Radical Formation in the Oxidation of 2,2′-Azo-2-methyl-6-heptene by Thianthrene Cation Radical

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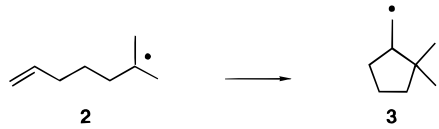
Reaction of 2,2′-azo-2-methyl-6-heptene (**1**) with thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) in CH_2Cl_2 solution containing 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) gave a mixture of nine C_8 hydrocarbons, namely, 1,1,2-trimethylcyclopentane (**4**, 2.2%), 6-methyl-1-heptene (**5**, 2.2%), 2-methyl-1,6-heptadiene (**6**, 9.8%), 2,2-dimethyl-1-methylenecyclopentane (**7**, 2.9%), 6-methyl-1,5-heptadiene (**8**, 39%), 3,3-dimethyl- (**9**, 7.6%), 4,4-dimethyl- (**10**, 11%), 1,2-dimethyl- (**11**, 5.4%), and 1,6-dimethylcyclohexene (**12**, 1.5%). The amounts of acyclic dienes (**6**, **8**) fell and of cyclohexenes (**9**, **10**) rose when DTBMP was omitted from or diminished in the solution. The results provide firm evidence (products **4**, **5**, and **7**) for the formation of the 2-methyl-6-hepten-2-yl radical (**2**), although the major fate of **2** is its oxidation to the corresponding cation **13**, the origin of the bulk of the other products.

The facile oxidative decomposition of azoalkanes was first reported in the reaction of 1,1′-azoadamantane (AdN═NAd) with thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$).[1] Most (91%) of the adamantyl groups in the AdN═NAd were converted by two-electron oxidation into the adamantyl cation (Ad^+), trapped subsequently, for example, by the solvent acetonitrile. Circumstantial evidence for the formation of the adamantyl radical ($Ad^{\bullet}$) was adduced for the small amount (0.2%) of adamantane and larger amount (5.5%) of adamantyl methyl ketone that were obtained. In the same year, one-electron transfer to solvent CCl_4 was attributed to the photolytic decomposition of cyclopropyl-substituted 2,3-diazabicyclo-[2.2.2]oct-2-enes.[2] Attempts to obtain further evidence for the initial formation of alkyl radicals in the oxidation of azoalkanes by $Th^{\bullet+}$, with the use of 1,4-diphenylazomethane[3] and 1,1′-azo-5-hexene,[4] were thwarted by the tautomerization of the azoalkane to the corresponding hydrazone. In the case of 1,4-diphenylazomethane, oxidative cycloaddition of the hydrazone, namely benzaldehyde benzylhydrazone, to solvent acetonitrile occurred and led to 1-benzyl-3-phenyl-5-methyl-1,2,4-triazole. The anticipated formation of benzyl radicals was not achieved. These initial reports were followed by a number of others, particularly on the reactions of diazabicycloalkenes.[5,6] In these cases, one-electron oxidation led to deazatization and the formation of the cation radical of the corresponding cycloalkene or bicylcloalkane. Here, radical formation was deducible in the sense that the radical was part of a hydrocarbon cation radical, identifiable indirectly from its chemistry or directly with ESR spectroscopy. More concrete evidence for the formation of free alkyl radicals was provided by Zona and Goodman.[7] Irradiation of solutions of 2,2′-azo-2-methylpropane (azoisobutane) and 9,10-dicyanoanthracene (DCA) in acetonitrile and methanol solutions gave products attributable to the formation of $tBu^{\bullet}$ and its trapping by $DCA^{\bullet-}$.

Recently, Walborsky and co-workers reported the preparation and photolysis of 2,2′-azo-2-methyl-6-heptene (**1**).[8] The objective in the photolysis was to generate and explore the fate of the 2-methyl-6-hepten-2-yl radical (**2**), which is known to cyclize readily to the (2,2-dimethylcyclopentyl)methyl radical (**3**, eq 1).[9] Photolysis of a



(1)

dilute solution of **1** in ether solution gave three major products, 1,1,2-trimethylcyclopentane (**4**, 43%), 6-methyl-1-heptene (**5**, 26%), and 2-methyl-1,6-heptadiene (**6**, 22%) (Scheme 1). These products were attributed reasonably to the cyclization (for **4**) and disproportionation (for **5** and **6**) of radical **2**. Formation of 2,2-dimethyl-1-methylenecyclopentane (**7**), which would result from disproportionation of **3**, was not reported.

