

852. *Free Radicals and Radical Stability. Part XIV.*¹ (*Ethoxyphenyl*)diphenylmethanols and the Free Radical (*o*-Ethoxyphenyl)-diphenylmethyl.

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The basicity of triphenylmethanol is increased slightly more by the ethoxyl than by the methoxyl group.

Disproportionation of (*o*-ethoxyphenyl)diphenylmethyl in benzene is slow at room temperature, and the solid ethane can be isolated. Cryoscopic measurements show that the ethoxyl substituent promotes dissociation of the ethane slightly less than methoxyl does. In benzene at room temperature (*o*-ethoxyphenyl)diphenylmethyl iodide is dissociated to the same extent as the methoxyl derivative.

THE (*ethoxyphenyl*)diphenylmethanols were prepared for comparison of their basicities and of the salts with the corresponding methoxyl derivatives.¹⁻³ The introduction of a methoxyl group into triphenylmethanol increases the basicity, and generally leads to a bathochromic shift in the absorption spectrum of the sulphate, but these effects are slightly more marked with ethoxyl (see Table, where the basicity values are referred to that of triphenylmethanol as unity). The halochromic effect of the alkoxy group is greatest for *ortho*-substitution, whereas the basicity change is greatest for *para*-substitution and least for *meta*-substitution. There is no simple connection between the resistance of the salt to hydrolysis as expressed by the basicity, and the optical properties of the system.

Basicity and halochromism.

Diphenylmethanol	Basicity	Colour of sulphate	Diphenylmethanol	Basicity	Colour of sulphate
(<i>o</i> -Methoxyphenyl)- ...	2.0	Red	(<i>o</i> -Ethoxyphenyl)- ...	2.3	Red
(<i>m</i> -Methoxyphenyl)- ...	1.2	Orange-red	(<i>m</i> -Ethoxyphenyl)- ...	2.0	Reddish-brown
(<i>p</i> -Methoxyphenyl)- ...	6.5	Red	(<i>p</i> -Ethoxyphenyl)- ...	7.9	Orange-brown

In the thermal decomposition of formic acid solutions of (*o*-methoxyphenyl)diphenylmethanol at 77° the evolution of carbon dioxide is more rapid and more nearly approaches the theoretical value than for similar solutions of triphenylmethanol, and the favourable influence of *o*-methoxyl is further shown by the higher yield of triarylmethane.⁴ The behaviour of the solution of (*o*-ethoxyphenyl)diphenylmethanol, however, differs markedly from that of the *o*-methoxyl derivative inasmuch as the reaction is more rapid in the initial stages, but slows down sharply when about 0.3 mol. of the gas has been evolved: the colour of the (*o*-ethoxyphenyl)diphenylmethyl cation is discharged and the solution becomes brown, whereas solutions of the corresponding ions of triphenylmethyl and (*o*-methoxyphenyl)diphenylmethyl become colourless. The overall inhibiting influence of the ethoxyl substituent on the reduction process arises from secondary reactions which lead to coloured products without liberation of carbon dioxide. Although (*p*-ethoxyphenyl)diphenylmethane may be isolated from the solution, the compound is more readily prepared by reduction of the alcohol with zinc and acetic acid.

(*o*-Ethoxyphenyl)diphenylmethyl chloride dissolves in non-ionizing solvents to form colourless solutions, and is reduced to the free radical by mercury or silver. In bromobenzene solution at 18° reduction by molecular silver is slower than that of triphenylmethyl chloride. A 2% solution of (*o*-ethoxyphenyl)diphenylmethyl in benzene is yellowish-red, and there is no appreciable change of colour in 4 days in the dark. The radical rapidly absorbs 0.95 mol. of oxygen, and forms a normal peroxide. Although the

¹ Part XIII, preceding paper.

² Gomberg and Nishida, *J. Amer. Chem. Soc.*, 1922, **45**, 190.

³ Gomberg and Buchler, *ibid.*, p. 207.

⁴ Part VIII, *J.*, 1940, 874.

radical is much more prone to disproportionate and/or isomerize than triphenylmethyl, these reactions are slow at room temperature—solutions which are 24 hr. old absorb practically the same amount of oxygen as the freshly prepared solution.

Di-(*o*-ethoxyphenyl)tetraphenylethane in 2% benzene solution at the freezing point is about 20% dissociated, which is slightly less than for the methoxyl derivative.¹ The ethane, which may be isolated in the solid state from acetone solution, dissolves in organic solvents to yield the characteristic colour of the radical, but forms a red solution in liquid sulphur dioxide owing to ionization. Solutions of the free radical absorb iodine until an equilibrium is established with (*o*-ethoxyphenyl)diphenylmethyl iodide. In benzene at 15° the amount of halogen absorbed is only slightly lower than for the *o*-methoxyl derivative.

