CIV.—*Mobile Anion Tautomerism. Part VI. The Activation of the Three-carbon Anionotropic System by Polynuclear Aryl Groups.*

By Harold Burton.

In Parts II and III (J., 1928, 1650; 1929, 455) it was shown that the activation of the three-carbon anionotropic system

$$\text{(I) Ph·CHX·CH:CHR} \longrightarrow \text{Ph·CH:CH·CHRX (II)}$$

by the phenyl group causes a complete conversion of (I) into (II) in a solvent such as acetic anhydride, when R is a hydrogen atom or a methyl group, and X is the acetoxy- or *p*-nitrobenzoyloxy-group. It has been emphasised that the completeness of the change shows the facile activating power of the aryl group. Since aryl groups are also able to promote activation in prototropic systems [(I) $\rightleftharpoons$ (II) when X = H] (Ingold and Shoppee, J., 1929, 447), it is at once apparent that the aryl group is able to absorb an electric charge of either sign produced on the adjacent carbon atom by the ionisation of an attached atom or group. This property, which is undoubtedly due to the fact that aryl groups contain an available mechanism (tautomeric electron-displacement) for the distribution of an ionic charge of either sign, has been shown by Burton and Ingold (*Proc. Leeds Phil. Soc.*, 1929, **1**, 421) to afford a satisfactory hypothesis for the explanation of the existence and stability of free radicals. One consequence of this hypothesis is that polynuclear aromatic systems should act more powerfully than phenyl in promoting the dissociation of hexa-arylethanes, because the rings of a polynuclear group which are more distant from the ethane carbon atom will act as an additional charge-absorbing mechanism, that is, they will facilitate the distribution of the charge. Reference to the literature shows that naphthyl groups do promote the dissociation of hexa-arylethanes to a greater extent than phenyl; the actual order is α-naphthyl > β-naphthyl > phenyl.

The investigation now described was undertaken to see if the simple three-carbon anionotropic * system is activated to a greater extent by a polynuclear aryl group than by the phenyl group, as would be expected from the above consideration. Experimental difficulties have limited the cases studied to two, namely, the α- and β-*naphthylvinylcarbinols*, which were prepared, not in a state of absolute purity, from acraldehyde and the requisite magnesium naphthyl bromide. Acetylation of these alcohols with boiling acetic anhydride gives, as expected, the acetates of the isomeric γ-1- and γ-2-*naphthylallyl alcohols.* The results obtained from a study of the *p*-nitrobenzoylation of the naphthylvinylcarbinols in pyridine solution show definitely that the α- and the β-naphthyl group have a greater activating power than the phenyl group.

All the α-arylallyl alcohols (arylvinylcarbinols) examined previously (Parts I and II) have given, by *p*-nitrobenzoylation in pyridine, the corresponding *p*-nitrobenzoates. This can be ascribed to the relatively low temperature (water-bath) at which the reaction is carried out and also to the relatively low dielectric constant of pyridine. It has been shown (Part II) that the ease of rearrangement of an α-arylallyl *p*-nitrobenzoate into the γ-arylallyl *p*-nitrobenzoate depends on the temperature, the medium in which the reaction is carried out, and the time of heating. Treatment of α-naphthylvinylcarbinol with *p*-nitrobenzoyl chloride in pyridine during a short period at the water-bath temperature gives a small amount of the corresponding *p*-nitrobenzoate, but when the time of reaction is increased, this ester is no longer isolated; a small amount of the isomeric γ-1-*naphthylallyl* p-*nitrobenzoate* can, however, be isolated from the reaction mixture. The β-naphthylvinylcarbinol is undoubtedly similar in its behaviour, but, in this case, it was not possible to show the intermediate formation of the naphthylvinylcarbinyl *p*-nitrobenzoate (slow rate of reaction), but γ-2-*naphthylallyl* p-*nitrobenzoate* was isolated from reaction mixtures which had been heated for a relatively long time. Repeated preparation of α-phenylallyl *p*-nitrobenzoate under the same experimental conditions as those used in the formation of the γ-naphthylallyl ester has never given any cinnamyl *p*-nitrobenzoate. Furthermore, cinnamyl *p*-nitrobenzoate cannot be isolated, even in small amount, when a solution of α-phenylallyl *p*-nitrobenzoate in pyridine is heated on the water-bath for 24 hours, whereas, under the same

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* Analogous experiments in the case of prototropic systems are being undertaken by Dr. C. W. Shoppee.

conditions, α-naphthylvinylcarbinyl *p*-nitrobenzoate is readily converted into its isomeride.

EXPERIMENTAL.

α-Naphthylvinylcarbinol (*α-1-Naphthylallyl Alcohol*), $C_{10}H_7\cdot CH(OH)\cdot CH\colon CH_2$.—The Grignard reagent, prepared by the method of Gilman and McCracken (*J. Amer. Chem. Soc.*, 1923, **45**, 2463) from magnesium (12 g.), α-bromonaphthalene (104 g.), ether (200 c.c.), and a trace of iodine, was cooled below 0°, and a solution of acraldehyde (33 c.c.) in ether (100 c.c.) added during 2 hours. The mixture was stirred for a further 4 hours and then decomposed with ice and saturated ammonium chloride solution. Distillation of the residue from the dried ethereal extract gave naphthalene, and then 49 g. of a viscous oil, b. p. 184—188°/19 mm. Further distillation gave the nearly pure *alcohol*, b. p. 186—187°/19 mm. (Found : C, 83·7; H, 6·4. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%). The impurity is a small amount of bromonaphthalene. The alcohol was characterised further by means of its *phenylurethane*, which crystallised from light petroleum in clusters of fine needles, m. p. 108—109° (Found : C, 79·0; H, 5·8. $C_{20}H_{17}O_2N$ requires C, 79·2; H, 5·6%).