We have now turned to the use of **1** for seeking further evidence for radical formation in oxidations by $Th^{\bullet+}$.

Results and Discussion

Oxidation of **1** by $Th^{\bullet+}$ in CH_2Cl_2 solution was carried out by dropwise addition of a solution of **1**, 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), and nonane (GC standard) to a stirred suspension of $Th^{\bullet+}ClO_4^-$. Gas chromatographic (GC) analysis of the solution, after addition of a small amount of aqueous K_2CO_3, yielded nine identifiable C_8 hydrocarbons, namely, **4**−**7**, 6-methyl-1,5-heptadiene (**8**), 3,3-dimethylcyclohexene (**9**), 4,4-dimethylcyclohexene (**10**), 1,2-dimethylcyclohexene (**11**), and 1,6-dimethylcyclohexene (**12**) (Scheme 2). The amounts of these products, totaling 82% of the available hydrocarbon

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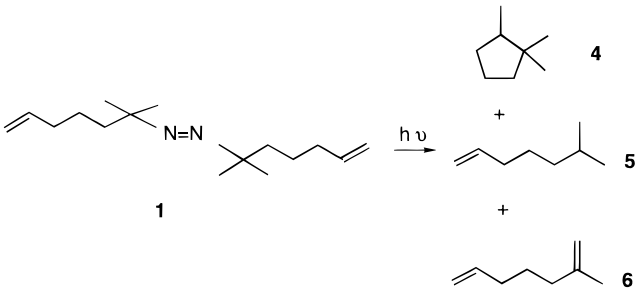
Scheme 1



Scheme 2

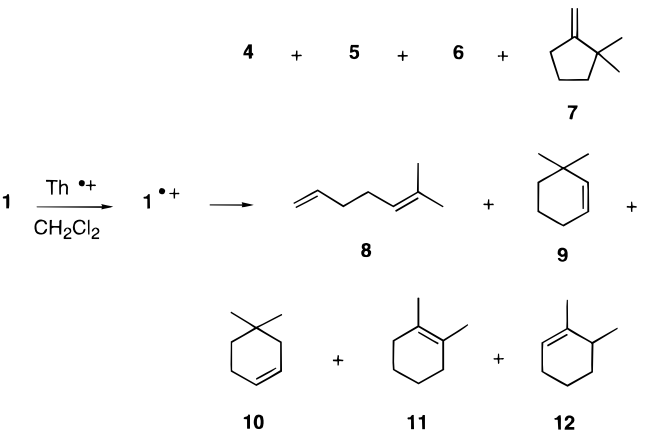


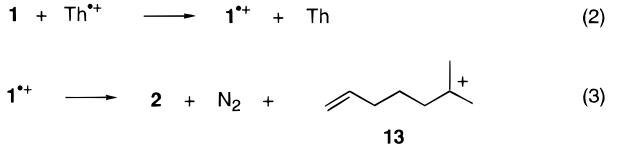
Table 1. Products of Reaction of 2,2′-Azo-2-methyl-6-heptene (1) with $Th^{\bullet+}ClO_4^-$

	products mmol[a] and %[b]										
run	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	Th	ThO
1	3.72	3.86	16.8	4.62	68.0	13.2	19.2	9.69	2.43	182	2.9
2	3.69	3.91	16.9	5.24	67.2	13.3	19.1	9.43	2.57	180	3.1
3	3.71	3.75	16.4	5.23	64.7	12.5	18.2	9.11	2.59	179	4.8
4	3.88	3.18	16.6	4.82	66.1	13.1	18.9	8.43	2.52	176	4.1
av[c]	3.75	3.67	16.8	4.98	66.5	13.0	18.9	9.17	2.53	179	3.7
	2.2	2.2	9.8	2.9	39	7.6	11	5.4	1.5	98	2.2
5[d]	3.63	1.30	tr	3.69	8.05	38.7	54.0	11.0	2.67	161	6.7
	2.3	0.82		2.3	5.1	24	34	6.9	1.7	96	4.0
6[e]	3.54	1.07	0.54	2.24	15.0	30.2	42.5	13.4	3.11	177	9.6
	2.2	0.67	0.34	1.4	9.4	19	27	8.4	1.9	95	5.1

