J. Org. Chem. **1995**, *60*, 4504–4509

The Reaction of 2,2,5,5-Tetramethyl-3,4-diphenylhexane with D_2. Stereochemical Effects in a High-Temperature Reaction

Robert D. Guthrie,[*,†] Rustem V. Sharipov,[†] Sreekumar Ramakrishnan,[†] Buchang Shi,[‡] and
Burtron H. Davis[‡]

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, and Center for Applied Energy Research, 3572 Iron Works Pike, Lexington, Kentucky 40511

Received February 23, 1995[®]

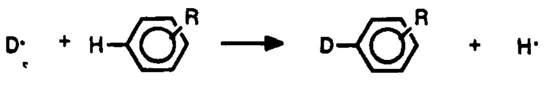
The thermolysis of 2,2,5,5-tetramethyl-3,4-diphenylhexane was carried out at temperatures above 300 °C in the absence and presence of D_2 (14 MPa). The presence of D_2 results in a greatly increased yield of the major product, neopentylbenzene. However, at higher concentrations of starting material, up to 50% of the neopentylbenzene formed avoids deuterium incorporation, an outcome believed to result partly from participation of the phenylneopentyl radical in radical disproportionation reactions. The *meso*-isomer of starting material produces a substantial yield of stilbene in both the absence and presence of D_2. Under D_2, 1,2-diphenylethane is produced, and it is believed that stilbene and other alkenes present serve as D atom traps producing radicals which then participate in termination by disproportionation. Remarkably, the *d,l*-diastereomer gives a different product distribution than the *meso*-isomer, giving very little stilbene or other products of *tert*-butyl group loss. However, both systems produce 1-phenyl-2-methyl-2-propene by methyl radical loss from the phenylneopentyl radical. The formation of such alkenes and the path to termination they provide is blamed for the absence of efficient kinetic chains involving D atoms.

Introduction

In a recent paper, we described the thermolysis of 1,2-diphenylethane, DPE (bibenzyl), and 1,2,3,4-tetraphenylbutane under D_2 pressure.[1] From results presented therein, it seemed clear that benzylic radicals present in the reaction mixture were capable of reacting with D_2 to remove D atoms as shown in eq 1. This reaction is

$$\mathrm{Ar{-}\overset{|}{\underset{|}{C}}\cdot \ + \ D_2 \longrightarrow Ar{-}\overset{|}{\underset{|}{C}}{-}D \ + \ D\cdot} \qquad (1)$$

endothermic by about 20 kcal/mol but, as pointed out by Poutsma,[2] is favored by the high pressure of D_2 (*ca.* 14 MPa in our study) present in the reaction vessel. For the reaction of DPE, the benzyl radicals generated from DPE cleavage produced only a small amount of toluene-d_1, reacting preferentially with DPE to form 1,2-diphenylethyl radicals, DPE•. As a result, the dominant reactant with D_2 *via* eq 1 was this secondary radical. The reaction of eq 1 produces a D atom which can displace either H atoms (eq 2) or alkyl radicals as proposed by Vernon (eq 3).[3] The reactions of eqs 2 or 3 coupled with eq 4 formally



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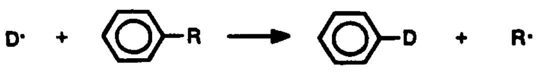

(3)

constitute a chain process. However, operative chain

$$\mathrm{H\cdot \ or \ R\cdot \ + \ D_2 \longrightarrow HD \ or \ RD \ + \ D\cdot} \qquad (4)$$

lengths are near 1. The reason for this is that, in the DPE case and similar systems, the radical population consists primarily of 1,2-diaryl radicals. Chain termination can occur either by radical–radical coupling or by disproportionation. Manka and Stein have shown that coupling dominates for benzylic radicals at lower temperatures.[4] But, at the temperatures used for our studies, radical couplings of benzylic radicals are reversible and do not provide viable termination routes. It therefore appeared that the most important termination step in the DPE system, and probably for 1,2-diaryl radicals in general, is disproportionation of two 1,2-diaryl radicals to give 1,2-diarylalkene and 1,2-diarylalkane as shown in eq 5.

$$\mathrm{2\ Ar\dot{C}HCH_2Ar \longrightarrow ArCH{=}CHAr \ + \ ArCH_2CH_2Ar} \qquad (5)$$

Because efficient H atom chains (eqs 3 and 4) would be highly desirable for hydroliquefaction of fossil fuels, we became curious to see whether such processes were possible. In the DPE study, lowering the DPE concentration increased the competitiveness of eq 1, but it seemed clear that while eq 5 became less important at low concentration, it remained the major barrier to increasing chain length. Radicals generated from several similar systems (*e.g.* cumyl and fluorenyl) also find disproportionation pathways to termination.[5] In an attempt to study a system for which the disproportionation pathway is closed down, we decided to investigate 2,2,5,5-tetramethyl-3,4-diphenylhexane (TMDH). The expected phenylneopentyl radical, **1**•, from TMDH (eq 5) would not able to disproportionate, and benzylic H atom

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[†] University of Kentucky.

