69. *Free Radicals and Radical Stability. Part IV. Diphenyl-3-acenaphthylmethyl.*

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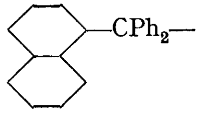
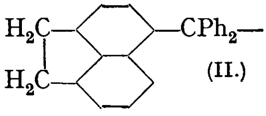
The free radical diphenyl-3-acenaphthylmethyl has been prepared and isolated in the solid state; it is bluish-red in benzene and bluish-green in nitrobenzene. No direct comparison of the radical stability in benzene could be made with that of diphenyl-α-naphthylmethyl, owing to doubt as to the accuracy of Schlenk and Renning's results. In nitrobenzene, however, the stability of the two radicals is approximately the same, and the influence of the $-CH_2\cdot CH_2-$ group on the electromeric effects responsible for stabilisation of the radical appears to be too slight for measurement by the molecular-weight method. Oxidation of the free radical leads to the partial discharge of the colour and the formation of a normal peroxide.

Although the two radicals differ little in stability, diphenyl-3-acenaphthylcarbinol is more basic than diphenyl-α-naphthylcarbinol and its halochromic salts are more deeply coloured. When diphenyl-α-naphthylmethyl formate is heated at 99°, there is evolution of carbon dioxide and formation of the corresponding methane, but no carbon dioxide is evolved on similar treatment of the 3-acenaphthyl analogue.

With a view to ascertain the influence of the $-CH_2\cdot CH_2-$ grouping when substituted in the naphthyl ring of diphenyl-α-naphthylmethyl (I), we have prepared the radical diphenyl-3-acenaphthylmethyl (II). This may be isolated as a pale yellow, microcrystalline solid from acetone solution and gives a deep red solution in benzene, but a deep green in liquid sulphur dioxide. The radical exhibits the characteristic reactivity of triarylmethyls and combines rapidly with oxygen to form a peroxide. Cryoscopic determinations of the molecular weight in benzene indicate that it exists in the unimolecular condition to the extent of 70%, and roughly the same order of stability is found in nitrobenzene.


(I.)


(II.)

The radical stability of diphenyl-α-naphthylmethyl in benzene was first examined by Schlenk and Renning (*Annalen*, 1912, **394**, 194), who stated that they worked with 2·4 and 2·8% solutions. Subsequently, in a series of careful cryoscopic experiments, Gomberg and Schoepfle (*J. Amer. Chem. Soc.*, 1919, **41**, 1655) could not reproduce these results, and found the solubility to be less than 2% in freezing benzene. If Schlenk and Renning's material was of the same purity as Gomberg and Schoepfle's, it follows that the observed value of the molecular weight is too high owing to the separation of solute during the freezing of the solution, and therefore that the recorded value of the radical stability in benzene is too low. This difficulty was not encountered in our experiments with diphenyl-3-acenaphthylmethyl, and as the radicals are more soluble in nitrobenzene there is no possibility of solute separation at the dilutions employed. Our results with diphenyl-3-acenaphthylmethyl show that this radical has roughly the same stability as diphenyl-α-naphthylmethyl. The effect of the $-CH_2{\cdot}CH_2-$ group to be anticipated on the basis of Burton and Ingold's theory of radical stability (*Proc. Leeds Phil. Soc.*, 1929, **1**, 421; *Trans. Faraday Soc.*, 1934, **30**, 52) is too small for precise measurement by the cryoscopic method.

The basicity of *diphenyl-3-acenaphthylcarbinol*, however, is appreciably higher than that of the α-naphthyl analogue, and the halochromic salts are bluish-green and green, respectively. The two carbinols yield highly coloured formates on treatment with anhydrous formic acid. The thermal decomposition of diphenyl-α-naphthylmethyl formate proceeds slowly at 99° with formation of the corresponding methane and evolution of carbon dioxide. Diphenyl-3-acenaphthylmethyl formate, however, does not evolve carbon dioxide under these conditions.

EXPERIMENTAL.