[a] The yield of each product (mmol) is an average of 10 or more GC measurements. [b] Entries in rows 6, 8, and 10. The percentage is based on millimoles of C_8 groups in **1** after compensation for recovered **1**. [c] Average of runs 1−4. Standard deviation in the order **4**−**12** was 0.088, 0.34, 0.12, 0.31, 1.43, 0.40, 0.42, 0.071. In each run, 85.5×10^{-3} mmol of **1**, 312×10^{-3} mmol of DTBMP, and GC standard in 1 mL of CH_2Cl_2 was added dropwise to a stirred suspension of 183×10^{-3} mmol of $Th^{\bullet+}ClO_4^-$ in 1 mL of CH_2Cl_2. [d] 79.5×10^{-3} mmol of **1**, 141×10^{-3} mmol of DTBMP and 167×10^{-3} mmol of $Th^{\bullet+}ClO_4^-$. [e] 80.2×10^{-3} mmol of **1**, no DTBMP, and 187×10^{-3} mmol of $Th^{\bullet+}ClO_4^-$.

groups in **1,** are listed in Table 1. Small amounts of other hydrocarbon products were formed but were not identified. Also, GC traces and GC/MS data suggested that some radicals had been trapped by $Th^{\bullet+}$ to form 1- and 2-substituted thianthrenes, a reaction that has been observed in other work with $Th^{\bullet+}$.[10] No attempt was made to identify and assay these products.

Oxidation of **1** by $Th^{\bullet+}$ must lead initially to $\mathbf{1}^{\bullet+}$, which we treat as next decomposing into the radical **2** and the corresponding cation **13** (eqs 2 and 3). The products **4**−**12** are derived, then, from **2** and **13**.



Radical **2** has served as a radical clock[9] and also as a radical probe in a number of diverse reactions. The products that may be expected from **2** are, therefore, well-recorded in the literature. Thus, Chatgilialoglu and co-workers, in reactions of 6-bromo-6-methyl-1-heptene (**14**) with $(Me_3Si)_3SiH$ obtained **4** and **5** (in relative amounts that varied with the concentration of $(Me_3Si)_3SiH$ and 1,1-dimethylcyclohexane (**15**).[9] The last product **15**, whose yield was not given, arose evidently from the less common endo-trig cyclization of **2**. The same products were reported by Ashby and co-workers in the amounts 68%, 11.8%, and 7.3% in the investigation of the Grignard reagent made from 6-chloro-6-methyl-1-heptene (**16**).[11] In the reactions of **2** in CCl_4, Giese and Hartung[12] obtained as major products **16** and 1-(chloromethyl)-2,2-dimethylcyclopentane, corresponding with chlorine abstraction by **2** and by **3**. Only a minor amount of 1-chloro-3,3-dimethylcyclohexane, the product that would follow from endo-trig cyclization of **2**, was obtained. Toi and co-workers,[13] from reaction of **16** with Bu_3SnH, obtained not only **4** (40%), **5** (50%), and **15** (5%) but also **8** (5%). Other workers, in various reactions, on the other hand, were able either to trap or identify only the radicals **2** and **3**.[14−16]

In contrast with **2**, information in the literature on **13** is sparse. The kinetics but not the products of solvolysis of **16** in 80% ethanol have been reported.[17] The only work with the chemistry of **13** that we have been able to find is by Toi and co-workers.[13] Reduction of **16** by the ate complex prepared from *B*-butyl-9-borabicyclo[3.3.1]nonane and butyllithium gave 33% of **5**, 7% each of **8** and **15**, and 3.4% of **6**. None of **4** was obtained, signifying[13] that in that reaction of **16**, **13** rather than **2** was involved.