EXPERIMENTAL

(*p*-Ethoxyphenyl)diphenylmethanol.—Hydrolysis of the interaction product of *p*-phenethylmagnesium bromide and benzophenone gave the alcohol as an oil which, however, was obtained crystalline as follows. Etheral *p*-ethoxybenzophenone⁵ (0.1 mole) was added slowly to a filtered solution of phenylmagnesium bromide (0.1 mole) and, after reaction had completely subsided, the mixture was heated under reflux for 30 min. under a soda-lime guard-tube. The mixture was hydrolysed and acidified with sulphuric acid, and the etheral layer was washed and dried (Na₂SO₄). The oil obtained on evaporation solidified after prolonged trituration with light petroleum. Recrystallization from 1 : 4 ether–light petroleum gave the colourless alcohol, m. p. 54° (Found: C, 82.4; H, 6.8. C₂₁H₂₀O₂ requires C, 82.9; H, 6.6%).

(*p*-Ethoxyphenyl)diphenylmethane, previously obtained from (*p*-ethoxyphenyl)diphenylmethyl ethyl ether⁶ and from (*p*-hydroxyphenyl)diphenylmethane,⁷ was prepared by heating the alcohol (2 g.) with acetic acid (25 ml.) and zinc dust (7 g.) under reflux for 2 hr. The mixture was filtered while hot, and the yellow oil, which was deposited on cooling, was separated and triturated with ligroin until it solidified. Recrystallized from alcohol, the methane was obtained colourless, with m. p. 68° (Found: C, 87.0; H, 6.6. Calc. for C₂₁H₂₀O: C, 87.5; H, 7.0%).

(*m*-Ethoxyphenyl)diphenylmethanol.—To a filtered solution of phenylmagnesium bromide (0.22 mole) etheral ethyl *m*-ethoxybenzoate⁸ (0.1 mole) was added dropwise, and the mixture was heated under reflux in a dry atmosphere for 90 min. The product was hydrolysed and acidified. The crude alcohol deposited from the etheral solution was washed with light petroleum and recrystallized from alcohol; it had m. p. 90° (Found: C, 82.4; H, 6.3. C₂₁H₂₀O₂ requires C, 82.9; H, 6.6%).

(*o*-Ethoxyphenyl)diphenylmethanol.—The compound was prepared by heating together etheral solutions of phenylmagnesium bromide (0.22 mole) and ethyl *o*-ethoxybenzoate⁷ (0.1 mole) for 3 hr., and hydrolyzing the product. The etheral solution was washed with water and dried (Na₂SO₄). On removal of the bulk of the solvent, the alcohol was deposited as a yellow solid, which became colourless on recrystallizing from alcohol, and had m. p. 136–137° (Found: C, 82.7; H, 6.5. C₂₁H₂₀O₂ requires C, 82.9; H, 6.6%).

Basicity of Alcohols.—The basicity was determined by the method of Baeyer and Villiger.⁹

Potassium (o-Ethoxyphenyl)diphenylmethoxide.—A solution of the alcohol (3 g.) in xylene (25 ml.) was boiled with metallic potassium (0.4 g.) in dry nitrogen for 3 hr. After cooling, the unchanged metal was removed by means of a pointed rod, and the solution was reduced to one-third of its bulk by distillation in a stream of nitrogen. The crystals deposited on cooling consisted of potassium (*o*-ethoxyphenyl)diphenylmethoxide with 1 mol. of xylene of crystallization [Found: K, 8.7. C₂₁H₁₉O₂K.C₆H₄(CH₃)₂ requires K, 8.9%]. 27% of the solvent is retained after 1 hr. at 145°/20 mm. in a stream of nitrogen. The compound is rapidly hydrolyzed by moisture.

(*o*-Ethoxyphenyl)diphenylmethane.—Since the compound is obtained in very low yield by heating (*o*-ethoxyphenyl)diphenylacetic acid,¹⁰ we employed the following methods.

(a) The solution obtained by refluxing the alcohol (5 g.) in acetic acid (25 ml.) with zinc dust

⁵ Gattermann, Ehrhardt, and Maisch, *Ber.*, 1890, **23**, 1199.

⁶ Bistrzycki and Herbst, *Ber.*, 1902, **35**, 3135.

⁷ Bistrzycki and Herbst, *Ber.*, 1903, **36**, 3571.

⁸ Cohen and Dudley, *J.*, 1910, **97**, 1741.

⁹ Baeyer and Villiger, *Ber.*, 1902, **35**, 1189.

¹⁰ Liebig, *Annalen*, 1908, **360**, 216.

(6 g.) for 2 hr. was filtered and allowed to cool. The methane deposited (3.3 g.) was repeatedly crystallized from alcohol; it had m. p. 67° (Found: C, 86.8; H, 6.9. Calc. for $C_{21}H_{20}O$: C, 87.5; H, 7.0%).