3-Bromoacenaphthene.—This was prepared by a slight modification of the method of Graebe and Guinsbourg (*Annalen*, 1903, **327**, 85). A boiling solution of acenaphthene (200 g.) in chloroform (700 c.c.) was treated dropwise (2 hours) with bromine (200 g.) dissolved in chloroform (200 c.c.), and boiling continued until evolution of hydrogen bromide had ceased. After distillation of the solvent, the residual 3-bromoacenaphthene was obtained as a light yellow oil, b. p. 198—220°/29 mm. It was further purified by dissolution in warm alcohol, the coloured impurities being reduced by means of a small amount of zinc dust and hydrochloric acid. After recrystallisation from alcohol, it melted at 52°.

Phenyl 3-Acenaphthyl Ketone.—For the preparation of this compound (Graebe and Haas, *Annalen*, 1903, **327**, 96) the following procedure gave the purest product. Acenaphthene (100 g.), freshly distilled benzoyl chloride (140 g.), and pure carbon disulphide (750 c.c.) were treated with small quantities of aluminium chloride (100 g.) during 90 minutes, and the mixture boiled for 3 hours. The mixture was decomposed by trituration under ice and hydrochloric acid, the carbon disulphide removed by distillation, and steam passed through the residue. The ketone was washed with water, and a solution in chloroform dried over calcium chloride. After removal of the solvent, the ketone was distilled under ordinary pressure (excessive frothing occurred under reduced pressure). The product, b. p. 360—390°, was a light red oil which crystallised as a pale yellow solid from glacial acetic acid and melted at 85° after recrystallisation from alcohol.

Diphenyl-3-acenaphthylcarbinol.—(*a*) To a filtered solution of phenylmagnesium bromide (from bromobenzene, 22·5 g.; magnesium, 4·0 g.; ether, 40 c.c.), a fine suspension of phenyl 3-acenaphthyl ketone (30 g.) in ether was added, the mixture being vigorously shaken after each addition. The solution became green, and the product was deposited as a gummy solid. After 3 hours' heating, the mixture was decomposed with ice and sulphuric acid, and the precipitated *carbinol* removed by filtration, more being recovered from the ethereal layer. Twice recrystallised from benzene, it melted at 196° (Found: C, 88·7; H, 6·1. $C_{25}H_{20}O$ requires C, 89·1; H, 6·0%).

(*b*) To magnesium powder (1·8 g.), strongly activated *in situ* by Baeyer's method, freshly distilled 3-bromoacenaphthene (20 g.) was added, and ether (60 c.c.) distilled directly into the apparatus through a long column of freshly-drawn sodium wire. After the mixture had been boiled for ½ hour, the characteristic brown colour of 3-acenaphthylmagnesium bromide was developed. The solution was heated until there was no further separation of the slightly soluble magnesium derivative (10 hours). To the cold mixture, an ethereal solution of benzophenone (20 g.) was added during ¾ hour, and the whole was heated for 3 hours. The reaction mixture was hydrolysed in the usual manner, and the carbinol isolated by adding light petroleum to the concentrated ethereal solution. The yield was lower than that obtained by method (*a*) and the product was not so readily purified.

Diphenyl-3-acenaphthylcarbinol produces green halochromic salts with several strong acids. With concentrated sulphuric acid it forms an intense bluish-green solution from which the carbinol is precipitated on dilution with water. Similar, highly coloured solutions are given by formic, perchloric, and phosphoric acids. An approximate measure of the basicity of the carbinol was obtained by Baeyer's method (*Ber.*, 1902, **35**, 1189). The carbinol, however, is not very soluble in glacial acetic acid, and on warming, a purplish-brown solution was obtained. The colour changed to an intense bluish-green on addition of 10% sulphuric acid. Hydrolysis of the solution was effected by adding aqueous alcohol until the green colour was discharged.

The same procedure was applied to diphenyl-α-naphthylcarbinol, and the ratio of the basicity values was 1·3 : 1.