From our perspective, the sum of the results in the literature is that **2** will cyclize preferentially to **3** as expected, but also in small amounts, by the endo-trig route, to the 3,3-dimethylcyclohexyl radical (**17**). The amounts of the latter may be small enough to be overlooked or missed. On the other hand, there is no evidence in the (sparse) literature on **13** for its cyclization to anything but the 3,3-dimethylcyclohexyl cation (**18**). Our results are discussed, therefore, on the basis that none of our products **4** and **7** came from **13** and that we can ignore the amount of endo-trig cyclization (**17**) that may have contributed to the several cyclohexenes, **9**−**12**.

Compounds **4**, **5**, and **7** are certainly derived from radical **2**. Compounds **9**−**12** are almost as certainly derived from the corresponding cation (**13**). Walborsky found approximately equal amounts of **5** and **6**, whereas we have not only about five times more **6** than **5** but also large amounts of **8** (which was not obtained by Walbor-

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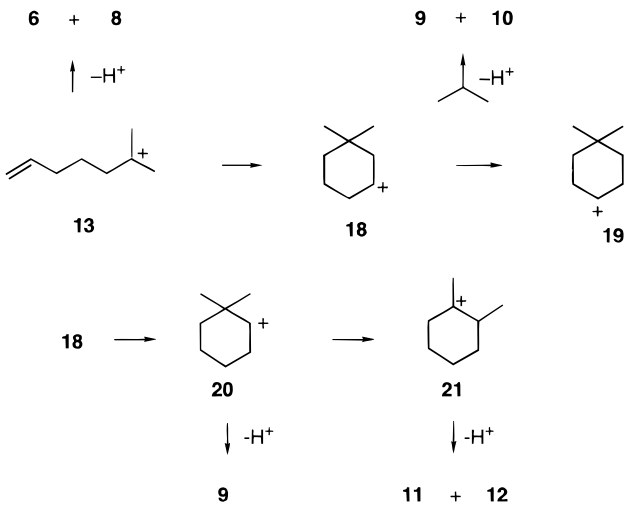
Scheme 3



sky). It is apparent, then, that most of **6** and **8** must have come from **13**. Thus, if we allow for obtaining equal amounts of **5** and **6** from disproportionation of **2**, the remaining amounts of **6** and **8** can be assigned to deprotonation of **13**. The summation is that about 10% of the products is attributable to **2** and the remainder to **13**. The formation of products from **13** is shown in Scheme 3. It appears that either cyclization of **2,** in spite of its rapid rate (10^6 s^{-1}),[9] does not compete well with oxidation by an excess of $Th^{\bullet+}$, or that two-electron oxidation of **1** prevails before $\mathbf{1}^{\bullet+}$ can fragment. Ready oxidation of the tertiary radical **2** to the tertiary cation **13** is understandable and is a built-in liability of using a branched azoalkane in order to avoid its tautomerization to a hydrazone. Our work nevertheless shows the formation of and survival of the radical **2**, albeit in the minor reaction pathway.

Walborsky found approximately equal amounts of **5** and **6** and attributed them to disproportionation of **2**. None of **7** and **8** was reported by Walborsky, so that the ratio of the amounts of products **4**/(**5** + **6**) that were obtained from a dilute solution of **1** was 0.9.[8] In our work (runs 1−4), if we assume that an amount of **6**, by disproportionation of **2**, equal to that of **5** was formed, the ratio of amounts of cyclic to acyclic, radical-derived products, (**4** + **7**)/(**2** × **5**), is 1.2, not far from that of Walborsky. Our major product was **8**, consistent with deprotonation of **13**. We assume also that the larger portion (7.6%) of **6** came from **13**, although some may have formed from disproportionation of radical **2**, too. The cyclic products **9**−**12** have their origin in the cyclization of **13**, as shown in Scheme 3. Among these products are **11** and **12,** whose formation must have been preceded by hydride and methyl rearrangements. When reaction was carried out in the presence of a smaller amount of base (run 5) and in the absence of base (run 6), the distribution of some products changed considerably. The amounts of acyclic dienes (**6** and **8**) fell and the amounts of cyclohexenes rose, particularly of products **9** and **10**. Assuming that an amount of **6** equal to that of **5** would be formed in disproportionation of radical **2**, the sum (**8** + **6** − **5**) falls from nearly 47% in runs 1−4 to nearly 4% and 9% in runs 5 and 6, while correspondingly, the sum of **9**−**12** rises from nearly 26% to nearly 67% and 56%. The data point to competition in deprotonation and cyclization of the cation **13**, cyclization becoming dominant when the concentration of DTBMP was diminished.

