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Wallach Rearrangement Mechanisms for Hexamethylazoxybenzene. General Acid Catalysis in Strongly Acidic Solutions[1]

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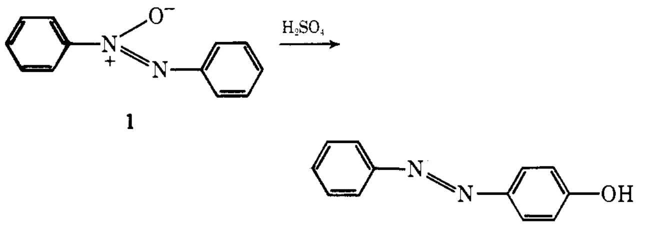
Abstract: The kinetics of the reaction of 2,2′,4,4′,6,6′-hexamethylazoxybenzene (**6**) to give 4-hydroxymethyl-2,2′,4′,6,6′-pentamethylazobenzene (**7**) in strong H_2SO_4 solutions have been investigated. The acidity dependence is complex, but the total reaction can be separated into two processes, one dominant below, and the other above ~80% H_2SO_4. Consideration of possible mechanisms leads to linear correlations of log k_ψ − log [$C_{SH^+}/(C_S + C_{SH^+})$] with 2 log $a_{HSO_4^-}$ and with log $a_{H_2SO_4}$, for these two processes, rather than with $-H_0$ or other acidity functions. These correlations lead to the following proposals of the reaction mechanism. The low-acidity process undergone by **6** involves rate-determining nucleophilic attack by HSO_4^-, subsequent to proton loss (para methyl) from the monoprotonated substrate to HSO_4^- acting as a base. In the other mechanism, the monoprotonated substrate undergoes a rate-determining proton transfer to oxygen of ^+NOH with loss of H_2O, giving an intermediate dication. The latter undergoes fast proton loss and nucleophilic attack, leading to the observed products. The dicationic mechanism thus represents general acid catalysis by H_2SO_4 species in the acid region 80% H_2SO_4 and above.

The Wallach rearrangement[2] of azoxybenzene (**1**) to give *p*-hydroxyazobenzene (**2**) in sulfuric acid has been investigated recently in several laboratories.[3-7] Apart from a requirement for the involvement of more than one proton and an intermediate which can react symmetrically, little agreement exists on the mechanism of this reaction.[8,9] As a reaction intermediate, this group[5] has favored the dication **3**,[10] but others prefer **4**, in unprotonated,[3] mono-,[4] or diprotonated form,[6] and another group believes that **5** is more likely.[7]



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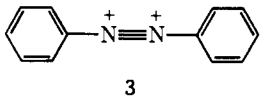

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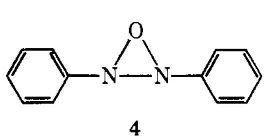

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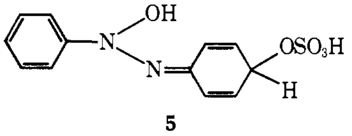

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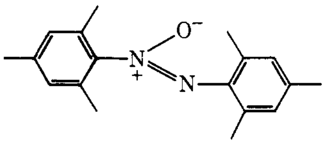
In an attempt to shed further light on this problem, a study of the Wallach rearrangement of hexamethylazoxybenzene (**6**) has been undertaken. The methyl groups should stabilize structures like **3**, if formed, and help to prevent complications due to sulfonation previously found with **1** in the 95-100% H_2SO_4 region.[11] The formation of **7**, somewhat unexpectedly, as the product of the reaction of **6** in 85% H_2SO_4, has already been reported;[12] in this paper, the kinetics of this process are discussed. The results have yielded further information on the relevance of general acid catalysis in highly acidic solutions to the Wallach rearrangement pathways.[5,13]



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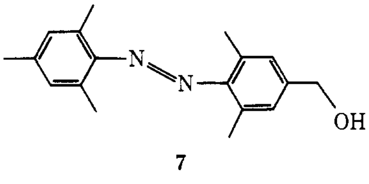

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Experimental Section

The preparation of 2,2′,4,4′,6,6′-hexamethylazoxybenzene (**6**) and the isolation and identification of the reaction product 4-hydroxymethyl-2,2′,4′,6,6′-pentamethylazobenzene (**7**) have been previously described,[12] as well as the pK_a determination, by standard methods.[14]

