

1149. *Polar Influences in Radical Reactions. Part III.* The Abstraction of Benzylic Hydrogen Atoms from Dibenzyl Ethers by Benzyl Radicals.*

By R. L. HUANG, H. H. LEE, and M. S. MALHOTRA.

The benzyl and *p*-methoxybenzyl radicals, when generated by thermolysis of the azo-compounds $\text{Ar}\cdot\text{CH}_2\cdot\text{N}:\text{N}\cdot\text{CH}_2\cdot\text{Ar}$ ($\text{Ar} = \text{Ph}$ or *p*- $\text{C}_6\text{H}_4\cdot\text{OMe}$) in dibenzyl ether, abstract benzylic hydrogen atoms from the substrate, to markedly different degrees (14% and 63%, respectively, at 170°). A study of substituent effects showed that dehydrogenation by the latter radical at 140–150° is virtually free from polar influences.

The triphenylmethyl radical, liberated from triphenylchloromethane by the action of zinc at 130°, also dehydrogenates dibenzyl ether to the extent of 50%. Its efficacy in hydrogen-abstraction, relative to that of free benzyl, is discussed.

AMONG studies on the participation of polar effects in radical reactions, the majority concern abstraction of α -hydrogen atoms from aromatic side-chains. The abstracting radicals hitherto investigated have in the main been electronegative in nature, *e.g.*, the halogens (bromine and chlorine), alkoxy-, acyloxy-, and peroxy-radicals, and free trichloromethyl.¹ Radicals of an electropositive character have not as yet received attention. This paper reports the same abstraction reaction by a number of radicals of this type, namely, free benzyl, *p*-methoxybenzyl, and triphenylmethyl.

* Part II, preceding Paper.

¹ For references see Part I, R. L. Huang, H. H. Lee, and S. H. Ong, *J.*, 1962, 3336.

For the study of side-chain reactivity the system so far found to be the most versatile has been substituted toluenes, and much work using this system has been published. When the abstracting entity is a benzyl radical, however, difficulties are expected. Although free benzyl, a resonance-stabilised radical, is known readily to abstract halogen atoms (bromine and chlorine) from molecular halogens, alkyl hypohalites, and bromotrichloromethane, and hydrogen atoms from phenols, its displacement of hydrogen from a carbon atom can hardly be expected to be facile. Thus, the "identity reaction"



has been shown by Eliel *et al.*² to occur only to a negligible extent, and Jackson³ has recently found only slight exchange between free benzyl and chlorotoluene, at moderate temperatures. In view of the high reactivity of the α -hydrogen atoms in dibenzyl ether,¹ it was thought that this might be a suitable substrate for study with the benzyl radical, especially as it has been demonstrated by Huang and Yeo⁴ that, in the dehydrogenation of dibenzyl ethers by *t*-butoxy-radicals, the benzyl and substituted-benzyl radicals generated in the system also partake in the abstraction of benzylic hydrogen atoms, in favourable cases up to 24%. Accordingly, we studied the dehydrogenation of dibenzyl ether by benzyl, *p*-methoxybenzyl, and triphenylmethyl radicals. The first two were generated by thermolysis of the azo-compounds $\text{Ar}\cdot\text{CH}_2\cdot\text{N}:\text{N}\cdot\text{CH}_2\cdot\text{Ar}$ ($\text{Ar} = \text{Ph}$ or *p*- $\text{C}_6\text{H}_4\cdot\text{OMe}$), whilst triphenylmethyl was produced *in situ* by the action of zinc on triphenylchloromethane.

Thermolysis of $\omega\omega'$ -azotoluene is known⁵ to yield nitrogen and benzyl radicals. Bickel and Waters,⁶ who decomposed the compound in boiling decalin, obtained nitrogen (84%), bibenzyl (39%), toluene (12.5%), stilbene (10.5%), and traces of tetraphenylbutane. We have confirmed this work (94% nitrogen), obtaining also small quantities (*ca.* 5%) of benzaldehyde which probably arose from the hydrazone $\text{Ph}\cdot\text{CH}:\text{N}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{Ph}$ ⁶ or from the azine $\text{Ph}\cdot\text{CH}:\text{N}:\text{N}:\text{CH}\cdot\text{Ph}$ (see below).