(b) A solution of the methanol (0.3 g.) in 98% formic acid (5 ml.) was kept at 100° until colourless. After cooling, it was poured into water, and the precipitated methane was repeatedly crystallized from alcohol. Its m. p. (66°) was unchanged by admixture with a specimen prepared by method (a).

Thermal Decomposition of Formates.—Measurements of the rate of evolution of carbon dioxide from solutions of triphenylmethanol (0.260 g.) and the *o*-methoxyl (0.290 g.) and the *o*-ethoxyl derivative (0.304 g.) in 98% formic acid (5 ml.) at 77° gave the annexed results.

The first two solutions were completely decolorized, but the solution of the ethoxyl derivative became brown as the characteristic colour of the cation was discharged.

Time (min.).....	5	15	20	30	40	50	60	80	100
CO ₂ (%)	5.3	29.9	38.6	53.5	63.1	67.5	70.6	73.2	75.3
Time (min.).....	10	20	30	40	50	60	70	80	90
CO ₂ (%)	43.5		60.3	74.0	82.1	88.0	93.5	97.0	98.5
Time (min.).....	4	8	14	22	30	40	60	80	100
CO ₂ (%)	22.4	27.6	34.2	38.6	41.7	46.5	53.1	56.9	62.2

(*o*-Ethoxyphenyl)diphenylmethyl Chloride.—(a) A solution of the alcohol (2 g.) in benzene (10 ml.) containing anhydrous calcium chloride was saturated with hydrogen chloride and kept for 12 hr. in a stoppered flask. The solution was siphoned off and concentrated to half-bulk. The deposited (*o*-ethoxyphenyl)diphenylmethyl chloride was filtered off, and recrystallized from light petroleum in a dry atmosphere. The colourless crystals had m. p. 144° (Found: Cl, 11.1. $C_{21}H_{19}OCl$ requires Cl, 10.9%).

(b) A suspension of the alcohol (2 g.) in light petroleum (10 ml.) was treated with acetyl chloride (2 ml.), and boiled for 45 min., then kept overnight, and the deposited (*o*-ethoxyphenyl)diphenylmethyl chloride was recrystallized from the same solvent. It had m. p. 115° (Found: Cl, 10.7%). This procedure gave a more readily purified product than method (a).

The ferric chloride addition compound was prepared by adding an ethereal solution of anhydrous ferric chloride to a solution of (*o*-ethoxyphenyl)diphenylmethyl chloride in 1:1 ether-benzene. It was a greenish-black solid (Found: Cl, 28.7. $C_{21}H_{19}OCl, FeCl_3$ requires Cl, 29.2%). The zinc chloride addition compound was obtained similarly as a black oil which solidified in a desiccator in 3 days (Found: Cl, 24.3. $C_{21}H_{19}OCl, ZnCl_2$ requires Cl, 23.2%). The stannic chloride addition compound was deposited as a reddish-brown oil from benzene (Found: Cl, 31.1. $C_{21}H_{19}OCl, SnCl_4$ requires Cl, 30.4%).

Alkyl (o-Ethoxyphenyl)diphenylmethyl Ethers.—A solution of (*o*-ethoxyphenyl)diphenylmethyl chloride (2 g.) in methanol (25 ml.) was kept at 66° in a dry atmosphere for 10 min. On concentration to half bulk and cooling, (*o*-ethoxyphenyl)diphenylmethyl methyl ether was deposited; recrystallized from ligroin, it had m. p. 121° (Found: C, 82.6; H, 7.0. $C_{22}H_{22}O_2$ requires C, 83.0; H, 7.0%). The chloride and ethanol gave similarly (*o*-ethoxyphenyl)diphenylmethyl ethyl ether, m. p. 124° (from ligroin) (Found: C, 83.05; H, 7.0. $C_{23}H_{24}O_2$ requires C, 83.1; H, 7.3%).

(*o*-Ethoxyphenyl)diphenylmethyl Phenyl Ether.—Metallic potassium (0.4 g.) was dissolved in molten phenol (7.5 g.). To the cold mass a solution of (*o*-ethoxyphenyl)diphenylmethyl chloride (1.2 g.) in ether (25 ml.) was added, and the mixture was heated on the water-bath for 30 min. The cooled mixture was extracted with ether, and the combined extracts were washed repeatedly with sodium hydroxide solution. The ethereal solution was heated to remove the solvent, and the residual (*o*-ethoxyphenyl)diphenylmethyl phenyl ether was converted into a white powder by trituration with light petroleum. After recrystallization from 1:1 ether-light petroleum, it had m. p. 110° (Found: C, 84.5; H, 5.7. $C_{27}H_{24}O_2$ requires C, 85.2; H, 6.4%).