[‡] Center for Applied Energy Research.

[®] Abstract published in *Advance ACS Abstracts,* June 15, 1995.

[1] (a) Guthrie, R. D.; Shi, B.; Rajagopal, V.; Ramakrishnan, S.; Davis, B. H. *J. Org. Chem.* **1994**, *59*, 7426–7432. See also: (b) Guthrie, R. D.; Shi, B.; Sharipov, R.; Davis, B. *ACS Div. Fuel Chem. Prepr.* **1993**, *38*, 526–533. (c) Rajagopal, V.; Guthrie, R. D.; Shi, B.; Davis, B. H. *ACS Div. Fuel Chem. Prepr.* **1993**, *38*, 1114. (d) Ramakrishnan, S.; Guthrie, R. D.; Shi, B.; Davis, B. H. *ACS Div. Fuel Chem. Prepr.* **1993**, *38*, 1122. (e) Shi, B.; Ji, Y.; Guthrie, R. D.; Davis, B. H. *Energy Fuels* **1994**, *8*, 1268–1275.

[2] Poutsma, M. L. *Energy Fuels* **1990**, *4*, 113–131 (see p 122).

[3] Vernon, L. W. *Fuel* **1980**, *59*, 102.

[4] Manka, M. J.; Stein, S. E. *J. Phys. Chem.* **1984**, *88*, 1514–1519.

[5] Guthrie, R. D.; Ramakrishnan, S.; Davis, B. H. Unpublished research. See also ref 1d.

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Table 1. Product Distribution[a] from Thermolysis of *meso*-TMDH under Vacuum, N_2, and D_2 at 350 °C

		time (min)				
compound	conditions	5	10	20	30	40
meso-TMDH	V[b]	35.2	9.0	<0.5	<0.5	<0.5
meso-TMDH	N_2	37.5	3.5	<0.5	<0.5	<0.5
meso-TMDH	D_2	15.9	2.1	<0.5	<0.5	<0.5
d,l-TMDH	V[b]	28.5	14.5	5.3	2.3	1.7
d,l-TMDH	N_2	15.5	16.7	9.9	8.9	4.8
d,l-TMDH	D_2	17.8	8.4	4.1	2.7	1.6
1	V[b]	3.5	11.5	11.9	11.3	12.0
1	N_2	3.5	11.3	11.6	12.0	12.3
1	D_2	36.9	53.9	59.6	58.1	57.7
2	V[b]	6.9	17.3	17.2	17.8	17.7
2	N_2	8.2	19.6	17.6	17.8	17.9
2	D_2	12.0	11.4	10.5	9.9	10.9
3	V[b]	2.7	7.8	7.9	7.9	7.9
3	N_2	4.4	9.1	7.6	7.6	7.5
3	D_2	3.5	2.6	2.6	2.3	2.3
4	V[b]	7.3	11.5	13.4	13.2	13.3
4	N_2	0.6	2.6	2.5	2.5	2.7
4	D_2	1.8	2.6	2.3	2.6	2.8
5	V[b]	3.2	7.8	9.7	9.7	9.6
5	N_2	0.6	2.5	2.5	2.5	2.5
5	D_2	<0.5	<0.5	<0.5	<0.5	<0.5
6	V[b]	4.2	15.3	14.5	14.8	15.0
6	N_2	4.9	22.8	22.2	23.3	24.3
6	D_2	2.5	3.3	3.9	4.2	3.9
7	V[b]	1.8	2.5	3.7	3.2	3.7
7	N_2	2.3	6.0	5.4	5.5	5.6
7	D_2	<0.5	<0.5	<0.5	<0.5	<0.5
DPE	V[b]	<0.5	<0.5	<0.5	<0.5	<0.5
DPE	N_2	<0.5	<0.5	<0.5	<0.5	<0.5
DPE	D_2	1.1	4.8	6.6	8.2	9.0
8	V[b]	<0.5	<0.5	<0.5	<0.5	<0.5
8	N_2	<0.5	<0.5	<0.5	<0.5	<0.5
8	D_2	1.6	2.8	2.9	4.4	4.7

[a] All yield data in this table and the following tables are given in mole percent of observed products calculated on the basis of measured GC response factors where possible. [b] Run in evacuated ampules.