Berson *et al.*⁷ have shown that evolution of nitrogen from 2-azobornane decreased from 95% to 42% when the concentration of the azo-compound was increased from 0.0056M to 0.17M, and attributed this to secondary attack, by the 2-bornyl radical, on the carbon atom adjacent to the azo-group, resulting ultimately in the formation of the corresponding azine. In the decomposition of azotoluene in dibenzyl ether, therefore, a large excess of the ether was employed, a high yield of nitrogen (73%) being thus obtained after 4 hr. at 160–170° (at 135–140°, decomposition dropped to 30%). Formation of some hydrazone and/or azine, however, apparently could not be avoided, as indicated by the increase of benzaldehyde between the time the reaction was completed and the time the products were worked up. The products were toluene (14% based on azo-compound decomposed), benzaldehyde (13%), traces of tetraphenylbutane, and some resinous material. (Bibenzyl was probably present, although its isolation and identification in the presence of a large excess of dibenzyl ether proved difficult and was not pursued.) The low yield of benzaldehyde indicates that, of all the benzyl radicals generated, only a few (13%) abstracted α -hydrogens from the ether. This radical is, therefore, not a suitable abstracting agent with which to study substituent effects.

To ascertain whether the benzaldehyde produced from the ether might have suffered attack by the benzyl radicals, the decomposition of $\omega\omega'$ -azotoluene in boiling benzaldehyde (179°) was also studied. The products consisted of toluene (18%), bibenzyl (11%), stilbene (11%), and small quantities of tetraphenylbutane and nitrogen-containing substances. Since no trace of the dibenzoate, $\text{Bz}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{O}\cdot\text{Bz}$, known to be formed in good yield from the benzoyl radical under much the same conditions,⁸ could be found, it seemed reason-

² E. L. Eliel, P. H. Wilken, F. T. Fang, and S. H. Wilen, *J. Amer. Chem. Soc.*, 1958, **80**, 3303.

³ R. A. Jackson, *J.*, 1963, 5284.

⁴ R. L. Huang and O. K. Yeo, *J.*, 1959, 3190.

⁵ G. Williams and A. S. C. Lawrence, *Proc. Roy. Soc.*, 1936, **A**, 156, 455.

⁶ A. F. Bickel and W. A. Waters, *Rec. Trav. chim.* 1950, **69**, 312.

⁷ J. A. Berson, C. J. Olsen, and J. S. Walia, *J. Amer. Chem. Soc.*, 1962, **84**, 3337.

⁸ R. L. Huang and S. S. Si-Hoe, "Vistas in Free Radical Chemistry," ed. W. A. Waters, Pergamon Press, London, 1959, p. 242.

able to conclude that the toluene found was derived from the benzyl radical through abstraction of α -hydrogen atoms not from benzaldehyde, but from the azo-compound and/or bibenzyl. From the latter would thus arise the bibenzyl radical $\text{Ph}\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_2\cdot\text{Ph}$ which would account for tetraphenylbutane and stilbene. The inability of the benzyl radical to attack benzaldehyde is consistent with the almost identical bond-dissociation energies attributed to the benzylic C-H bonds in toluene and benzaldehyde (78 and 79 kcal., respectively).⁹

Abstraction by the *p*-methoxybenzyl radical was next investigated. Thermal decomposition of 4,4'-dimethoxy- $\omega\omega'$ -azotoluene in decalin at 150–160° gave nitrogen (28%), and small quantities of 4,4'-dimethoxybibenzyl, 4,4'-dimethoxystilbene, and anisalazine. The generation of the free *p*-methoxybenzyl radical thus appears well substantiated, whilst its rôle as the hydrogen-abstracting radical, when the decomposition was carried out in dibenzyl ether, was attested by the isolation of *p*-methoxytoluene, in at least 46% yield. As an abstracting radical it proved to be considerably more efficient than free benzyl, giving under similar conditions a much higher yield of benzaldehyde (63% against 13%). Under optimum conditions, found to be a 100-fold excess of the ether at 165–175°, decomposition was 86% complete and the yield of benzaldehyde nearly quantitative (96%). Despite an allowance to be made for abstraction due to free benzyl generated from the ether radical, the yield of benzaldehyde arising from abstraction by the *p*-methoxybenzyl radical must have been over 80%. It appears therefore that under these conditions, abstraction of hydrogen becomes the main reaction, while dimerisation, occurring either in the solvent "cage" or by recombination, hardly takes place.

