

REACTION OF 1,2,3,4-TETRAPHENYLBUTANE WITH D₂ AT 400 °C

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INTRODUCTION

In an earlier preprint,¹ we have described the reaction of diphenylethane, DPE, with D₂ at 450 °C to promote D incorporation in both starting DPE and reaction products. A previous study by Vernon² had suggested that when the reaction is carried out under H₂ with tetralin present, benzyl radicals produced in the thermolysis react with H₂ to give toluene and H-atoms and that the H atoms react with DPE to give 2-phenylethyl radicals and benzene. Our earlier results are consistent with this suggestion in that the Vernon process would provoke D incorporation for the reaction under D₂. However, in our experiments, the amount of D in initially formed toluene as well as in benzene and ethylbenzene was substantially less than one atom of D per molecule demanding the conclusion that radicals present also react with DPE to give 1,2-diphenylethyl radicals. In fact, the amount of aliphatic deuterium present in unreacted DPE was quite similar to that in the formed toluene. The similarity was then explained by further experiments in which DPE-1,1-d₂ was shown to undergo extensive scrambling under the reaction conditions and that toluene-1,1,1-d₃ undergoes exchange with DPE under the reaction conditions.³ As this agreed with existing literature which provided a number of examples of exchange of H atoms between benzylic positions,⁴ it was clear that it would be difficult to identify the radical primarily responsible for removing D atoms from D₂ because the initial landing sites of D-atoms become obscured by exchange.

Although it seemed reasonable that both benzyl and 1,2-diphenylethyl radicals were capable of carrying out this reaction, the roles played by each were not separable. It seemed likely that the 1,2-diphenylethyl radical being rendered more stable by its "secondary" structure would be less reactive. On the other hand, the equilibrium between the benzyl and diphenylethyl radicals would allow the latter to accumulate in the reaction mixture for the same reason. To establish the 1,2-diphenylethyl radical as a candidate for reaction with D₂ we undertook to produce it by a route which did not also generate benzyl radicals. We thus secured 1,2,3,4-tetraphenylbutane, TPB, by a literature preparation,⁵ and undertook to study its thermolysis in the presence of D₂.

RESULTS AND DISCUSSION

1,2,3,4-Tetraphenylbutane

TPB underwent thermolytic reaction at 400 °C to give 1,2-diphenylethane, 1, and stilbene, 2, as major products. Small amounts of 1,2,3-triphenylpropane, 3, toluene, 4, and smaller amounts of benzene, 5, ethylbenzene, 6, and styrene, 7, were observed at high conversions. The product distribution is presented in Table I. It seems clear that the major reaction pathway for thermolysis of TPB is homolysis of the 2,3 bond to give two 1,2-diphenylethyl radicals, 8, which then react, predominantly, by disproportionation to give 1 and 2. Compounds 3 and 4 are presumably formed via homolysis of the 1,2 bond to give benzyl radicals, 9, and 1,2,3-triphenylprop-1-yl radicals, 10. Interestingly, the amount of 3 + 4 increases relative to 1 + 2 as the reaction progresses suggesting the possible production of some of 3 and 4 from 1 and 2. It is clear that the formation of 2 constitutes the only source of hydrogen atoms. Formation of two molecules of 1 from one TBP requires that two atoms of H be provided externally unless 2 is formed concurrently. The formation of 3 and 4 also requires a source of H or D.

As the reaction proceeds, the total moles of 1, 3, and 4 formed exceeds the moles of 2. This fact alone, in the absence of other unsaturated products, clearly predicts the consumption of D₂. Products were analyzed for deuterium content by gas chromatography/mass spectrometry (GC/MS) and, indeed, contained substantial amounts of deuterium as detailed in Table II.

Interpretation of GC/MS data obtained for recovered TPB is rendered difficult by the fact that the original molecular ion ($m/z = 362$) fragments readily to give daughter ions at ($m/z = 181$). However, the pattern of ion intensities in the $m/z = 181$ region is, within experimental error, identical to that for starting TPB suggesting that no deuterium has been incorporated. This is confirmed by ²H NMR experiments which fail to detect the presence of D atoms (upper limit of 5%). In previous experiments with more volatile substrates, we have usually found significant amounts of deuterium in all aromatic compounds present. Apparently the reaction with D atoms occurs largely in the gas phase and unreacted liquid TPB is protected in this instance by its low vapor pressure.

Most of the deuterium atoms predicted to be present are found in the diphenylethane, 1, formed. Roughly 50% of the molecules of 1 contain one or more atoms of D. Rough calculation suggests that the amount of D present in 1, plus small amounts present in other components of the reaction mixture, is sufficient to explain the excess of 1, 3, and 4 over 2. Interestingly, the stilbene present contains a relatively small amount of D. Although we have not yet been able to determine its exact location by NMR, earlier experiments suggest that this amount of D is roughly that expected for the aromatic ring exchange reaction associated with D-atom production and D-atom addition to the double bond of 2 would incorporate some D at the vinyl positions after disproportionation.