removal from TMDH by **1**$^\bullet$ seemed sterically prohibitive. Moreover, central bond scission in TMDH and related compounds had been shown by Rüchardt and co-workers[6] to occur under relatively mild conditions, offering the opportunity to see whether reaction with D_2 could be induced at temperatures below those normally used in hydroliquefaction. The results of our investigation are the subject of this paper.[7]

Experimental Section

Equipment and procedures have for the most part been described in earlier publications.[1] The key feature of our experimental apparatus is a *ca.* 12 mL glass reaction bulb with a long capillary neck housed in a stainless steel tube reactor. Control experiments with the present system showed high recoveries, although a large collection of minor, unidentified products accounts for the fact that the total of product percentages listed in Table 1 is approximately 93%. When mixtures of products were subjected to the reaction conditions, recovery was greater than 95% and there was no measurable depletion of the more volatile materials.

Starting materials were prepared by literature methods[6b,8] and some details given earlier.[7]

Identification of Reaction Products. Compounds **1**, **2**, **6**, **8**, and DPE were obtained commercially and compared by GC, GC/MS, and NMR with isolated materials. Compound **3** showed no parent ion: MS for **3** *m/z* 148, 147, 105, *91*, 57. Compound **3** was isolated in a small amount, and its NMR spectrum was identical to that of a literature spectrum of **3**.[9] Compound **4** was synthesized by a literature procedure:[10] ^{1}H NMR ($CDCl_3$), 0.97 (s, 9 H, *t*-Bu), 2.91, 3.15 (2 d, 2 H, CH_2), 2.61 (t, 1 H, CH), 6.9–7.2 (m, 10 H, Ph); MS *m/z* = 237, 182, 167 (small), 105, *91*, 57. It was shown to be identical to the reaction product. Compound **7** was separated in a small amount: ^{1}H NMR ($CDCl_3$) 0.9 (s, 9 H, *t*-Bu), 0.93 (d, 3 H, CH_3), 2.3 (m, 1 H, CH), 7.0–7.2 (m, 5 H, Ph); MS *m/z* 162, 147, *105*, 91, 57. Compound **5** was not isolated, but its structure was tentatively assigned on the basis of mass spectral data: MS *m/z* 238, 182, *167*, 105, 91, 77, 57.

Deuterium Content. Deuterium analyses were carried out by GC/MS (gas chromatography/mass spectrometry) as described earlier using authentic samples to determine P-1 percentages where necessary.[1a] None of the compounds for which analyses are reported presented significant proton-loss problems. The total amount of D_2 present in the glass reaction vessel is estimated to be approximately 26 mmole which is more than 100 times the amount of substrate even for 50 mg runs. Thus, the amounts of deuterium incorporated which are listed in Tables 2, 3, and 6 are far from equilibrium values, and the amount of HD built up during the reaction should not be more than a few percent, even assuming that there is no mixing between D_2 inside and outside of the glass bulb.

Results and Discussion

Product Distribution from *meso*-TMDH. Thermolysis of *meso*-TMDH in an evacuated ampule at 300 °C resulted in the conversion of the *meso*-isomer (76% remaining) to the *d,l*-isomer (12%) in 15 min. Coincident with this conversion was formation of 1-phenyl-2,2-dimethylpropane (neopentylbenzene, 2.3%, **1**), stilbene (**2**, 4.2%), and 2,2,4,4-tetramethyl-3-phenylpentane (**3**, 1.7%).

The reaction was then carried out at 350 °C under three sets of conditions: in an evacuated ampule, under N_2 (*ca.* 14 MPa), and under D_2 (*ca.* 14 MPa). The reactions are too fast at this temperature to allow for meaningful calculation of kinetic parameters, but they show the important differences in product distribution. The reaction is effectively over after 20 min, and longer time data simply illustrate product stability and distribution reproducibility. Product distributions from these runs are shown in Table 1. In addition to **1**–**3**, the vacuum and N_2 runs produced 3,3-dimethyl-1,2-diphenylbutane (**4**), 3,3-dimethyl-1,1-diphenylbutane (**5**), 2-methyl-1-phenylpropene (**6**), and 2,2-dimethyl-3-phenylbutane (**7**). The run under D_2 added 1,2-diphenylethane (DPE) and 2-methyl-1-phenylpropane (**8**) to the collection of products.