Kinetic runs were carried out in the thermostated cell compartment of a Unicam SP 800 uv-visible spectrophotometer, using the

Table I. Rate Constants for Conversion of **6** to **7** in Aqueous Sulfuric Acid at 44.4° and Solution Acidity Parameters Used in Rate Correlations

% H_2SO_4 (w/w)	$-H_0$[a]	$a_{HSO_4^-}$[b]	$a_{H_2SO_4}$[c]	$C_{SH^+}/(C_S + C_{SH^+})$[d]	k_ψ,[e] sec^{-1}	$k_\psi{}^S$,[f] sec^{-1}
60.81[g]	4.36	7.67		0.205	1.16×10^{-5}	
63.69[g]	4.70	8.53		0.457	3.91×10^{-5}	
64.02	4.74	8.63		0.491	3.07×10^{-5}	
66.67[g]	5.09	9.57		0.765	8.65×10^{-5}	
67.01	5.14	9.68		0.795	9.16×10^{-5}	
69.61	5.48	10.7		0.927	1.03×10^{-4}	
71.93	5.79	11.5		0.974	1.24×10^{-4}	
73.22	5.95	12.0		0.985	1.24×10^{-4}	
76.54	6.40	13.1	0.0054	0.997	1.86×10^{-4}	0.18×10^{-4}
79.63	6.89	13.7	0.0156	0.999	3.30×10^{-4}	1.40×10^{-4}
80.82	7.07	13.8	0.0230	1.000	4.30×10^{-4}	2.39×10^{-4}
84.11	7.58	13.3	0.0644	1.000	1.13×10^{-3}	0.92×10^{-3}
86.53	7.96	12.5	0.123	1.000	2.26×10^{-3}	2.10×10^{-3}
89.61	8.43	10.8	0.249	1.000	4.76×10^{-3}	4.65×10^{-3}
92.23[g]	8.84	9.10	0.395	1.000	8.04×10^{-3}	7.16×10^{-3}
93.68[g]	9.06	7.96	0.490	1.000	1.07×10^{-2}	1.06×10^{-3}
95.71[g]	9.45	6.11	0.646	1.000	1.16×10^{-2}	1.16×10^{-3}
96.12	9.54	5.72	0.676	1.000	1.14×10^{-2}	1.14×10^{-2}
98.10[g]	9.92	3.47	0.838	1.000	1.32×10^{-2}	1.32×10^{-2}

[a] H_0 values at 45° are taken from ref 16. [b] Reference 22. [c] Reference 18; values at 45°. [d] Calculated from $1/m \log (C_{SH^+}/C_S) = pK_{SH^+} - H_0$, with $pK_{SH^+} = -4.75$ and $m = 1.51$ (ref 12). [e] Observed pseudo-first-order rate constants; average values of 2–3 kinetic runs generally. [f] Calculated rate constants for "strong acid mechanism" (see text). [g] Medium contains 1% methanol.

Table II. Acidity and Rate Data for the Conversion of **6** to **7** at 25.2°[a]

% H_2SO_4 (w/w)	$-H_0$	$a_{H_2SO_4}$	$C_{SH^+}/(C_S + C_{SH^+})$	k_ψ, sec^{-1}
76.54	6.62	0.0034	0.998	1.16×10^{-5}
80.82	7.30	0.0167	1.000	3.68×10^{-5}
85.58	8.04	0.0826	1.000	1.81×10^{-4}
89.61	8.70	0.232	1.000	5.75×10^{-4}
92.63	9.22	0.408	1.000	9.75×10^{-4}
96.12	9.86	0.668	1.000	1.79×10^{-3}

[a] Footnotes as in Table I but with H_0 and $a_{H_2SO_4}$ values referring to 25°.