Thus, it seems clear that one-third to one-half of the 1,2-diphenylethyl radicals produced through scission of the 2,3-bond in TPB react with D₂ to give 1-d, plus a D-atom. The remainder disproportionate to give 1 plus 2. The D-atoms formed react with all gas-phase aromatic compounds to give ring exchange. We find that these results make it difficult to avoid the conclusion that 1,2-

diphenylethyl radical is a viable partner in the reaction with D_2 .

Interestingly, the small amount of toluene, 4, produced in this reaction contains about the same level of D as does 1. While we cannot say unequivocally that benzyl radicals also react with D_2 in this system, it seems unlikely that the relatively high levels of D in 4 could arise through D-atom removal from 1.

As might be expected, triphenylpropane, 3, formed also contains D. The amount is somewhat less, for reasons that are not clearly understood. One possible explanation is that the 1,2,3-triphenylprop-1-yl radical remains in the liquid phase and therefore has less ready access to gaseous D_2 .

The processes which seem likely to explain the data described are given in equations 1,2,3 and 4 in Figure 1. It will be noted that the only termination steps suggested are those in eq 2. It is clear that the amount of 2 produced is insufficient to account for all of the necessary termination processes. Whether termination reactions involving $R \cdot + D \cdot$ are involved or other processes must be invoked, is not clear at the present time. It will be noted that in runs to high conversion, we do not list 100% of the material balance. This is because a large assortment of minor products are formed, not all of which have been identified.

2,3-Dimethyl-2,3-diphenylbutane

From the results described above as well as those in the following paper in this series, it seemed likely that the reaction with D_2 is general for radicals of a variety of structural types. To this point the radicals studied were either monosubstituted (primary) or disubstituted (secondary). It was thus of interest to extend the scope to tertiary radicals and preliminary experiments have now been carried out with 2,3-dimethyl-2,3-diphenylbutane (bicumyl), 11. When 11 was subjected to thermolysis at 450 °C under D_2 for 30 min, the products were found to be cumene, 12, (70%) and 2-phenylpropene, 13, (30%), the latter clearly arising from disproportionation of 2-phenylprop-2-yl radical (cumyl), 14. Thus about 40% excess 12 is produced and this presumably is obtaining D from D_2 .

GC/MS studies showed that molecules of 12 were 62% d_0 , 26% d_1 and 11% d_2 . 1H and 2H NMR studies show that deuterium is being incorporated at both aliphatic positions in 12. About 55% of the aliphatic D is at the methine (CH) position and 45% is in the CH_2 groups. This suggests that when cumyl radicals react with D_2 , the D atoms produced react to a significant extent at the methylene (CH_2) group in 13, rather than at aromatic positions as observed with the diphenylethane system. The resultant deuterated cumyl radicals disproportionate and place deuterium at all positions in both 12 and 13. The sequence of events for the reaction of 11 is shown in Figure 2.

EXPERIMENTAL SECTION

Synthesis of 1,2,3,4-Tetraphenylbutane, TPB. The synthesis was carried out as described in the literature.⁵ The product was a white crystalline solid, mp 183 °C. 1H NMR δ ($CDCl_3$) 2.8 (m, 2 H), 3.1 (m, 4 H), 7.4 (m, 20 H).

Synthesis of 2,3-Dimethyl-2,3-diphenylbutane, 11. This compound was prepared by a literature procedure.⁶ The product was sublimed to give white crystals, mp 119 °C. 1H NMR δ ($CDCl_3$) 1.25 (s, 12 H), 7.10

(m, 10 H).

Thermolysis of 1,2,3,4-Tetraphenylbutane, TPB, and 2,3-Dimethyl-2,3-diphenylbutane, 11, 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 comparison with authentic samples.

REFERENCES

1. Guthrie, R. D.; Shi, B.; Sharipov, R.; Davis, B. H. Prepr., Div. Fuel Chem., Am. Chem. Soc. 1993, **38**, 526-533.
2. Vernon, L. W. FUEL 1980, **59**, 102-106.
3. Rajagopal, V.; Guthrie, R. D.; Shi, B.; Davis, B. H. Prepr., Div. Fuel Chem., Am. Chem. Soc. 1993, **38**, this volume.
4. (a) Poutsma, M. L.; Dyer, C. W. J. Org. Chem. 1982, **42**, 4903. (b) Buchanan, A. C.; Dunstan, T. S. J.; Douglas, E. C.; Poutsma, M. L. J. Am. Chem. Soc. 1986, **108**, 7703. (d) Bockrath, B.; Bittner, D.; McGrew, J. J. Am. Chem. Soc. 1984, **106**, 135-138. (e) McMillen, D. G.; Malhotra, R.; Chang, S.-J.; Ogier, W. C.; Nigenda, S. E.; Fleming, R. H. FUEL, 1987, **66**, 1611-1620.
5. Wyman, D. P. J. Org. Chem. 1962, **27**, 3712. See also, Brook, A. G.; Tai, K. N.; Gilman, H. J. Am. Chem. Soc. 1955, **77**, 6219, and Smith, L. I.; Hoehn, H. H. J. Am. Chem. Soc. 1941, **63**, 1184.
6. Bors, D.; Kaufman, M. J.; Streitwieser, A., Jr. J. Am. Chem. Soc. 1985, **107**, 6975-6982.