The *p*-methoxybenzyl radical having proved to be an effective dehydrogenating agent for dibenzyl ether, a study of substituent effects was carried out by decomposing the azo-compound in a series of substituted ethers containing the *m*- and *p*-chloro-, *m*-bromo-, and *p*-*t*-butyl-groups. Since polar effect decreases with increasing temperature, and since the azo-compound decomposes very slowly below 130°, the temperature range of 140–150°, at which decomposition was moderate, was chosen for the present study.

As with azotoluene, formation of the hydrazone and/or the azine occurred, giving rise to anisaldehyde. Analysis of products from each ether therefore involved the separation of three aldehydes, namely, benzaldehyde, a substituted benzaldehyde, and anisaldehyde. This imposes a limitation on the choice of substituted dibenzyl ethers but, for those named above, separation of the three aldehydes was in each case effectively done by the method developed earlier.¹ Another experimental difficulty encountered was the total inhibition of decomposition in some experiments, without apparent reason. This has been experienced with related substances^{7,10} and attributed to presence of traces of impurities in the solvents. However, despite careful purification of materials, inhibition could not always be avoided.

Results of abstraction experiments with substituted dibenzyl ethers are given in the Table (see Experimental). A plot of the logarithms of the molar ratio substituted-benzaldehyde:benzaldehyde against the σ or σ^+ constants of the substituents shows no linear relationship (σ correlation: $r = 0.65$; σ^+ correlation: $r = 0.5$) indicating the absence of polar effects. Since, for each methoxybenzyl radical which abstracts a hydrogen atom from the ether a secondary benzyl or substituted benzyl radical is liberated through disproportionation of the ether radical, the abstracting species is in actual fact a mixture of benzyl radicals, in which, however, free *p*-methoxybenzyl predominates.

In view of a recent report¹¹ that the triphenylmethyl radical, generated *in situ* by the action of zinc on triphenylchloromethane at 125–130°, abstracts benzylic hydrogen atoms from the xylenes, in favourable cases to the extent of 43%, it became of interest to study the dehydrogenation of dibenzyl ether by the same radical. Reaction using the reported method gave benzaldehyde in 50% yield based on the triphenylchloromethane used, triphenyl-

⁹ P. Gray and G. Williams, *Chem. Rev.*, 1959, **59**, 239; L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, 1957, **27**, 416.

¹⁰ R. C. Peterson and S. D. Ross, *Tetrahedron Letters*, 1960, No. 23, 18.

¹¹ R. A. Benkeser, J. L. Bach, and R. G. St. Clair, *J. Org. Chem.*, 1961, **26**, 1404.

methane in 43% yield, small quantities of 1,1,1,2-tetraphenylethane (3%), and a substituted product of dibenzyl ether, probably *p*-Ph₃C·C₆H₄·CH₂·O·CH₂·Ph. Isolation of triphenylmethane, in approximately the same yield as benzaldehyde, is strongly indicative of the triphenylmethyl radical being the abstracting radical and, judging from the amount of benzaldehyde produced, it would appear that this radical is considerably more reactive than the benzyl radical, which abstracts to the extent of 14% only. A more plausible explanation can probably be found in the equilibria existing between these radicals and their respective dimers at the reaction temperatures: whilst hexaphenylethane would be expected to be largely dissociated to the triphenylmethyl radical, bibenzyl, on the contrary, is completely stable. The concentration of the former radical therefore, must have been considerably higher than that of the latter in the respective reaction systems. A similar explanation would seem reasonable to account for the apparently different abstracting capacities of the benzyl and *p*-methoxybenzyl radicals, namely, that the difference is due not so much to the intrinsic ability of the radicals to abstract hydrogen as to the rate at which the radicals are eliminated from the system through dimerisation. The *p*-methoxybenzyl radical, in which the benzylic carbon atom is polarised due to the presence of the *p*-substituent, would be expected to combine with a like radical less readily than would the unsubstituted benzyl radical. This postulate is consistent with the finding⁴ that both the *p*-methoxyl and the *m*-chlorobenzyl-radicals abstract hydrogen relatively well, when these are generated from the respective substituted dibenzyl ethers following dehydrogenation by *t*-butoxy-radicals.