Compound **1** is expected from scission of the central bond in TMDH as shown in eq 6 followed by reaction of the resultant **1**$^\bullet$ with an H atom donor. At least initially, the only H atom donor is TMDH itself, and thus, eq 7 must be considered. Equation 7 would generate **1**, 2-methylpropene (**9**), and the 3,3-dimethyl-1,2-diphenylbutyl radical (**4**$^\bullet$). Radical **4**$^\bullet$ could then lose a *tert*-butyl radical to give **2** as shown in eq 8. Of course, **4**$^\bullet$ could

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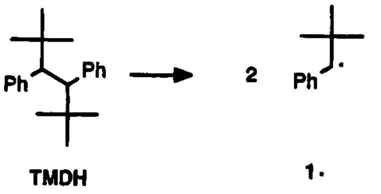
[6] (a) Eichin, K.-H.; Beckhaus, H.-D.; Hellmann, S.; Fritz, H.; Peters, E.-M.; Peters, K.; von Schnering, H.-G.; Ruchardt, C. *Chem. Ber.* **1983**, *116*, 1787–1821. (b) Hellmann, G.; Beckhaus, H.-D.; Ruchardt, C. *Chem. Ber.* **1979**, *112*, 1808–1834. (c) Beckhaus, H.-D.; Ruchardt, C. *Chem. Ber.* **1977**, *110*, 878–895. (d) Kratt, G.; Beckhaus, H.-D.; Lindner, H. J.; Ruchardt, C. *Chem. Ber.* **1983**, *116*, 3265–3263. (e) Kratt, G.; Beckhaus, H.-D.; Lindner, H. J.; Ruchardt, C. *Chem. Ber.* **1984**, *117*, 1748–1764.

[7] A preliminary report has appeared: Sharipov, R.; Guthrie, R. D.; Shi, B.; Davis, B. H. *ACS Div. Fuel Chem. Prepr.* **1993**, *38*, 1129.

[8] (a) Conant, J. B.; Blatt, A. T. *J. Am. Chem. Soc.* **1928**, *50*, 554. (b) Masada, H.; Murotani, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1181.

[9] Van Meurs, F.; Van der Toorn, J. M.; Van Bekkum, H. *J. Organomet. Chem.* **1976**, *113*, 341–351.

[10] Clin, B.; Jousseaume, B.; Duboudin, J.-G. *Bull. Soc. Chim. Fr.* **1974**, 1293–1296.



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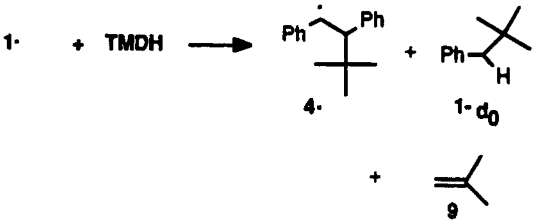

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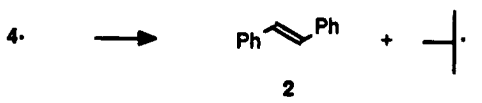
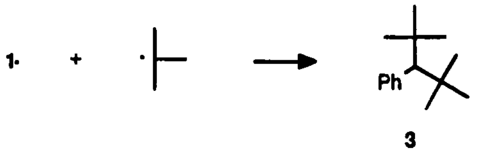


(8)

also be generated by simple homolysis of the 2,3-bond in TMDH. The fact that, in the vacuum and N_2 reactions, **1** was not the predominant product as it had been when the reaction was carried out by Rüchardt and co-workers in a hydrogen donor solvent[6a] along with the fact that **2** was a major product for us and was formed in only 2–6% in Rüchardt's reactions strongly suggests that the stripping of *tert*-butyl groups from TMDH is radical-induced. Equation 8 generates *tert*-butyl radicals which can give **3** by eq 9. Evidence for the intermediacy of **4**$^\bullet$ is found in



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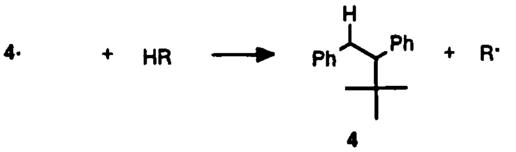

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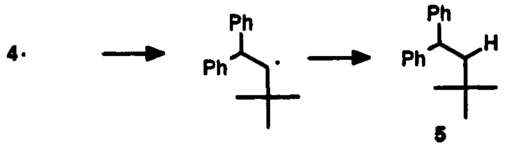

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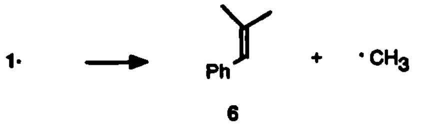

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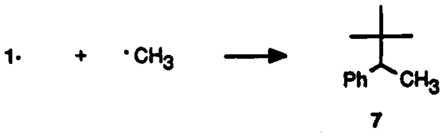

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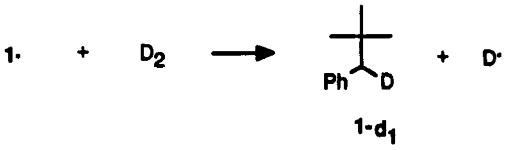
the presence of **4**, formed by H atom abstraction, eq 10. Rearrangement of this radical in the manner previously observed for DPE$^\bullet$ accounts for **5** (eq 11). **1**$^\bullet$ must also split out a methyl radical to give **6** as shown in eq 12, and the methyl radical can proceed by eq 13 to give **7**.

