

REACTION OF 2,2,5,5-TETRAMETHYL-3,4-DIPHENYLHEXANE
WITH D₂ AT 300-350 °C

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INTRODUCTION

In previous preprints we have described the thermolysis of 1,2-diphenylethane (bibenzyl)^{1,2} and 1,2,3,4-tetraphenylbutane under D₂.³ We have also described preliminary results with 2,3-diphenyl-2,3-dimethylbutane (bicumyl).³ In these cases the resulting pattern of deuterium incorporation into reaction products and recovered starting materials was interpreted in terms of benzylic radicals reacting with D₂ to produce D atoms which then reacted both to reverse the processes involved in their formation and also to add to unsaturated centers in the molecules present. An important mechanistic consideration for reactions of the compounds listed turned out to be the availability of a disproportionation process as the probable dominant termination step in each case. For both diphenylethane and tetraphenylbutane, a 1,2-diphenylethyl radical is formed which disproportionates to stilbene and diphenylethane. Cumyl radical can similarly give cumene and α -methylstyrene. It was thus of interest to see what might happen in a system where this option was missing. We also wished to explore temperature limitations for the reaction with D₂.

For these and other reasons, we decided to investigate the thermolysis of 2,2,5,5-tetramethyl-3,4-diphenylhexane (TMDH) under D₂. This substrate had been synthesized earlier and its thermolysis kinetics studied by Ruchardt.⁴ Thermolysis of this compound produced a rich assortment of products suggesting a complex network of reaction steps. The situation was somewhat simpler in the presence of D₂ and led to some interesting mechanistic conclusions as described below.

RESULTS AND DISCUSSION

meso-TMDH undergoes thermolysis at 300 °C, and the most abundant product after 30 min is the *d*,*l*-isomer (approx. 55 wt%). Other products are 1-phenyl-2,2-dimethylpropane (neopentylbenzene), 1, stilbene, 2, 1-phenyl-2-methylprop-1-ene,³ 2,2,4,4-tetramethyl-3-phenylpentane, 4, 1,2-diphenyl-3,3-dimethylbutane, 5, 1,1-diphenyl-3,3-dimethylbutane, 6, and other minor products. Amounts of neopentylbenzene and stilbene in the products mixture suggest the possibility of two paths for isomerization of TMDH. First by cleavage of the central C-C bond (as anticipated from the work of Ruchardt⁴) and second by cleavage of the

C-C bond between alpha and beta carbons. On further heating (at 350°C) either in vacuum or under N₂, the mixture of meso- and d,l-TMDH is completely converted to the mixture of products indicated above. The distribution of products for the reaction carried out in vacuum is given in Table I.

When the 350 °C reaction of TMDH is carried out under D₂, the proportion of neopentylbenzene in the product mixture becomes quite large: 63% as compared to 13% when run in vacuum, strongly suggesting that 1-phenylneopentyl radicals are being intercepted by D₂. It is also significant that while there is no significant amount of 1,2-diphenylethane, 7, present in the vacuum or N₂ reactions, this product develops in the D₂ reaction. The amount of stilbene, 2, formed under D₂ is smaller than the amount formed under N₂ and 7 grows in as the reaction proceeds. This suggests the possibility that 7 is formed from 2. Similarly, 1-phenyl-2-methylpropane, 8, is formed under D₂ at the expense of 3. The product 6, which is likely the rearrangement product of 1,2-diphenyl-3,3-dimethylbutyl radical, is also greatly diminished under D₂. The product distribution for the D₂ reaction is given in Table III. The results are compared graphically in Figures 1 and 2.