Diphenyl-3-*acenaphthylmethane*.—The carbinol was reduced by heating with zinc dust and acetic acid for 6 hours, the practically colourless solution was then poured into a large volume of water, and the precipitated greyish-white *hydrocarbon* was recrystallised from alcohol (charcoal); m. p. 167° (Found: C, 93·0; H, 6·5. $C_{25}H_{20}$ requires C, 93·75; H, 6·25%).

Action of Heat on the Formate.—The thermal stability of diphenyl-3-acenaphthylmethyl formate was compared with that of the diphenyl-α-naphthylmethyl ester by heating the carbinols with anhydrous formic acid at 99°. The latter ester is formed as a dark green solution by dissolving the carbinol in formic acid; it decomposed slowly with evolution of carbon dioxide and the colour was partly discharged during the heating. After an hour, about 20% of the theoretical amount of carbon dioxide had been evolved, and diphenyl-α-naphthylmethane separated from the cold solution. After recrystallisation from alcohol, this had m. p. 148—149°. Ullmann and Mourawiew-Winigradoff (*Ber.*, 1905, **38**, 2213) give m. p. 150° for the methane obtained, in much higher yield, by reduction of the carbinol with zinc and acetic acid.

The bluish-green solution of diphenyl-3-acenaphthylmethyl formate in formic acid was maintained at 99° for ¾ hour, but no measurable amount of carbon dioxide was evolved. The carbinol (1 g.) was therefore covered with anhydrous formic acid (10 c.c.) in a small flask provided with a ground-in condenser in direct communication with a liquid trap and a vessel charged with lime-water, and the mixture boiled vigorously while nitrogen was passed through the apparatus, but the test for carbon dioxide was negative. Although the colour of the solution slowly changed to light brown, the methane could not be isolated from the solution.

Diphenyl-3-*acenaphthylmethyl Chloride*.—The following methods were examined in connexion with the preparation of this compound:

(*a*) The carbinol (2 g.) was treated in dry benzene (2 c.c.) with slight excess of acetyl chloride in the halogenation apparatus previously described (Part II; this vol., p. 36). The green solution was heated for ½ hour at 40°, cooled, and light petroleum added. The *chloride* was slowly deposited, and by recrystallisation from benzene–light petroleum was obtained in practically colourless crystals, m. p. 141° (Found: Cl, 10·0. $C_{25}H_{19}Cl$ requires Cl, 10·0%). This is the most satisfactory method of preparing the substance for use in the preparation of the free radical.

(*b*) The carbinol (5 g.) was dissolved in benzene (50 c.c.) in a stout flask and treated with dry hydrogen chloride in the presence of a few lumps of anhydrous calcium chloride. The solution soon became deep blue-green in colour, and after saturation was complete, the flask was tightly stoppered and set aside for 12 hours. The solution was decanted from the hydrated calcium chloride, warmed with decolorising carbon, filtered, and concentrated to one-third bulk. The cold solution was treated to incipient turbidity with light petroleum; well-formed crystals of diphenyl-3-acenaphthylmethyl chloride were slowly deposited, and after recrystallisation as in (*a*) these were obtained colourless, m. p. 141° (Found: Cl, 10·1%).

(*c*) The chloride prepared by condensation of acenaphthene and diphenyldichloromethane in dry carbon disulphide solution by means of anhydrous aluminium chloride remained highly coloured after repeated crystallisation as in (*a*).

The chloride has the characteristic properties of triarylmethyl chlorides and forms halochromic derivatives with ferric, mercuric, and zinc halides.

Diphenyl-3-*acenaphthylmethyl Bromide*.—The carbinol (1 g.) in dry benzene (2 c.c.) was treated with acetyl bromide (2 c.c.), and the solution warmed and concentrated as for the chloride. The *bromide* was deposited in greenish-blue crystals, from which most of the colour was removed by repeated crystallisation as in (*a*), above; m. p. 135° (Found: Br, 20·0. $C_{25}H_{19}Br$ requires Br, 20·0%). Solutions of the bromide in non-polar media were rapidly reduced by silver with the formation of the free radical.