Table 2. Deuterium Distribution in 1 Formed from *meso*-TMDH with D_2 at 350 °C

time (min)	% d_0	% d_1	% d_2	% d_3	total D[a]	aromatic D[b]	aliphatic D[b]
5	38	51	11		0.73	0.20	0.50
10	39	46	13	2	0.80	0.30	0.52
20	40	47	11	2			
30	31	51	15	3			
40	33	50	15	2	0.88	0.32	0.54

[a] D atoms per molecule calculated from mass spectrum. D atoms per molecule values determined by NMR using an internal standard were in good agreement. [b] D atoms per molecule as determined by ^1H and ^2H NMR.

The sequence of eqs 6–13 would explain the products of reaction under N_2 or under vacuum. The most dramatic effect of carrying out the reaction under D_2 was the increased yield of **1**. We offer this as the most unambiguous evidence to date for reaction of a benzylic radical with D_2 as shown in eq 14. Although the yields



(14)

of the products of central bond homolysis are still not as high as those observed by Rüchardt in the presence of H donors such as mesitylene, xylene, and tetralin, the observed increase in yield of **1** clearly identifies D_2 as a D atom donor to **1**$^\bullet$. As will be seen, a significant fraction of **1** produced under D_2, more than the amount produced in the vacuum or N_2 runs, contains no D. This indicates that species generated by reactions of D atoms are serving as H atom donors to **1**$^\bullet$. Other effects of running the reaction under D_2 are reductions in the amounts of **2** and **6** with concomitant appearance of DPE and **8**. Rearrangement product **5**, while not prominent under N_2, disappears under D_2, suggesting that capture of **4**$^\bullet$ by D_2 and by D atom-generated species is efficient. Lower amounts of **3** and disappearance of **7** indicate the likelihood of a reaction between both *tert*-butyl radicals and methyl radicals with D_2. These observations agree with earlier findings of higher reactivity as indicated by reduced selectivity in the reactions of unconjugated radicals. In the present case, the bond energies of available C–H bonds are higher, making reaction with D_2 more competitive.

Deuterium Incorporation. Table 2 shows D incorporation in the major product **1**. As mentioned above, a significant fraction of **1** remains undeuterated in agreement with the suggestion that **1**$^\bullet$ can remove H atoms from the *tert*-butyl groups in TMDH. However, on the basis of the amount of **1** produced in the absence of D_2, this route cannot account for all of the **1-*d*$_0$**. Nevertheless, the amount of D incorporated at the benzylic position of **1** is greater than that at the methyl group of toluene formed from DPE in our earlier study which was carried out at a temperature 100 °C higher.[1] The somewhat lower (aromatic D/aliphatic D) incorporation for **1** relative to that observed for DPE and its hydrothermolysis products in our earlier study is somewhat surprising and suggests the possibility that D atoms produced by eq 14 and other reactions mentioned above may be more selective in their reactions at this lower temperature. In this regard, it is interesting to examine

Table 3. Atoms of D per Molecule in Other Products from Thermolysis of *meso*-TMDH under D_2 at 350 °C

	time (min)			
compound	5	10	30	40
3	0.68[a]	0.80[a]	0.84[a]	0.80[a]
DPE	2.02[b]	1.95[b]		3.25[b]
2	1.98	2.02		

[a] Approximately half of the D incorporated was in CH_3 groups. [b] In the 5 and 10 min runs, aromatic D exceeded aliphatic D by factors of 4 and 2, respectively. In the 40 min run, the amounts were nearly equal.