EXPERIMENTAL

Melting points were taken on a Kofler hot-stage apparatus. "Petroleum" refers to a fraction of b. p. 60–80°, and "alumina" to neutral, active aluminium oxide supplied by Merck & Co. The substituted dibenzyl ethers, including the hitherto unknown *m*-bromodibenzyl ether, b. p. 140–142°/0.6 mm., n_D^{23} 1.5858 (Found: C, 60.4; H, 4.9. C₁₄H₁₃BrO requires C, 60.7; H, 4.7%), were prepared as previously described,¹² and were spectroscopically pure (infrared). Microanalyses were carried out by Mrs. H. K. Tong of Singapore.

*Preparation of ωω'-Azotoluene.*⁶—Benzalazine (8 g.) in ethyl acetate (30 ml.) was hydrogenated at atmospheric pressure over 2% palladium–calcium carbonate (1 g.). After removal of the catalyst, the mixture was concentrated under reduced pressure (70 mm.), and the oily hydrazo-compound obtained was redissolved in ether and refluxed with mercuric oxide (6.5 g.). A further quantity of mercuric oxide (6.5 g.) was added after 30 min., and the mixture refluxed for 3 hr. with occasional shaking. Filtration and concentration under reduced pressure left a residue which solidified on cooling (–80°). After several recrystallisations from methanol at –80°, the product (4.0 g., 50%) was dried in a vacuum desiccator over phosphorus pentoxide (2 hr.), m. p. 29° (lit.,⁶ 27–29°). The azotoluene decomposed to a yellow liquid on standing at 25° for 5–6 hr.

The above procedure is a modification of that reported by Bickel and Waters,⁶ which in our hands gave ωω'-azotoluene in poor yield and contaminated by a compound of empirical formula C₁₄H₁₄N₂, m. p. 156–158° (Found: C, 80.7; H, 6.4; N, 13.1. Calc. for C₁₄H₁₄N₂: C, 80.0; H, 6.7; N, 13.3%).

*Preparation of 4,4'-Dimethoxy-ωω'-azotoluene.*¹³—A suspension of anisalazine (7.4 g.) in methanol (100 ml.) was hydrogenated in the presence of 20% palladium–charcoal (2 g.). After removal of the catalyst, copper sulphate solution (10%; 0.5 ml.) was added to the solution which was then shaken under oxygen with occasional cooling in ice. When no further uptake of oxygen was observed (400 ml.; 30 min.), the product was filtered off and recrystallised from methanol, yielding 4,4'-dimethoxy-ωω'-azotoluene (2.5 g., 30%) as colourless prisms, m. p. 93–94° (lit.,¹³ 92–93°), λ_{\max} . (EtOH) 276 and 356 m μ (log ϵ 3.60 and 1.95) [lit.,¹³ λ_{\max} . 275 and 356 m μ (log ϵ 3.60 and 1.89)]. 4,4'-Dimethoxy-ωω'-azotoluene is more stable than ωω'-azotoluene at room temperature.

Decomposition of ωω'-Azotoluene in Dibenzyl Ether.—(a) ωω'-Azotoluene (4.025 g., 19.2 mmoles) and dibenzyl ether (60 g., 300 mmoles) were placed in a two-neck flask fitted with a reflux condenser the top of which was connected to a gas-flow meter. The solution was heated from 27° to 170° (bath temp.) during 0.5 hr. and then kept at 160–170° for 3.5 hr. Nitrogen corresponding to 73%

¹² R. L. Huang and S. S. Si-Hoe, *J.*, 1957, 3988.