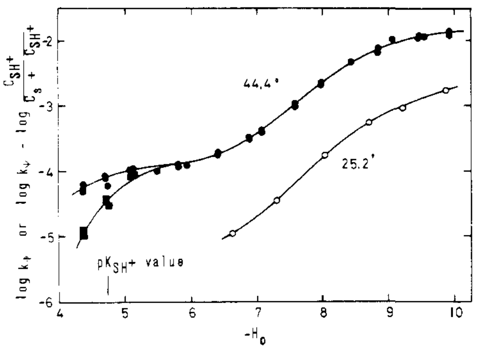
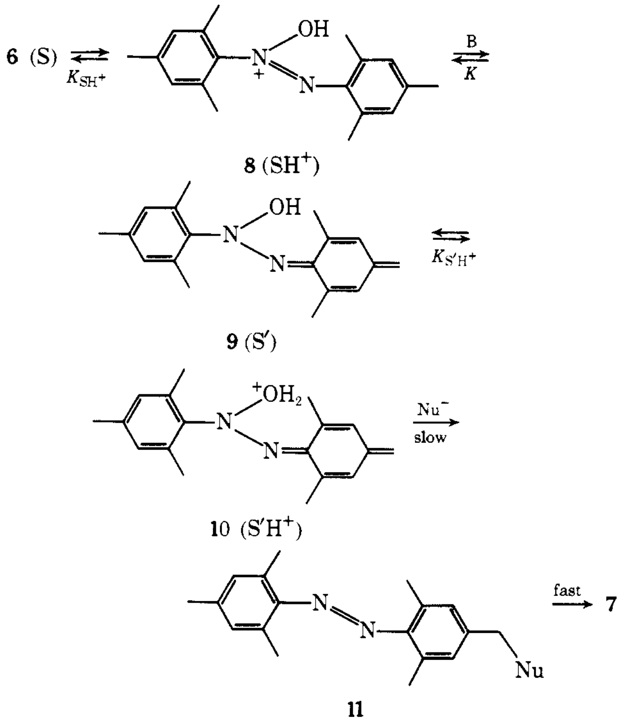


Figure 1. Graphs of log k_ψ (■) and log k_ψ − log $[C_{SH^+}/(C_S + C_{SH^+})]$ (● and ○) vs. $-H_0$, for the Wallach reaction **6** → **7** in aqueous H_2SO_4 at 25.2 and 44.4°.

Scheme I



"direct" method.[5] A stock solution of the substrate in methanol was pipetted into a 1-cm cuvette. The methanol was evaporated before adding acid, except where needed to aid solubility (weak acids), or for fast reactions, where the substrate solution was added directly to the acid by syringe. Rate differences in reactions with and without methanol (1% of the total volume) were negligible. In the case of the faster reactions, rapid mixing was accomplished by use of a nitrogen-driven semimicro stirrer. Substrate insolubility did not present a problem; the same rate constant, within experimental error, was obtained for the weakest acid used at a quarter of the usual substrate concentration (using a 4-cm cuvette). The reaction was followed by monitoring the appearance of the product peak at 463 nm[12] by periodic scanning or at constant wavelength as appropriate. The product was formed in quantitative yield except at the highest acidities where slight decomposition was observed. Pseudo-first-order rate constants (k_ψ) were obtained from the slopes of log (OD_∞ − OD) vs. time plots, which were linear over several half-lives, or, for the slowest reactions, from Guggenheim plots.[15]

The data for the acidity function and other correlations were obtained from the following sources. The H_0 scales at 45 and 25° are taken from ref 16 and 17. Values of $a_{H_2SO_4}$ at 25 and 45° were taken from the extensive compilation of Kort and Cerfontain,[18,19] derived from original measurements by Giauque et al.[20] The J_0 scale used is from Rochester.[21] Values of $a_{H_3O^+}$ and $a_{HSO_4^-}$ are from Kort and Cerfontain,[18] of C_{H^+} and $C_{HSO_4^-}$ from Robertson and Dunford.[22]

Results and Discussion

Kinetic data for the conversion of **6** to **7** determined at various acidities are given in Tables I (44.4°) and II (25.2°). A plot of log k_ψ vs. $-H_0$ is given in Figure 1. Also plotted in Figure 1 is the function log k_ψ − log $[C_{SH^+}/(C_S + C_{SH^+})]$, the use of which is preferable,[23,24] as it takes into account the fact that the substrate is not fully protonated at

H_0 values near pK_{SH^+}. The pK_{SH^+} value of **6** was found to be −4.75;[12] the slope of the log (C_{SH^+}/C_S) vs. $-H_0$ plot used in this determination was 1.51. Both these numbers were used in calculating the values of $C_{SH^+}/(C_S + C_{SH^+})$ given in Tables I and II; this is equivalent to allowing the substrate to define its own acidity function for monoprotonation.[25]

It is apparent from Figure 1 that this reaction is not a simple one, as multiple curvature in H_0 plots is almost always indicative of mechanistic change.[24-26] Since the part of the reaction at low acidity appears to be almost acidity independent after allowing for initial substrate protonation, the mechanism shown in Scheme I, modified from a suggestion of Duffey and Hendley,[7] will be considered first.

