenide and stibide ions, which causes the scrambling of aryl rings. It is suggested that the low-lying π^* MO of the quinolyl moiety prevents C-As bond breaking of the radical anion intermediate.

The photostimulated reaction of potassium diphenylarsenide with *p*-halotoluenes and *p*-haloanisoles (chloro, bromo, iodo) in liquid ammonia gave four arsines as products: triphenylarsine, diphenylarylsarsine, phenyldiarylsarsine, and triarylsarsine (aryl = *p*-tolyl, *p*-anisyl) (eq 1).²

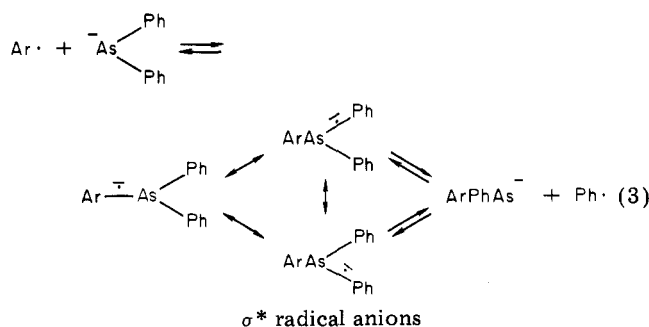


These results were explained in terms of the $S_{RN}1$ mechanism,³ where the radical anion formed from the coupling of an aryl radical with the nucleophile suffers competitive reactions: reversion to starting materials, bond fragmentation leading to scrambling of aryl rings, and electron transfer leading to the substitution products. Scheme I is a representation of the intermediate involved and the products obtained.

On the other hand, the photostimulated reaction of diphenylarsenide ion with 4-chlorobenzophenone gave only one arsine, namely, the straightforward substitution product. There is evidence that this reaction also occurred by the $S_{RN}1$ mechanism,² but the radical anion intermediate formed does not fragment, and the only reaction observed is the electron transfer leading to the substitution product (eq 2).



It was suggested that the predominance of the bond-fragmentation or electron-transfer pathways depends on the relative energies of the σ^* and π^* molecular orbitals (MO's). The low-lying MO's of the radical anion intermediate when *p*-tolyl or *p*-anisyl radicals couple with diphenylarsenide ion are the σ^* of the C-As bond, and lead to bond fragmentation of any of the three C-As bonds (eq 3).^{2,4}



On the other hand, in the coupling reaction of 4-benzoylphenyl radical with diphenylarsenide ion, the low-lying MO of the radical anion intermediate is the π^* MO of the 4-benzoylphenyl moiety, and the only process

(1) Presented in part at the 5th IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, 1980, p 97. Based in part on the Ph.D. Thesis of Ruben A. Alonso, Universidad Nacional de Córdoba, Argentina, Aug 1981.

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(3) Bunnett, J. F. *Acc. Chem. Res.* 1978, 11, 413.

(4) Rossi, R. A. *J. Chem. Educ.*, in press.