¹³ G. Fodor and P. Szarvas, *Ber.*, 1943, 76, 334.

decomposition of the azo-compound was collected. Analysis of an aliquot of the reaction mixture by infrared spectroscopy showed benzaldehyde (1709 cm.^{-1} , ϵ 720) to be present to the extent of 3.5 moles (13%, based on 73% decomposition of azotoluene). The mixture was fractionated under nitrogen giving (i) material, b. p. $30-108^{\circ}/0.3\text{ mm.}$ (1.86 g.), (ii) unchanged dibenzyl ether (54 g.), b. p. $106-108^{\circ}/0.3\text{ mm.}$, and (iii) residue (4.1 g.). Fraction (i) was again analysed for benzaldehyde by infrared spectroscopy and found to contain 5.5 mmoles (20%). Vapour-phase chromatography of fraction (i) indicated the presence of toluene (14%). Short-path distillation of fraction (iii) afforded (a) 1,2,3,4-tetraphenylbutane (ca. 20 mg.), m. p. $180-182^{\circ}$ (lit.,¹⁴ $179-180^{\circ}$), (b) unchanged dibenzyl ether (3 g.), and (c) intractable oils (0.8 g.).

(b) In another experiment, the azotoluene (2.75 g., 13.1 mmoles) and dibenzyl ether (49 g.) were heated at $135-140^{\circ}$ for 5 hr. (30% decomposition). Fractionation gave (i) material, b. p. $30-108^{\circ}/0.3\text{ mm.}$ (0.6 g.), (ii) unchanged dibenzyl ether (46 g.), b. p. $106-108^{\circ}/0.3\text{ mm.}$, and (iii) a yellow residue (5 g.). Fraction (i) was shown by infrared spectroscopy to contain 3 mmoles of benzaldehyde (38%). Short-path distillation of fraction (iii) yielded (a) unchanged dibenzyl ether (3.8 g.), and (b) intractable oils (1.1 g.).

Decomposition of $\omega\omega'$ -Azotoluene in Decalin.—A solution of $\omega\omega'$ -azotoluene (1.98 g., 9.4 mmoles) in decalin (23.7 g., 170 mmoles) was refluxed ($187-193^{\circ}$) for 4.5 hr., when the volume of nitrogen evolved indicated that 94% of the azo-compound had decomposed. Examination of the mixture by infrared spectroscopy showed no detectable amount of benzaldehyde. However, after being set aside for 12 hr., fractionation gave a forerun (4.5 g.), b. p. $80-100^{\circ}/30\text{ mm.}$, which was shown by infrared spectroscopy to contain benzaldehyde (1.0 mmole, 5.6%).

Decomposition of $\omega\omega'$ -Azotoluene in Benzaldehyde.—A solution of $\omega\omega'$ -azotoluene (3.79 g., 18 mmoles) in benzaldehyde (9.0 g., 85 mmoles) after being refluxed for 4.5 hr. (70% decomposition) gave, on distillation, (i) a forerun, b. p. $40-84^{\circ}/70\text{ mm.}$ (3.3 g.), (ii) unchanged benzaldehyde (5.0 g.), b. p. $840^{\circ}/70\text{ mm.}$, and (iii) a residue (4.5 g.). Vapour-phase chromatography of (i) showed the presence of toluene (4.6 mmoles, 18% based on azo-compound decomposed). A portion of the residue (2.75 g.) was chromatographed on alumina (145 g.) and eluted with petroleum containing benzene (5–10%) to give (a) bibenzyl (0.30 g., 11%), m. p. and mixed m. p. $48-50^{\circ}$, (b) stilbene (0.28 g., 11%), m. p. and mixed m. p. $123-124^{\circ}$, and (c) 1,2,3,4-tetraphenylbutane (30 mg.), m. p. $181-182^{\circ}$, λ_{max} . (EtOH) 254, 259, 262, 265, and 269 m μ . ($\log \epsilon$ 2.79, 2.77, 2.83, 2.89, and 2.69). Elution with benzene and benzene-ether gave four nitrogen-containing compounds in traces.