Table 4. Product Distribution from Thermolysis of *meso*-TMDH under D_2 at 400 °C

	time (min)				
compound	5	10	20	30	40
meso-TMDH	6.6	2.7	>0.2	>0.2	>0.2
d,l-TMDH	0.2	>0.2	>0.2	>0.2	>0.2
1	43.1	43.3	41.8	42.0	42.3
2	6.4	4.3	3.5	1.3	0.8
3	0.7	>0.2	>0.2	>0.2	>0.2
4	5.4	4.5	3.7	2.4	1.6
6	7.4	3.5	2.5	1.6	1.0
DPE	11.4	19.3	20.6	21.9	23.4
8	7.8	14.5	15.3	16.1	16.4

Table 5. Comparison of Product Distributions from Thermolysis of *d,l*-TMDH[a] and *meso*-TMDH[a] under D_2 at 350 °C

	time (min)				
compound	5	10	20	30	40
meso-TMDH (from *d,l*)	>0.2	>0.2	>0.2	>0.2	>0.2
meso-TMDH (from *meso*)		>0.5 (2.1)	>0.5	>0.5	
d,l-TMDH (from *d,l*)	47.0	10.5	5.1	1.9	1.1
d,l-TMDH (from *meso*)		>0.5 (8.4)	>0.5 (4.1)	>0.5 (2.7)	
1 (from *d,l*)	30.7	65.6	71.3	71.8	71.6
1 (from *meso*)		52.6 (53.9)	51.3 (59.6)	56.0 (58.1)	
2 (from *d,l*)	1.3	1.8	1.0	1.1	1.1
2 (from *meso*)		4.2 (11.4)	3.3 (10.5)	2.3 (9.9)	
3 (from *d,l*)	>0.2	>0.2	>0.2	>0.2	>0.2
3 (from *meso*)		>0.2 (2.6)	>0.2 (2.6)	>0.2 (2.3)	
4 (from *d,l*)	>0.2	>0.2	>0.2	>0.2	>0.2
4 (from *meso*)		5.9 (2.6)	4.0 (2.3)	4.8 (2.6)	
6 (from *d,l*)	4.8	4.8	5.9	5.2	5.3
6 (from *meso*)		6.2 (3.3)	5.4 (3.9)	5.4 (3.2)	
DPE (from *d,l*)	0.9	0.5	0.5	0.5	0.5
DPE (from *meso*)		8.3 (4.8)	10.0 (6.6)	11.2 (8.2)	
8 (from *d,l*)	5.1	5.1	5.8	6.7	7.2
8 (from *meso*)		6.9 (2.8)	8.7 (2.9)	10.8 (4.4)	

[a] Data for the *d,l*-isomer were run with 5 mg of substrate in a *ca.* 12 mL bulb. For the *meso*-isomer, the number listed first was obtained with 5 mg of substrate, and the second (in parentheses) is the corresponding number from Table 1 obtained using 50 mg of substrate.

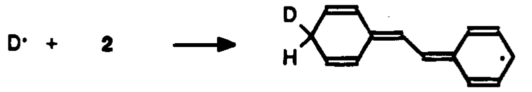
Table 6. Deuterium Distribution in 1 Formed from *d,l*- and *meso*-TMDH at Low Concentration[a] at 350 °C[b]

time (min)	% d_0	% d_1	% d_2	% d_3	% d_4
5 (*d,l*)	6	58	30	6	–
10 (*d,l*)	7	52	34	7	–
10 (*meso*)	13	51	28	7	1
20 (*d,l*)	2	59	34	5	–
20 (*meso*)	10	47	32	10	1
30 (*meso*)	7	44	35	13	2

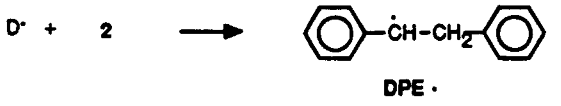
[a] Reactions were run with 5 mg of TMDH in a 12 mL reactor as contrasted with 50 mg for the runs of Table 2. [b] In comparison with the 50 mg runs, D content in DPE was higher, 3.5–4 atoms/molecule, in the runs with *meso*-TMDH (see Table 3). The D content of **2** was about 1.5 atoms of D/molecule in these runs. **8** contained from 2.3–2.9 atoms of D/molecule, but **6** contained 0.5–0.6 atoms/molecule.

D incorporation in some of the other reaction products as summarized in Table 3.

The unexpectedly high deuterium content in both **2** and DPE suggests that, after **2** is formed by eq 8, it then serves as a selective scavenger of D atoms. The high aromatic D content of DPE suggests that **2** accumulates D atoms at aromatic sites by eq 2 at least twice as efficiently as the other aromatic compounds present; for example, **1** contained a maximum of 0.3 atoms of aromatic D per molecule, whereas DPE initially contained 0.75 atoms of aromatic D per ring. Perhaps the extended conjugation for D atom adducts to aromatic sites of **2** (eq 15) accounts for its enhanced reactivity. We have as yet been unable to test this hypothesis. DPE is at least partly formed through the reaction of **2** with D atoms at vinyl sites (eq 16) followed by disproportionation (eq 5).