The origin of products **4** and **7** is certainly the cyclization of radical **2**, evidence for which we were seeking. Our data show on the other hand that if **2** and **13** are formed in the initial cleavage of $\mathbf{1}^{\bullet+}$, most of the **2** is next oxidized by the relatively large excess of $Th^{\bullet+}$ to **13**. This finding is analogous to that with the oxidation of azo-*tert*-octane, in which products of the 2-methyl-2-heptyl cation were dominant.[18] In the present work, more of **8** than **6** was obtained, as would be expected from **13**. More of **10** was obtained (from **18** and **19**) than **9** (from **18** and **20**). Finally, as would be expected, more of **11** than **12** was formed from **21**. We searched for but could not find **15** among our products.

In conclusion, the formation of an alkyl radical (here, **2**) from cation−radical oxidation of an azoalkane (here, **1**) has been certified.

Experimental Section

Dichloromethane, dimethyl sulfoxide (DMSO), hexamethylphosphordiamide (HMPA), and triethylamine (Et_3N) were distilled from CaH_2. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Dimethylformamide (DMF) was distilled from CaH_2 under reduced pressure. Diethyl ether was distilled from $LiAlH_4$. ^1H and ^{13}C NMR spectra were recorded with a 200 MHz Bruker spectrometer with $CDCl_3$ solvent unless noted otherwise. GC/MS analyses were made with a Hewlett-Packard instrument, model 5988A and a Supelco SEP-5 capillary column, 30 m × 0.32 mm. GC analyses of product mixtures were made with a Varian model 3700 gas chromatograph attached to a Spectra Physics model 4290 integrator. Two capillary columns were used: Supelco SE-54 and SPB-20, each 30 m × 0.25 mm, and 0.25 μm film thickness.

The SE-54 was used for all analyses, while the SPB-20 was used only for **6** and **9** which were inseparable on the SE-54 column. Each column was held initially at 36 °C for 4 min and was programmed for 12 °C/min increase until 250 °C. The injector and FID detector were held at 250 °C.

1,1,2-Trimethylcyclopentane (**4**) was purchased from the API inventory at Carnegie Institute of Technology. 6-Methyl-1-heptene (**5**), 6-methyl-1,5-heptadiene (**8**), 4,4- (**10**), 1,2- (**11**), and 1,6-dimethylcyclohexene (**12**) were purchased from Wiley Organics. A sample of **8** was also initially donated by Professor G. A. Molander. 1,1-Dimethylcyclohexane (**15**) and 1,3-dimethylcyclohexene, which were sought but not found among the products of reaction, were also purchased from Wiley Organics. Compounds **6**, **7**, and **9** were prepared as described later. All other reagents were purchased from Aldrich Chemical Company.

2-Methyl-1,6-heptadiene (**6**) was prepared essentially as described by Walborsky[8] from **6-hepten-2-one**, with the exception that the ylide $Ph_3P{=}CH_2$ was prepared in DMSO from the reaction of methyltriphenylphosphonium bromide with NaH.[19] After chromatographic purification of the pentane solution of **6** by passage through a silica gel column, the **6** was distilled through a small Vigreux column and had the same ^1H NMR properties as described.[8]