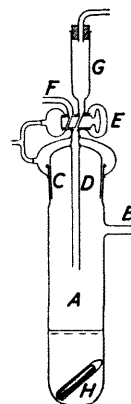
The Free Radical, (o-Ethoxyphenyl)diphenylmethyl.—Absorption of oxygen by a bromobenzene solution (10 ml.) of (*o*-ethoxyphenyl)diphenylmethyl chloride (0.462 g.) when agitated with molecular silver (6.4 g.) at 17° was slower than for triphenylmethyl chloride.

A 2% benzene solution of (*o*-ethoxyphenyl)diphenylmethyl undergoes no appreciable change in colour (Lovibond tintometer) in a sealed tube for 3 days in the dark. After longer periods, the colour is discharged; the radical is more prone than triphenylmethyl to undergo disproportionation and/or isomerization. The rapid absorption characteristic of the oxidation of the radical corresponds to 0.95 mol. of oxygen, and is practically the same as that recorded for

triphenylmethyls containing methoxyl substituents. Solutions of (*o*-ethoxyphenyl)diphenylmethyl are rapidly decolorized in sunlight owing to photochemical decomposition.

The ethane was isolated in an apparatus (Figure), which has several advantages over the Gomberg isolation unit.¹¹ It consists of a boiling tube *A* (13 cm. long; 2.9 cm. diam.) with a side-tube *B* and a glass stopper *C* through which passes a tube *D* sealed to a 3-way stopcock *E* in communication with a gas inlet tube *F* and a funnel *G* (6 cm. long; 1.8 cm. diam.). The vessel contains a sealed tube *H* charged with mercury and roughened on the outside to serve as "internal scratcher" for inducing crystallization. To prevent intrusion of atmospheric oxygen into the apparatus during the concentration and drying, the ground-glass joint and the stopcock are surrounded with small balloons which are kept inflated with carbon dioxide from an auxiliary generator.

A 10% solution of the radical in benzene was prepared in a Schlenk tube in the dark, and introduced under pressure of carbon dioxide into the isolation unit through the funnel *G*, which was then fitted with a stopper carrying an inlet tube in communication with the gas circuit. With the stopcock open to *F*, the lower part of the isolation unit was immersed in water at 40°, and the benzene was distilled through the side-tube under reduced pressure in a stream of carbon dioxide. On cooling of the concentrated solution, the ethane was deposited as a brown oil. Light petroleum (5 ml.) was introduced from the funnel *G*, and the oil was triturated with the solvent by oscillating the scratcher *H*. The petroleum was decanted through the side-tube *B* into a trap, and the trituration was repeated with further quantities of light petroleum until the oil was converted into a yellowish-brown powder. The ethane was deposited as yellow crystals on cooling of its solution in acetone, and was dried under reduced pressure in a stream of carbon dioxide. In an evacuated tube it had m. p. 144° (decomp.); it dissolved readily in liquid sulphur dioxide to form a red solution.



Dissociation of Di-(o-ethoxyphenyl)tetraphenylethane.—The degree of dissociation of the ethane in benzene was determined by the indirect cryoscopic method¹⁰ with the annexed results. Each set of determinations was completed within 3 hr., during which disproportionation was negligible.

M of radical = 287.36. M of the ethane = 574.7.

Benzene, $K = 52.5^\circ$.

Solvent (g.)	Chloride (g.)	Radical (g.)	Δ	M	Dissocn. of ethane (%)
21.98	0.4802	0.4275	0.220°	464.1	23.8
	0.6148	0.5474	0.272	480.7	19.6
17.58	0.2850	0.2337	0.157	482.6	19.1
	0.4014	0.3573	0.225	474.3	21.1
21.98	0.3682	0.3277	0.162	483.7	18.9
	0.5264	0.4686	0.236	474.3	21.1

After completion of the measurements the reddish-yellow solution was decanted from silver and silver chloride and allowed to evaporate in the air. (*o*-Ethoxyphenyl)diphenylmethyl peroxide was deposited, and after rapid recrystallization from benzene had m. p. 143—144° (Found: C, 82.9; H, 6.7. $C_{42}H_{38}O_4$ requires C, 83.1; H, 6.3%).

Absorption of Iodine by the Radical.—A solution of the chloride (0.4234 g.) in benzene (8 ml.) was reduced with molecular silver in a sealed tube with a thin-walled bulb at the bottom. The tube was broken under carbon dioxide in a sintered-glass filter-tube so that the solution passed into a flask where it was titrated with 0.1*N*-iodine in benzene. The weight of halogen absorbed at 15° was 0.1664 g., which is 60.3% of the amount required for complete conversion of the radical into (*o*-ethoxyphenyl)diphenylmethyl iodide.

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¹¹ Part II, *J.*, 1939, 39.