Diphenyl-3-*acenaphthylmethyl Peroxide*.—The chloride was dissolved in a mixture of equal parts of dry benzene and ether, and the solution reduced by shaking with an excess of molecular silver in a sealed tube for 3 hours. The finely divided silver chloride was allowed to settle, and the blue-red solution of the radical siphoned into another vessel, where it was oxidised by the passage of air. The blue-red colour was rapidly discharged, but the solution still preserved a pale yellow colour after completion of the peroxide reaction. The solvent was rapidly evaporated, and the thick, oily residue washed and repeatedly triturated with light petroleum until it was converted into a yellow powder. The *peroxide* was fairly readily soluble in cold ether, benzene, and acetone, but could not be readily crystallised from these solvents. It was recrystallised from carbon disulphide, but could not be obtained completely free from colour. It melted at 167° (Found : C, 89·0; H, 5·8. $C_{50}H_{38}O_2$ requires C, 89·6; H, 5·7%).

*Radical Stability of Diphenyl-*3*-acenaphthylmethyl.*—The molecular weight of the radical was determined by the indirect, cryoscopic method under pure nitrogen in the apparatus previously described (Part II; *loc. cit.*). Before use, the chloride was freshly recrystallised, finely powdered, and stored for at least 24 hours in an evacuated desiccator containing soda-lime and shavings of paraffin-wax. The reduction of the chloride is rapidly effected by six times the calculated weight of molecular silver, but with the more concentrated solutions it was advisable to add a further supply of silver from a suitable precipitating device held in the side-tube of the Beckmann vessel. The results obtained with benzene and nitrobenzene solutions of the radical are given in the following table.

*Stability of Diphenyl-*3*-acenaphthylmethyl.*

Molecular weight of tetraphenyldi-3-acenaphthylethane = 638.
Molecular weight of diphenyl-3-acenaphthylmethyl = 319.
Benzene, K = 52·5°; nitrobenzene, K = 71·2°.

In benzene.

Solvent, g.	Chloride, g.	Radical concn., %.	Δ.	*M.*	Radical stability, %.	Solvent, g.	Chloride, g.	Radical concn., %.	Δ.	*M.*	Radical stability, %.
18·98	0·1665	0·8	0·112°	370	72·5	19·01	0·2689	1·3	0·178°	376	70·0
	0·2822	1·3	0·185	380	68·2		0·5035	2·4	0·327	383	66·9
	0·5703	2·7	0·373	381	67·8		0·7186	3·4	0·472	378	68·7
	0·7827	3·7	0·522	373	71·1	18·87	0·3848	1·8	0·256	376	69·7
							0·6027	2·9	0·403	374	70·5
In nitrobenzene.											
22·97	0·3819	1·5	0·299	355	79·7	22·50	0·4459	1·8	0·351	361	77·0
	0·6705	2·6	0·509	366	74·3		0·7713	3·1	0·587	373	71·1

Very striking colour effects were observed during the formation of the free radical in nitrobenzene. Immediately after the addition of the chloride to the liquid, the solution was pale green, but on being stirred with silver the solution became blue owing to the formation of the radical. When reduction was complete, the solution was deep bluish-green.

Isolation of the Free Radical.—Pure diphenyl-3-acenaphthylmethyl chloride (3 g.) was dissolved in sodium-dried benzene (40 c.c.), and the solution shaken with molecular silver (3 g.) in a sealed tube on a rotary agitator for 3—4 hours. The radical solution was transferred under carbon dioxide into the concentrating apparatus as described previously (Part II; *loc. cit.*). After evaporation of the solvent at 45—50° under reduced pressure in a slow stream of carbon dioxide, the residual gummy mass proved to be only slightly soluble in warm ether. It dissolved readily in warm acetone, and the impure hydrocarbon crystallised comparatively rapidly on cooling. Two recrystallisations from the same solvent did not remove all the colour from the solid. The material was dried *in situ* under reduced pressure for 2 hours. The pale yellow crystalline hydrocarbon melted at 155° (vac.) and dissolved in liquid sulphur dioxide to form a very deep blue-green solution.

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