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Table I. Weight % of Products from the Thermolysis of 1,2,3,4-Tetraphenylbutane under D₂ at 400 °C.

Compound	Time (min)				
	5	10	15	20	30
TPB	92	71	41	29	16
1	2.1	16.2	22.6	26.3	33.6
2	3.5	7.4	15.2	12.4	12.7
3	0.2	3.2	3.3	11	9.6
4	<0.1	0.5	1.1	1.6	3.3
5	<0.1	0.2	0.2	--	0.4
6	<0.1	0.1	0.1	--	0.5
7	<0.1	0.1	0.1	--	0.2

Table II. Deuterium Content of Products from Thermolysis of TPB under D₂ at 400 °C.

Product	% of d _n at Time (min)				
	5	10	15	20	30
TPB-d ₀	>95	>95	>95		>95
TBP-d ₁	<5	<5	<5		<5
1-d ₀	50.5	49.8	43.8	28.6	29.8
1-d ₁	40.6	41.5	44.0	46.2	44.1
1-d ₂	8.0	7.8	10.4	20.5	20.7
1-d ₃	0.8	0.7	1.5	4.7	4.9
2-d ₀	88.0	88.5	83.1	61.6	63.0
2-d ₁	11.6	10.7	14.2	29.2	31.0
2-d ₂	0.3	0.8	1.9	6.6	6.6
3-d ₀	75	74	68		
3-d ₁	25	26	32		
4-d ₀			43.2	25.6	30.5
4-d ₁			46.2	57.7	55.3
4-d ₂			8.4	16.7	14.3

Figure 1

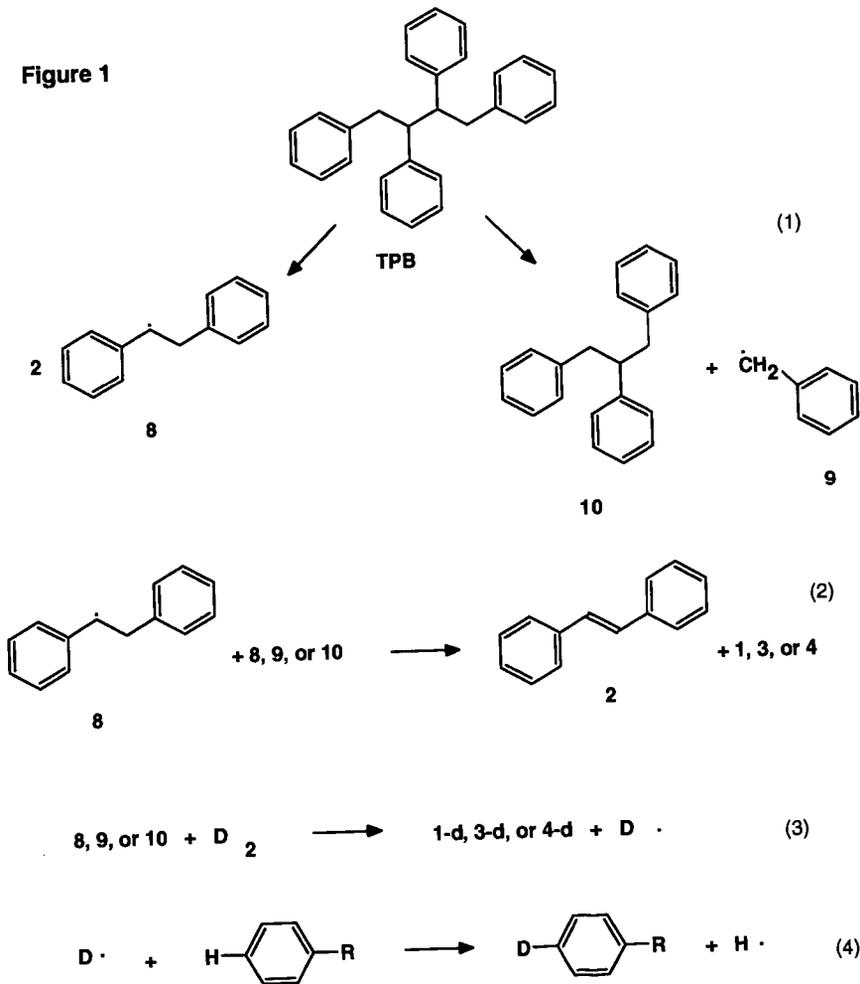


Figure 2