When the alcohol (9·2 g.) was heated with *p*-nitrobenzoyl chloride (10·2 g.) and pyridine (60 c.c.) on the water-bath for 3 hours, and the mixture poured into water, an oil was precipitated. This was separated from the supernatant liquid by decantation, washed with water, and dissolved in warm alcohol. The alcoholic solution was kept at about 0° for 2 days, crystalline material (2·5 g.) separating. Recrystallisation of this from alcohol gave *α-naphthylvinylcarbinyl* p-*nitrobenzoate* in flat prisms, m. p. 79—80° (Found : C, 71·95; H, 4·65. $C_{20}H_{15}O_4N$ requires C, 72·1; H, 4·5%). The ester has a great tendency to separate as an oil from solvents in which it is moderately easily soluble.

When a similar mixture of the alcohol, *p*-nitrobenzoyl chloride, and pyridine was heated on the water-bath for 16 hours, and the resultant dark-coloured solution poured on ice, a semi-solid product was obtained. This was separated, washed with water (decantation), and dissolved in alcohol (charcoal). The alcoholic solution, when kept at about 0°, gradually deposited crystals of γ-1-naphthylallyl *p*-nitrobenzoate (see below), m. p. 138—139° after crystallisation from acetic acid.

γ-1-Naphthylallyl Alcohol, $C_{10}H_7\cdot CH\colon CH\cdot CH_2\cdot OH$.—A mixture of α-naphthylvinylcarbinol (15 g.) and acetic anhydride (20 c.c.) was boiled for 6 hours and then fractionated. The γ-1-naphthylallyl acetate, b. p. 210—211°/9 mm., obtained was hydrolysed with an excess of 5% alcoholic potassium hydroxide solution, giving γ-1-*naphthylallyl alcohol*, b. p. 209—210°/18 mm., which gradually solidified to a crystalline mass, m. p. 39—40° (Found: C, 84·0; H, 6·5. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%). The alcohol could not be recrystallised satisfactorily owing to its great tendency to separate as an oil from various solvents. The *phenylurethane* crystallised from benzene–light petroleum in needles, m. p. 120° (Found: C, 79·3; H, 5·6. $C_{20}H_{17}O_2N$ requires C, 79·2; H, 5·6%).

The alcohol was readily *p*-nitrobenzoylated in pyridine; γ-1-*naphthylallyl* p-*nitrobenzoate* crystallised from acetic acid in needles, m. p. 138—139° (Found: C, 71·7; H, 4·5. $C_{20}H_{15}O_4N$ requires C, 72·1; H, 4·5%). The ester is also obtained when a solution of α-naphthylvinylcarbinyl *p*-nitrobenzoate in acetic anhydride is boiled for 6 hours, the solution poured into water, and the precipitated solid crystallised from acetic acid.

β-*Naphthylvinylcarbinol* (α-2-*Naphthylallyl Alcohol*), $C_{10}H_7\cdot CH(OH)\cdot CH{:}CH_2$.—The Grignard reagent from magnesium (12 g.), β-bromonaphthalene (100 g.), ether (400 c.c.), and a trace of iodine was treated with acraldehyde (33 c.c.) in ether (200 c.c.) in a similar manner to its isomeride. The *alcohol* was obtained as a viscous oil, b. p. 195—198°/21 mm., contaminated with a little bromonaphthalene (Found: C, 84·0; H, 6·5. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%). The yield was 25% of the theoretical. The *phenylurethane* separated from benzene–light petroleum in colourless prisms, m. p. 134—135° (Found: C, 79·1; H, 5·7. $C_{20}H_{17}O_2N$ requires C, 79·2; H, 5·6%).

No solid derivative was obtained when the alcohol was heated with *p*-nitrobenzoyl chloride (1·1 mols.) in pyridine solution for 3 hours. When the mixture was heated for 16 hours and then worked up as described for the analogous α-derivative, a small amount of γ-2-naphthylallyl *p*-nitrobenzoate (see below) (Found: C, 72·1; H, 4·5%) was obtained. This melted at 148° after two crystallisations from alcohol.

γ-2-*Naphthylallyl Alcohol*, $C_{10}H_7\cdot CH{:}CH\cdot CH_2\cdot OH$.—A mixture of β-naphthylvinylcarbinol (10 g.) and acetic anhydride (15 c.c.) was boiled for 6 hours, and the solution poured into water. The solid acetate (yield, almost quantitative) was hydrolysed, without further purification, with an excess of 10% alcoholic potassium hydroxide. Dilution of the alkaline mixture with water precipitated the *alcohol*, which crystallised from benzene in needles, m. p. 116° after slight previous sintering (Found: C, 84·6; H, 6·6. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%).

p-Nitrobenzoylation was accomplished readily by the pyridine method. The p-*nitrobenzoate* crystallised from alcohol, in which it was only sparingly soluble, in thin plates, m. p. 148°. It is identical (mixed m. p.) with that formed from β-naphthylvinylcarbinol (Found: C, 72·0; H, 4·6. $C_{20}H_{15}O_4N$ requires C, 72·1; H, 4·5%).

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