Mass spectrometric analysis of the major reaction product, 1, gives the results shown in Table II. Results of ¹H and ²H NMR for this compound are shown in Table IV. It will be noted that even after 5 min, at which time about 35% of the mixture of meso- and d,l-11 remains, the amount of deuterium in the 1-position of neopentylbenzene is 50% of one atom of D. The distribution does not change significantly with time. We see little alternative to the conclusion that the phenylneopentyl radical formed from dissociation of TMDH removes D from D₂ making this the clearest example so far of the reaction R[•] + D₂ → R-D + D[•]. We have no information to indicate the source of the H atoms which are required to produce the 1-d₀ produced. The most likely possibility is a termination process involving H atom removal from the tert-butyl radicals which would seem likely side products to the formation of 2, 5, and 7. The presence of compound 4 in substantial amounts in the vacuum and N₂ reactions indicate the presence of tert-butyl radicals and demonstrate the viability of a coupling with phenylneopentyl radicals. As H atom removal is an expected companion reaction to coupling, this makes the tert-butyl radical a logical source of H.

It is interesting that the level of incorporation of D in the aromatic rings of 1 and recovered TMDH is much lower relative to the aliphatic D when compared with results from the diphenylethane system. This suggests the possibility that D atoms are being scavenged by species present in the reaction mixture. A logical possibility is the 2-methylpropene expected as a product of the reaction of tert-butyl radicals with H-atom acceptors and the observance of D in the methyl groups of 4, but not of 1 confirms this suggestion. Reaction of D atoms with stilbene, 2, and 3 also seemed likely. This would seem to explain the unexpectedly high levels of D found in diphenylethane, 7, both at aromatic and aliphatic positions as shown in Table V. The possibility that stilbene can serve as an efficient scavenger for D atoms is presently under investigation. The stilbene present in the D₂ reaction was also found to contain high levels of D.

The various observations described above lead us to suggest the reaction scheme shown in Figure 3 as representing the most significant processes involved in the thermolysis of TMDH under D₂. In addition to demonstrating the viability of a number of processes having basic importance in the understanding of hydroliquefaction chemistry, this

study documents the uncatalyzed reaction of an organic compound with D₂ at an unusually low temperature.

EXPERIMENTAL SECTION

Equipment and Procedures. These have been described elsewhere.^{1,2,3}

Synthesis of 1-phenyl-2,2-dimethylpropanol. This material was synthesized by a literature method.⁵ The product was a colorless liquid, 17.5 g (53.7 %) with pleasant honey smell. ¹H NMR (CDCl₃), : 0.93 (9H,s, t-Bu); 2.65 (1H, -OH); 4.35 (1H,s, C-H); 7.3 (5H,s, -Ph).

1-Bromo-1-phenyl-2,2-dimethylpropane. This material was prepared by a literature synthesis.⁶ ¹H NMR (CDCl₃), : 1.1 (9H,s, t-Bu); 4.9 (1H,s,C-H); 7.3-7.5 (5H,m, -Ph).

meso-2,2,5,5-Tetramethyl-3,4-diphenylhexane, (1) This material was prepared by a literature synthesis.⁴ For use in the reaction with D₂ it was twice recrystallized from acetic acid, then twice from petroleum ether - stout prisms, m.p. 181 °C, ¹H NMR (CDCl₃), : 0.53 (18H,s, t-Bu); 3.05 (2H,d,-CH-); 7.15-7.3,7.5 (10H,m, -Ph).

Thermolysis of 2,2,5,5-tetramethyl-3,4-diphenylhexane. Thermolysis of the model compound was conducted in sealed evacuated 4 mL Pyrex ampules in a silicone oil bath at 300-320 °C and in a sand bath at 330-400 °C. For each experiment 5 mg of compound was used. After pyrolysis, reaction mixture was analyzed by GC-MS.

Thermolysis of 2,2,5,5-tetramethyl-3,4-diphenylhexane under D₂ gas pressure. The experiments with D₂ gas were conducted in a reaction bulb with a long capillary neck described earlier.¹ Normally 100 mg of model compound was placed in the reaction vessel. The reaction products were dissolved in 0.6 mL of carbon disulfide analyzed by GC and GC-MS then separated by preparative gas chromatography. Isolated compounds were analyzed by ¹H and ²H NMR, mass spectrometry and, where possible, comparison with authentic samples. Details of identification will be presented elsewhere.

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Table I. Product Distribution from the Reaction of meso-TMDH at 350 °C in Vacuum.