In this scheme, the protonated substrate **8** undergoes reversible proton loss from the para methyl group to base, giving a "new" substrate **9**, which in turn is protonated (the site of protonation determining whether **8** or **10** is formed). There follows rate-determining attack on the methylene carbon with loss of H_2O to yield the azo derivative **11.** In the case that Nu = HSO_4^-, rapid hydrolysis would take place, affording the primary alcohol **7** (cf. ref 27).

Using the usual terminology[28] and the nomenclature of Scheme I, rate eq 1 and 2 can be derived, the former being

$$\log k_\psi - \log [C_{SH^+}/(C_S + C_{SH^+})] = -H_0 + \log a_{Nu}a_{B:} + \log kK/K_{S'H^+} + \log (f_{SH^+}f_{InH^+}/f_\ddagger f_{In}) \quad (1)$$

$$\log k_\psi - \log [C_{SH^+}/(C_S + C_{SH^+})] = \log a_{Nu}a_{B:} + \log kK + \log (f_{SH^+}f_{S'H^+}/f_\ddagger f_{S'}) \quad (2)$$

applicable to the case that **9** is essentially unprotonated, while in the latter, complete protonation to **10** is assumed. Activity coefficient terms such as those in eq 1 and 2 may behave in several ways as the acidity is varied: (i) they may be constant, i.e., the medium effect on each species involved would be the same; (ii) they may vary linearly, or with only slight curvature, with increasing acidity; or (iii) they may change in a highly nonlinear or discontinuous fashion. In view of previous work, by Schubert et al.[29] and others,[30] the behavior in ii is regarded as the most probable, with i and iii less likely but not impossible.[31] In the arguments which follow, it is assumed that the existence of the activity coefficient terms does not affect any linear correlations indicated by equations such as 1 and 2, but the slopes and intercepts may well be affected.

Returning to Scheme I, both B: and Nu^- are considered to be HSO_4^- ions. These are by far the predominant basic species in H_2SO_4,[13,22] and the fact that HSO_4^- is not solvated by H_2O in the medium[32] should increase its nucleophilicity. From Figure 1 it is apparent that the variation with H_0 is slight at low acidity, from which complete protonation of **9** to **10** can be assumed. Therefore the data of Table I are plotted according to eq 2 in Figure 2. It is seen that the correlation with 2 log $a_{HSO_4^-}$ is adequate, although the experimental scatter is considerable; the slope is 0.967 ± 0.086, and the correlation coefficient is 0.950. Deviation from this plot becomes serious above 77% H_2SO_4 ($H_0 < -6.5$) because of the advent of another mechanism which takes over at higher acidity.

For the region where both mechanisms appear important, the values of k_ψ were divided into contributions from the weak-acid mechanism (w) and the strong-acid mechanism (s), according to $k_\psi = k_\psi^w + k_\psi^s$. Values of k_ψ^w were calculated using the above correlation and subtracted from k_ψ. This is a small correction at high acidities; it only becomes important for a few points at moderate acidity. The derived values of log k_ψ^s are given in Table I.