6-Hepten-2-one. 4-Pentenyl 1-mesylate was obtained as an oil from reaction of 4-penten-1-ol with methanesulfonyl chloride in CH_2Cl_2 containing Et_3N.[20] The mesylate was converted into 4-pentene-1-nitrile as follows. A solution of 11.7 g (0.239 mol) of NaCN in DMSO was heated to 90 °C. To the solution was added 4-pentenyl 1-mesylate (32.0 g, 0.195 mol) over a period of 15 min at such a rate that the temperature did not exceed 150 °C. Stirring was continued without heating for 5 h. The mixture was poured into water, and the product was extracted with 4 × 50 mL of pentane. The pentane

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solution was washed with brine and dried over $MgSO_4$. Fractional distillation gave 15.3 g (0.161 mol, 83%) of 4-pentene-1-nitrile, bp 156−160 °C, having a satisfactory ^1H NMR spectrum.[21] Other workers have reported the preparation from 5-bromo-1-pentene, bp 59 °C/19 Torr[21] and bp 160−162 °C.[22] Hydrolysis of the nitrile was achieved by refluxing it (7.65 g, 80.5 mmol) for 15 h in a solution of 6.5 g of NaOH in 20 mL of water. Acidification with 9 mL of 50% H_2SO_4 and 10 mL of water gave 5-hexenoic acid as an oil. This was extracted with ether. Fractional distillation gave 6.0 g (52.6 mmol, 65%), bp 200−201 °C, having a satisfactory ^1H NMR spectrum.[23] Earlier preparations have been reported by oxidation of 5-hexen-1-ol[22] and from butenylmalonic acid, bp 103 °C/12 Torr.[24] 5-Hexenoic acid (3.42 g, 30 mmol) in 50 mL of THF was converted into 6-hepten-2-one by reaction with MeLi (90 mmol) using the general procedure of Rubottom and Kim.[25] The product (2.76 g, 24.6 mmol, 82%) had bp 141−142 °C and a satisfactory ^1H NMR spectrum.[26]

2,2-Dimethyl-1-methylenecyclopentane (**7**) was prepared in 61% yield from 2,2-dimethylcyclopentanone as described by Barfield and co-workers and had a satisfactory ^1H NMR spectrum.[27]

3,3-Dimethylcyclohexene (**9**) was obtained as a mixture with 4,4-dimethylcyclohexene (**10**) by decomposition of 3,3-dimethylcyclohexyl 1-tosylate on the SPB-20 column. With authentic **10** at hand, it was possible to assign a retention time to its isomer **9**, and by assuming that **9** and **10** have the same R_f, their relative yields of 41:59 were obtained. Isolation of **9** was not attempted. Distillation of 3,3-dimethylcyclohexanol from *p*-toluenesulfonic acid has been reported to give **9** and **10** in the ratio 35:65.[28]

3,3-Dimethylcyclohexyl 1-Tosylate. 3,3-Dimethylcyclohexanone was prepared by reaction of 3-methyl-2-cyclohexenone with $Me_2CuMgBr$ as described by Pelletier and Mody with use of Cu_2MeLi.[29] $Me_2CuMgBr$ was prepared from CH_3MgI (12.6 g CH_3I, 2.16 g Mg in 100 mL of ether) and a $CuBrMe_2S$ complex (7.73 g, 37.6 mmol) at −78 °C. Workup gave 3.2 g (25.4 mmol, 70%) of 3,3-dimethylcyclohexanone, bp 174−175 °C (lit.[29] bp 58−60 °C/15 Torr), having a satisfactory ^1H NMR spectrum. The ketone was reduced with $LiAlH_4$ to 3,3-dimethylcyclohexanol and this (230 mg, 1.81 mmol) was converted into the tosylate with 476 mg (2.50 mmol) of *p*-toluenesulfonyl chloride and 3.0 g (38 mmol) of pyridine according to the general procedure of Bartsch and Bunnett.[30] The product was not distilled and had ^1H NMR peaks at δ 0.80 (s, 3H), 0.89 (s, 3H), 1.09−1.60 (m, 8H), 2.42 (s, 3H), 4.48−4.63 (m, 1H), 7.28−7.35 (m, 2H), 7.74−7.83 (m, 2H).

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