Decomposition of 4,4'-Dimethoxy- $\omega\omega'$ -azotoluene in Decalin.—The azo-compound (0.95 g., 3.5 mmoles) in decalin (20 g., 98 mmoles) was heated at $150-160^{\circ}$ (bath) for 5 hr. (28% decomposition). The mixture, on cooling, deposited a white solid (0.36 g.), m. p. $80-95^{\circ}$, with infrared absorption almost identical to that of the starting azo-compound. Repeated recrystallization, however, failed to yield pure material. Concentration of the filtered solution under reduced pressure gave a residue (0.30 g.) which, on adsorbing on alumina and eluting with benzene, afforded (i) 4,4'-dimethoxybibenzyl (10 mg.), m. p. $120-122^{\circ}$ (lit.,¹⁴ 126°) and (ii) 4,4'-dimethoxystilbene (20 mg.), m. p. $214-215^{\circ}$ (lit.,¹⁴ 215°). Elution with benzene-ether (4:1) gave (iii) anisalazine (0.15 g.), m. p. and mixed m. p. $179-181^{\circ}$.

Decomposition of 4,4'-Dimethoxy- $\omega\omega'$ -azotoluene in Dibenzyl Ether.—(a) A solution of the azo-compound (3.37 g., 12.5 mmoles) in dibenzyl ether (110 g., 556 mmoles) was heated at $140-150^{\circ}$ (bath) for 4 hr., when nitrogen representing 50% decomposition of the azo-compound had been collected. Fractionation gave a forerun, b. p. $40-108^{\circ}/0.3\text{ mm.}$ (12 g.), containing mainly benzaldehyde and dibenzyl ether. To this was added ethanol (20 ml.), silver nitrate (5 g.), and, with stirring, aqueous sodium hydroxide (10%; 20 ml.). After 5 hr. the mixture was filtered and the filtrate diluted with water (200 ml.) and extracted with diethyl ether ($5 \times 50\text{ ml.}$). Concentration of the ethereal extracts followed by short-path distillation gave a fraction, b. p. $110-120^{\circ}/70\text{ mm.}$ (0.7 g.), n_D^{23} 1.5110, identified as *p*-methoxytoluene by infrared spectroscopy. The aqueous solution, on acidification and isolation with ether, gave benzoic acid (1.16 g.), m. p. and mixed m. p. $121-123^{\circ}$ (from water).

(b) A solution of the azo-compound (0.35 g., 1.3 mmoles) in dibenzyl ether (27.7 g., 140 mmoles), after being heated at $165-175^{\circ}$ for 4 hr. (86% decomposition), was distilled to give a forerun, b. p. $40-108^{\circ}/0.3\text{ mm.}$, which was treated with 2,4-dinitrophenylhydrazine.¹ Chromatography of the crude 2,4-dinitrophenylhydrazone on bentonite-kieselguhr¹ yielded mainly benzaldehyde 2,4-dinitrophenylhydrazone (0.60 g., 2.1 mmoles, 96% abstraction, based on azo-compound decomposed) and a small amount of anisaldehyde 2,4-dinitrophenylhydrazone (0.05 g.). A more con-

¹⁴ L. B. Howard, G. E. Hilbert, W. R. Wiebe, and V. L. Gaddy, *J. Amer. Chem. Soc.*, 1932, **54**, 3628.

centrated solution of azo-compound (5.6 mmoles) in dibenzyl ether (100 mmoles) under the same conditions gave a lower yield of nitrogen (14%) and of benzaldehyde (0.98 mmole, 63% abstraction.)

Decomposition of 4,4'-Dimethoxy- $\omega\omega'$ -azotoluene in Monosubstituted Dibenzyl Ethers.—This was conducted at 140–150° in the same manner as for dibenzyl ether. The reaction mixture was distilled and the forerun treated directly with 2,4-dinitrophenylhydrazine, and the hydrazone formed was separated by chromatography.¹ Results obtained are given in the Table.