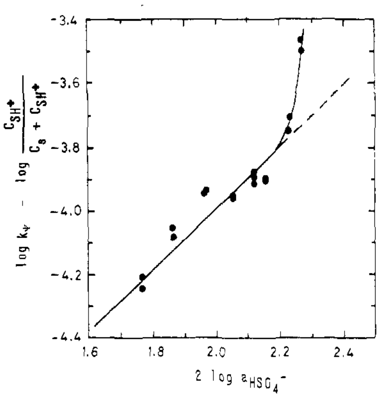
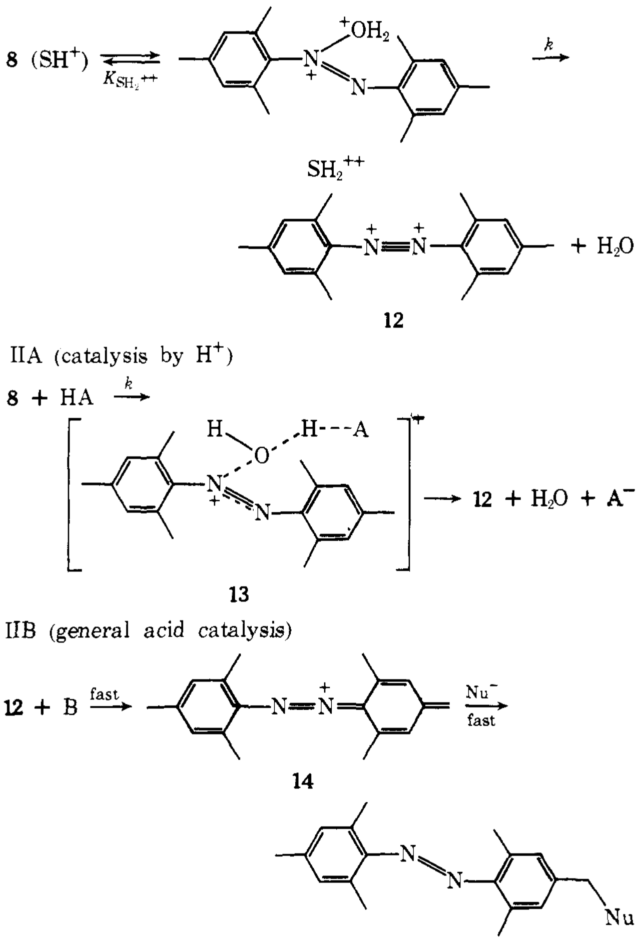


Figure 2. Plot of log k_ψ − log $[C_{SH^+}/(C_S + C_{SH^+})]$ against 2 log $a_{HSO_4^-}$, for the reaction of **6** in <80% H_2SO_4 at 44.4°.

Scheme II



The mechanism given in Scheme II will be considered for the reaction at high acidity; this is based on the two-proton mechanism proposed previously.[5] In Scheme IIA, a second equilibrium proton transfer is followed by rate-determining loss of H_2O to yield dication **12.** In contrast, Scheme IIB features rate-determining proton transfer to the oxygen function of **8** occurring concertedly with loss of H_2O via transition state **13.** The dication **12,** formed by either route, undergoes a series of fast steps to yield the product. From this scheme, eq 3 (for Scheme IIA) and 4 (for Scheme IIB)

$$\log k_\psi - \log [C_{SH^+}/(C_S + C_{SH^+})] = -H_+ + \log (k'/K_{SH_2^{++}}) + \log (f_{SH^+}f_{In^{++}}/f_\ddagger f_{In^+}) \quad (3)$$

$$\log k_\psi - \log [C_{SH^+}/(C_S + C_{SH^+})] = \log a_{HA} + \log k + \log (f_{SH^+}/f_\ddagger) \quad (4)$$

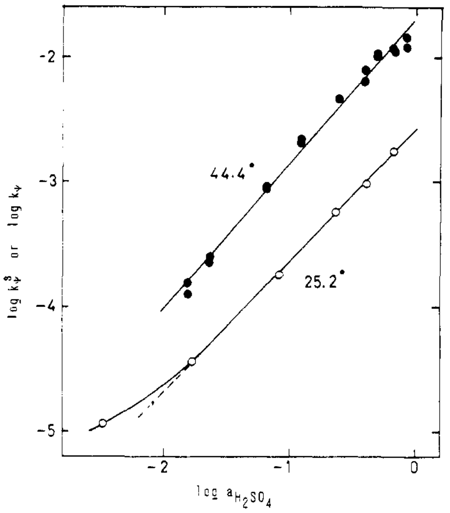


Figure 3. Plot of log k_ψ (O) and log k_ψ^s (●) vs. log $a_{H_2SO_4}$, for the reaction of **6** in >80% H_2SO_4 at 25.2 and 44.4°, respectively.

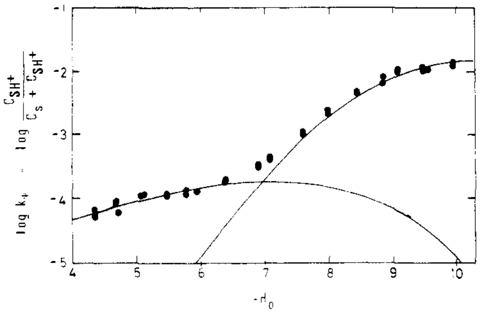


Figure 4. Comparison of theory with experiment in the Wallach reaction **6** → **7** in aqueous H_2SO_4 at 44.4°. The upper curve is drawn assuming correlation with log $a_{H_2SO_4}$ only, and the lower curve, with 2 log $a_{HSO_4^-}$ only. The points are experimental.