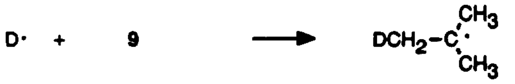


(15)



(16)

It was interesting to find D atoms in the CH_3 groups of **3**. Because no deuterium could be detected in the CH_3 groups of recovered TMDH, its appearance in **3** suggests the reaction of eq 17, followed by that of eq 9. D atoms also appeared at all of the aliphatic positions of **4**, suggesting that some of **4** comes from the addition of *tert*-butyl radicals to **2**.



$$D\cdot + \mathbf{9} \longrightarrow DCH_2\text{-}\overset{CH_3}{\underset{CH_3}{C\cdot}} \tag{17}$$

Product Distribution from *d,l*-TMDH. Most of our work was carried out using *meso*-TMDH, due to problems in the isolation of the *d,l*-diastereomer from synthetic mixtures. However, it was possible to obtain small amounts of reasonably pure samples of the *d,l*-isomer by partial thermolysis of *meso*-TMDH followed by gas chromatographic separation. The limited availability of the *d,l*-isomer required running the reaction at concentrations lower than those used for the data in Table 1 (5 mg rather than 50 mg in our *ca.* 12 mL reactors). Because we knew from our earlier work with DPE that lowering the concentration of starting compound would result in longer kinetic chains, it was therefore necessary to re-run *meso*-TMDH for comparison at the same concentration level.

Table 5 lists product distributions from the thermolysis of *d,l*-TMDH under D_2 at 350 °C. For the 10, 20, and 30 min runs, comparison data for the *meso*-compound run at the same concentration are listed along with (in parentheses) data from the higher concentration runs taken from Table 1. The most dramatic and clear difference between product distributions from *meso*-TMDH and *d,l*-TMDH is in the products from *tert*-butyl loss. Compounds **2**, **4**, and DPE are all greatly reduced for the reaction of the *d,l*-compound. The relative amounts of **2** and its hydrogenation product, DPE, produced from *meso*-TMDH change with the concentration of starting TMDH, but the sum yields of **2** and DPE are about 13% for the low-concentration run and 17% for the high-concentration run. By comparison, the combined yield of these products is about 2% from *d,l*-TMDH. Moreover, compound **4** resulting from the loss of one *tert*-butyl group, present at about 5% in the low-concentration runs for *meso*-TMDH, is virtually missing from the products from *d,l*-TMDH. Other differences are probably not significant. The yield of the major product **1** is higher from the *d,l*-isomer, probably because of the reduction in **2**, **4**, and DPE. Compounds **6** and **8** (methyl loss products) are present in comparable amounts from both diastereomers. There is an increase in the relative amount of the hydrogenation product **8** in the low-concentration runs as an expected result of longer kinetic chains. Compound **3** (from the coupling of *tert*-butyl radicals and $\mathbf{1}^{\bullet}$) is missing from the products from the *d,l*-isomer, as expected; but this also happens for the *meso*-isomer at low concentrations, and thus, no comparisons of *d,l*-TMDH and *meso*-TMDH can be made with this last piece of information.

Differences between the thermolysis behavior of the *d,l*-isomer and the *meso*-isomer run under D_2 are, for the most part, coincident with the elegant studies by Rüchardt carried out in H donor solvents, most completely for *p*-Cl-TMDH.[6a] Rüchardt showed that the *d,l*-isomer is the more stable and also the less reactive in the scission of the central bond. He also found a slightly greater activation barrier for the coupling of $\mathbf{1}^{\bullet}$ to give the *meso*-isomer. While we did not attempt detailed kinetic measurements, these findings explain our observation that the *meso*-isomer shows some isomerization to *d,l*-TMDH. Moreover, Rüchardt observed loss of *tert*-butyl groups to give *p,p'*-dichlorostilbene only with the *meso*-isomer and not with the *d,l*-compound.