Decomposition of 4,4'-dimethoxy- $\omega\omega'$ -azotoluene in monosubstituted dibenzyl ethers
R·C₆H₄·CH₂·O·CH₂·Ph at 140–150°.

Ether		Azo-cpd. (mmole)	Time (hr.)	Decompo- sition ^a (%)	Ph·CHO- DNP (mmole)	R·C ₆ H ₄ ·CHO- DNP (mmole)	<i>p</i> -OMe·C ₆ H ₄ CHO-DNP (mmole)	% Yield ^b of R·C ₆ H ₄ CHO + Ph·CHO	Molar ratio R·C ₆ H ₄ ·CHO: Ph·CHO
R	(mmole)								
H	210	3.00	6	62	3.6		0.28	97	
<i>p</i> -Cl	150	2.39	6	59	1.19	1.45	0.35	93	1.21
<i>p</i> -Cl	270	4.03	4.5	53	1.76	2.16	0.47	92	1.23
<i>m</i> -Cl	180	3.23	4	56	1.43	1.88	0.55	91	1.05
<i>p</i> -Bu ^t	110	2.51	4	50	1.25	1.18	0.64	97	0.94
<i>m</i> -Br	81	2.14	4.5	40	0.74	0.80	0.35	90	1.08

DNP = 2,4-dinitrophenylhydrazine. ^a Based on volume of nitrogen obtained. ^b Calculated on azo-compound decomposed.

Reaction of Dibenzyl Ether with Triphenylmethyl Radicals.—Zinc dust (6.6 g., 0.1 mole, dried at 150° before use) was added in one portion to a stirred solution of triphenylchloromethane (6.30 g., 23 mmoles) in dibenzyl ether (55.6 g., 280 mmoles) at 125–130° (bath) under nitrogen. The mixture was stirred at this temperature for 11 hr., filtered, the residue washed with petroleum, and the combined filtrate and washings were concentrated under nitrogen through a 6 in. Vigreux column. Distillation of the residue gave the following fractions: (i) material, b. p. 40–108°/0.3 mm. (6 g.), containing mainly benzaldehyde and dibenzyl ether, (ii) dibenzyl ether, b. p. 106–108°/0.3 mm., n_D^{22} 1.5602 (42 g.), and (iii) a viscous residue (10.4 g.). From fraction (i) benzaldehyde (0.6 g., 24% based on triphenylchloromethane) was isolated *via* the bisulphite adduct and identified as the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 240–242°. A portion (7.87 g.) of fraction (iii) was chromatographed on alumina (210 g.). Elution with petroleum afforded (a) triphenylmethane (1.8 g., 43%), m. p. and mixed m. p. 93–94° (from ethanol), (b) 1,1,1,2-tetraphenylethane (0.18 g., 3%), m. p. 144–145° (from ethanol) (lit.,¹⁵ 144°) (Found: C, 93.2; H, 6.8. Calc. for C₂₆H₂₂: C, 93.4; H, 6.6%), and (c) *benzyl p-triphenylmethylbenzyl ether* (0.03 g.), m. p. 169–170° (from ethanol) (Found: C, 89.9; H, 6.6. C₃₃H₂₈O requires C, 90.0; H, 6.4), ν_{\max} 1093, 1070, 1030, 696 cm.⁻¹. Further elution with petroleum–benzene (10:1) gave (d) dibenzyl ether (4.7 g.), identified by its infrared spectrum, and (e) intractable oils (0.9 g.).

In another experiment, triphenylchloromethane (6.03 g., 22 mmoles), dibenzyl ether (39.7 g., 200 mmoles), and zinc dust (6.6 g., 100 mmoles) were heated at 125–130° for 6 hr. and worked up as described above. The forerun b. p. 40–108°/0.3 mm. (8 g.) from distillation of the reaction mixture, on treatment with 2,4-dinitrophenylhydrazine, gave benzaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 241–243° (3.2 g., 50% based on triphenylchloromethane).

UNIVERSITY OF MALAYA, KUALA LUMPUR.

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¹⁵ M. Gomberg and L. H. Cone, *Ber.*, 1906, **39**, 1463.