can be readily derived.[5] These correspond to the Zucker–Hammett situations for A1 and A2 (one-proton) mechanisms.[33] Equation 3 is not found to be satisfactory, as plots of the left-hand side of eq 3 against both $-H_0$ (see Figure 1) and $-J_0$[34] are curved. For eq 4, plots of the left-hand side against log C_{H^+} (corresponding to the log [H_2SO_4] usually used) and log $a_{H_3O^+}$ are strongly curved with large initial slopes. However, plots against log $a_{H_2SO_4}$ prove to be linear, with slopes close to one, as can be seen from Figure 3. At 44.4°, the slope is 1.157 ± 0.024, correlation coefficient 0.996, and at 25.2°, 1.048 ± 0.018 and 0.999. Thus it seems reasonable to assign the mechanism in Scheme IIB as that which applies to this reaction in strong sulfuric acid, with undissociated H_2SO_4 acting as the acid catalyst HA.

Comparing the two mechanisms (Schemes I and II), it is reasonable that attack of Nu^- on **14** (Scheme II) should be fast, and that of Nu^- on **10** ($S'H^+$) should be slow. Thus **14** has a much lower charge density at CH_2 than does **10** because of the delocalization of positive charge in the former, which is absent in the latter. In addition, there is concomitant N-O bond rupture in reaction of **10** (Scheme I).

In Figure 4, theoretical curves for the two mechanisms, drawn according to the above correlations, are compared with the experimental results at 44.4°; the agreement is satisfactory. As can be seen, the strong-acid reaction takes over from the weak-acid one at 80% H_2SO_4, $H_0 = -6.9$. This is an acid region in which the activity of H_2SO_4 is rising rapidly,[13] while that of HSO_4^- is almost constant.

In summary, Schemes I and IIB represent the mechanism of the Wallach rearrangement of hexamethylazoxybenzene in sulfuric acid, at concentrations of less than and greater than ~80% H_2SO_4, respectively. Scheme I involves quinoid intermediates, while Scheme II features the dicationic intermediate formed in a general acid-catalyzed rate-determining proton-transfer process. General acid catalysis is not a new proposal for reactions in strong acids. For instance, Kresge et al.[35] use it to account for different reaction rates in mono- and polybasic acids, while Schubert and Myhre[36] propose acid catalysis by H_3O^+ and H_2SO_4 species in aromatic decarboxylations. However, it is felt that the correlations in Figure 2 and the analogous correlation observed for azoxybenzene[13] provide probably the most convincing evidence to date of this phenomenon in concentrated sulfuric acid.[37]

Acknowledgment. We gratefully acknowledge financial support of this research from the National Research Council of Canada.

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Radical Chlorination of *exo*- and *endo*-Tricyclo[3.2.1.0^{2,4}]octane and *exo,exo*- and *exo,endo*-Tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane with *tert*-Butyl Hypochlorite[1]

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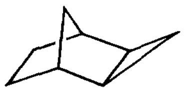
Abstract: Irradiation of *exo*-tricyclo[3.2.1.0^{2,4}]octane and *tert*-butyl hypochlorite at 40° in CCl_4 generates a mixture of monochlorides which consists of *exo*-6-chloro-, *endo*-6-chloro-, and 1-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane in a ratio of 67:12:17. In contrast, radical chlorination of *endo*-tricyclo[3.2.1.0^{2,4}]octane with *tert*-butyl hypochlorite results in a mixture of monochlorides consisting of *anti*-8-chloro-*endo*-tricyclo[3.2.1.0^{2,4}]octane, *endo*-2-chlorotricyclo[3.3.0.0^{4,6}]octane, and two incompletely characterized components in a 66:27:5:2 ratio. Analogous radical chlorination of *exo,exo*-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane with *tert*-butyl hypochlorite yields 1-chloro- and 2-chlorotetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane in a ratio of 71:22, while photochlorination of *exo,endo*-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane with *tert*-butyl hypochlorite gives 1-chloro- and 6-chloro-*exo,endo*-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane and *endo*-9-chloro-*exo*-tetracyclo[4.3.0.0^{2,4}.0^{5,7}]nonane in a ratio of 44:35:21. Abstraction at C-8 in the *endo*-tricyclooctane and C-9 in the *exo,endo*-tetracyclononane system is suggested to be due to anchimeric assistance to hydrogen abstraction, and the stereoselectivity of the rearranged radicals in both cases is discussed in terms of transannular interaction of cyclopropane.