Why does the *meso*-isomer show prominent *tert*-butyl loss while the *d,l*-isomer does not? In some preliminary presentations of these results,[11] we suggested the possibility that both *tert*-butyl groups were lost in a concerted elimination which, assuming the usual antiperiplanar transition state geometry, would lead to *trans*-**2** in the case of *meso*-TMDH and the less stable *cis*-**2** in the case of *d,l*-TMDH. This argument is illustrated in Figure 1. However, the presence of **4**, the structure of which has been confirmed by comparison with a synthetic sample, militates against this explanation. As **4** almost certainly arises via $\mathbf{4}^{\bullet}$, as shown in eq 10, it seems clear that this radical must then represent a local energy minimum on the path from TMDH to **2**. Thus, the relative propensity for *tert*-butyl loss from the *meso*-isomer must be the result of differing energetics for the reaction of eq 7 as a function of which diastereomer is used. As the 3,3-dimethyl-1,2-diphenylbutyl radical would be energetically the same when produced from either diastereomer, the difference in transition state energies for cleavage of the 2,3-bond and the 3,4-bond must be smaller for the *meso*-compound. Rüchardt[12] has calculated that the preferred conformation of the *meso*-compound is that with *anti-tert*-butyl groups. While the appearance of **4** would seem to rule out a concerted formation of *trans*-**2**, this conformation would, nevertheless, lead to the presumed low-energy conformation of radical $\mathbf{4}^{\bullet}$ shown as the lower path for *meso*-TMDH in Figure 1. The *d,l*-isomer also favors a conformation with *anti-tert*-butyl groups. However, in this case, loss of *tert*-butyl radical without conformational conversion would lead to an unfavorable conformation of the radical $\mathbf{4}^{\bullet}$ in which coplanarity of the phenyl ring with the radical center would require an unfavorable steric interaction. Of course, at these temperatures, the *d,l*-isomer can readily rotate into a conformation which would lead directly to the stable form of $\mathbf{4}^{\bullet}$, whereupon cleavage might be assumed to be facile. However, Rüchardt[6a,12] has pointed out that a substantial fraction of strain energy remains in effect at the transition state for these high-temperature homolyses, and our results insist that this is true in the case of *tert*-butyl radical loss from *d,l*-TMDH. It seems quite remarkable, but this reaction is stereospecific, even at 350 °C.

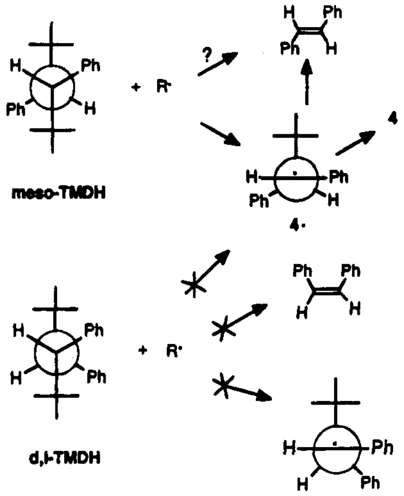


Figure 1. Stereoselectivity in TMDH thermolysis.

Summary and Conclusions

The presence of D_2 (14 MPa) during the thermolysis of TMDH leads to a 4–5-fold increase in the yield of reductive cleavage product **1**. Apparently, radicals, $\mathbf{1}^{\bullet}$, produced through central bond homolysis in TMDH which can couple to re-form TMDH, are trapped to give **1** when D_2 is present. Considering that, under the conditions used to obtain the data in Table 2, only about half of the trapping involves D_2 directly, other D atom-generated species must serve as H atom donors to $\mathbf{1}^{\bullet}$. The high deuterium incorporation in **2** and DPE suggests that D atoms generated by the reaction of various radicals with D_2 (eqs 1, 4, *etc.*) are trapped by the alkenes present in the manner of eqs 16 and 17, producing radicals which can then serve as H atom (or D atom) donors. The disproportionation reaction of eq 5 involving $DPE^{\bullet}$ as both H atom donor and H atom acceptor serves as a prototype for such processes. The presence of β-H atoms is a requirement for the donor, but any radical, including $\mathbf{1}^{\bullet}$, can serve as an acceptor. Thus, despite the fact that the main radical produced by thermolysis, $\mathbf{1}^{\bullet}$, is prevented from acting as an H atom donor by its lack of β-hydrogens, the formation of alkenes such as **2**, **6**, and **9** and their subsequent reaction with D atoms provide a source of donor radicals.

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[11] For example: Guthrie, R. D.; Shi, B.; Rajagopal, V.; Ramakrishnan, S.; Sharipov, R.; Davis, B. H. Organic Division Section of the American Chemical Society Meeting, Chicago, IL, August 1993; Poster 248.

[12] Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 429.

It would appear that the radical disproportionation reaction once again precludes the desired propagation efficiency necessary for the establishment of long kinetic chains. Further, it seems likely that any reactive alkene (or in the case of coal and other fossil fuel sources, some multiring arenes) can participate by trapping H or D atoms and thus promote termination. We hope in the future to study *d,l*-TMDH in more detail because a smaller fraction of the reaction products from this diastereomer are alkenes. Among other results, the present study illustrates how clever Nature can be at finding routes to termination of radical chain reactions by disproportionation. Given the structural diversity of typical coals, it seems certain that this problem will be unavoidable during hydroliquefaction in the absence of catalysts added to remove easily hydrogenated alkenes and arenes.

Acknowledgment. The authors thank the U. S. Department of Energy, Pittsburgh, for a grant, DE-FG22-91-PC91291, supporting this work.

JO9503421