Product	Time(min)				
	5	10	20	30	40
<u>meso</u> -TMDH	30.0	10.0	5.3	2.2	1.3
<u>d, l</u> -TMDH	37.0	16.0	6.1	2.6	2.0
1	3.7	12.7	13.6	13.2	12.9
2	4.5	11.7	12.1	12.6	12.6
3	3.5	13.0	13.3	13.6	13.8
4	3.8	11.4	12.4	12.6	12.6
5	3.4	7.0	9.1	6.1	2.0
6	6.3	10.3	12.4	8.3	3.1
7	--	--	--	--	--
8	--	--	--	--	--

Table II. Deuterium Distribution in 1-Phenyl-2,2-dimethylpropane Formed from Thermolysis of TMDH under D_2 at 350 °C (from GC/MS)

Time (min)	d_0	d_1	d_2	d_3
5	38	51	11	--
10	39	46	13	2
20	40	47	11	2
30	31	51	15	3
40	33	50	15	2

Table III. Product Distribution from the Reaction of meso-TMDH at 350 °C under D₂.

Product	Time(min)				
	5	10	20	30	40
<u>meso</u> -TMDH	16.7	2.3	1.0	0.5	0.3
<u>d,l</u> -TMDH	18.6	9.1	4.5	2.9	1.7
1	38.7	58.4	64.7	62.9	62.7
2	7.7	7.6	7.0	6.7	7.4
3	3.0	2.9	3.3	3.7	3.5
4	4.1	3.9	3.8	3.4	3.6
5	2.1	2.2	2.0	2.3	2.5
6	--	--	--	--	--
7	0.7	3.2	4.4	5.5	6.9
8	1.3	2.4	2.6	3.9	4.1

Table IV. Deuterium Incorporation in 1-Phenyl-2,2-dimethylpropane Formed from Thermolysis of TMDH under D₂ at 350 °C.

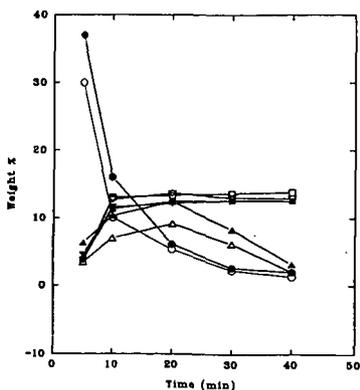
Time (min)	D/molecule (GC/MS)	D/molecule (NMR)	Aliphatic D (1-position)	Aromatic D
5	0.73	0.86	0.53	0.33
10	0.78	0.82	0.52	0.30
20	0.74			
30	0.89			
40	0.87	0.86	0.55	0.31

Table V. Deuterium Incorporation in 1,2-Diphenylethane Formed from Thermolysis of TMDH under D₂ at 350 °C.

Time (min)	D/molecule ^a (GC/MS)	D/molecule (NMR)	Aliphatic D	Aromatic D
5	2.02	2.04	0.44	1.60
10	1.95	1.98	0.67	1.31
20	2.6			
30	3.2			
40	3.3	3.37	1.55	1.82

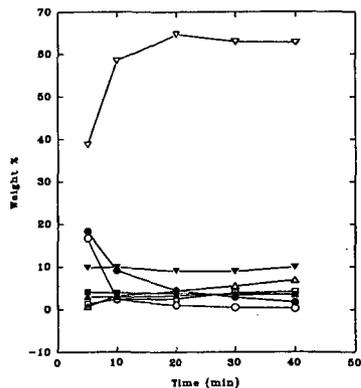
^a Because the amount of DPE formed was small, it was difficult to get reliable data. A good mass spectral analysis was produced only in the 20 min run. The distribution for this run was d₀ = 22%, d₁ = 32%, d₂ = 28%, d₃ = 13%, d₄ = 4%. The 30 and 40 min runs showed comparable distributions, but the experimental error was judged to be rather large.

Figure 1. Thermolysis of TMDH at 350 °C in Vacuum



○ - m,sc-TMDH
 □ - d,l-TMDH
 ▽ - 1

Figure 2. Thermolysis of TMDH at 350 °C Under D₂



○ - m,sc-TMDH
 □ - d,l-TMDH
 ▽ - 1

Figure 3