In recent years, there has been considerable interest in the characterization of radical intermediates which are structurally related to bridged carbonium ion intermediates, such as the 2-norbornyl,[2] 5- and 7-norbornenyl[2,3] and cholesteryl.[4] The reactions of these radical intermediates have, in all cases to date, been easily explained in terms of rearranging classical intermediates, rather than by invoking bridged delocalized intermediates.

Since in an earlier study we found that radical chlorination of bicyclo[3.1.0]hexane with *tert*-butyl hypochlorite results in substitution at C-2 and C-3, producing a ratio of *cis*-3- to *trans*-3-chlorobicyclo[3.1.0]hexane of 2:1,[5] in spite of the steric shielding of the cis face of the ring skeleton by the cyclopropane methylene, it appeared to be of considerable interest to carry out additional studies on 3-bicyclo[3.1.0]hexyl radical intermediates. A consideration of the anchimeric assistance found in the solvolyses of *exo*-5-norbornenyl (10^4),[6] *anti*-7-norbornenyl (10^{11}),[7] and *endo-anti*-tricyclo[3.2.1.0^{2,4}]oct-8-yl (10^{14})[8] substrates suggested that our investigation should focus attention on hydrogen abstraction from the *endo*-tricyclo[3.2.1.0^{2,4}]octane ring system (**2**). On this basis, we have chosen to consider radical chlorination reactions of *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]octane (**1** and **2**) and *exo,exo*- and *exo,endo*-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane (**3** and **4**) with *tert*-butyl hypochlorite.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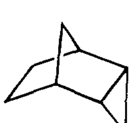
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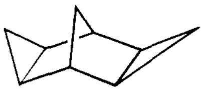
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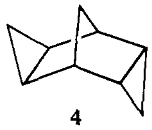
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Results

Irradiation of a 2:1 molar ratio of *exo*-tricyclo[3.2.1.0^{2,4}]octane and *tert*-butyl hypochlorite at 40° in CCl_4 produced a 27% yield of monochlorides, which consisted of *exo*-6-chloro- (**5**-Cl), *endo*-6-chloro- (**6**-Cl), and 1-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane (**7**-Cl) in a ratio of 67:12:17 with an unidentified component present to an extent of 3%. No dichlorides were detectable by VPC. Structural identification was based upon the reduction of the product chlorides to a single hydrocarbon, parent structure **1**, with tributyltin hydride (AIBN initiation, 95°), spectral analysis of the three major product components, and independent syntheses. The infrared and NMR spectral data of the 67% component were identical with those of an authentic sample of **5**-Cl prepared by addition of hydrogen chloride to *exo*-tricyclo[3.2.1.0^{2,4}]octene-**6**. The NMR spectrum of the 12% component [τ 5.88 (doublet of triplets, J = 9, 3.5 Hz, 1 H), 7.55 (m, 1 H), 7.71 (m, 1 H), 7.95 (m, 1 H), 8.65 (m, 2 H), 8.85–9.4 (m, 3 H), 9.6 (m, 1 H), 9.95 (quartet, J = 7 Hz, 1 H)] is consistent with that expected for the endo-6 isomer (**6**-Cl), and NMR and infrared comparison with a standard prepared by treatment of **5**-OH with triphenylphosphine and CCl_4[9] verified this assignment. Since the NMR spectrum of the 17% component exhibits no absorption for hydrogen α to chlorine, only one bridgehead hydrogen at τ 7.84, and an unsubstituted fused cyclopropane (C_3H_4) unit [τ 8.94 (triplet of doublets, J = 7, 3 Hz, 1 H), 9.13 (triplet of doublets, J = 7, 3 Hz, 1 H), 9.37 (overlapping pair of triplets, J = 7, 3 Hz, 1 H), 9.87 (quartet, J = 7 Hz, 1 H)], the correct structure must be that of bridgehead chloride **7**-Cl. As a second check on the ring skeleton, reduction of an isolated sample of the 17% component with tributyltin hydride (AIBN initiation) produced tricyclooctane **1** as the sole hydrocarbon, reinforcing the structural assignment. An independent synthetic route to

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