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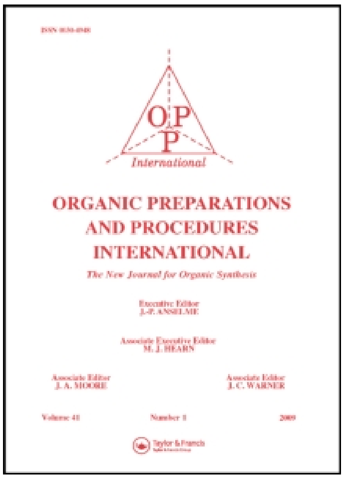

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SYNTHESES WITH BENZENEDIAZONIUM SALTS. DIPHENYLOCTADIENES AND TETRAPHENYLBUTANES

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Aryl radicals obtained easily from the decomposition of arenediazonium salts by reducing metal salts[1a,b], add to conjugated olefins; the resulting radical usually is oxidized by the metal in its higher valence state, as in the Meerwein arylation of olefins[2] in which Cu^+ is used.

When the reducing metal is Ti^{3+}, the aryl radicals are also obtained, as shown recently in a spectroscopic study[3] although their e.s.r. spectra were not recorded. However, in their addition to butadiene and styrene the resulting benzylic and allylic radicals gave rise instead to dimerization products, owing to the lesser oxidizing power of Ti^{4+}. The dimerization is also favoured by the presence of ferrous salts.[4]

With benzenediazonium salt and 1,3-butadiene the reaction product (74% yield) is a mixture of all four possible isomers, a clear indication of the radical character of the reaction : 1,8-diphenylocta-2,6-diene, corresponding to dimerization of two 1,4-addition moieties (47%); 1,6-diphenyl-5-vinyl-hex-2-ene(1,2 and 1,4 addition; 44%) and 1,4-diphenyl-2,3-divinylbutane (two diastereomers; 1,2 and 1,2 dimerization; 9%).

$$PhN_2^+ + Ti^{3+} \longrightarrow Ph\cdot + N_2 + Ti^{4+}$$

$$Ph\cdot + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow (Ph{-}C_4H_6{-})_2$$

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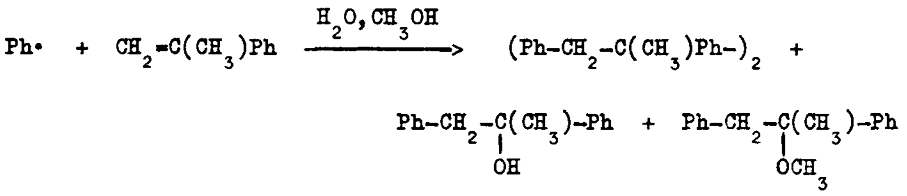
$$(Ph\text{-}C_4H_6\text{-})_2 = \begin{cases} (Ph\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-})_2 & \text{(I)} \quad 47\% \\ Ph\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH(CH{=}CH_2)CH_2Ph & \text{(II)} \quad 44\% \\ (Ph\text{-}CH_2\text{-}CH(CH{=}CH_2)\text{-})_2 & \text{(III)} \quad 9\% \end{cases}$$

With styrene 1,2,3,4-tetraphenylbutane is obtained, a mixture of about equal quantities of the meso and d,l forms, as expected[5] from dimerization of two benzylphenylcarbinyl radicals :

$$Ph\bullet \; + \; CH_2{=}CH\text{-}Ph \longrightarrow (Ph\text{-}CH_2\text{-}CHPh\text{-})_2$$

With α-methylstyrene the reaction leads to the corresponding dimerization product (always in about equal amount of the meso and d,l forms) but the yield is decreased (23.6%) by the presence of products arising from oxidation of the first formed adduct radical and subsequent reaction with the medium :



$$Ph\bullet \; + \; CH_2{=}C(CH_3)Ph \xrightarrow{H_2O,\,CH_3OH} (Ph\text{-}CH_2\text{-}C(CH_3)Ph\text{-})_2 \; + \; Ph\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)\text{-}Ph \; + \; Ph\text{-}CH_2\text{-}\underset{\displaystyle OCH_3}{\underset{|}{C}}(CH_3)\text{-}Ph$$

In this case the product which is less soluble and of higher m.p. is assumed to be the meso form on the analogy of the corresponding tetraphenylbutanes.[5]

Although the yields are not high, the synthetic value of these reactions lies in the fact that readily available starting materials are used and experimental conditions are very simple.

EXPERIMENTAL

Diphenyloctadienes. A solution of benzenediazonium salt was prepared in the usual way from aniline (9.3 g; 0.1 mole) dissolved in H_2O (70 ml) and conc H_2SO_4 (11.5 ml) by the addition of $NaNO_2$ (8 g; 0.116 mole) dissolved in H_2O (15 ml). This solution was added with stirring and

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under nitrogen atmosphere, to a mixture of 1,3-butadiene (25 ml; ~0.3 mole), $FeSO_4 \cdot 7H_2O$ (10 g; ~0.036 mole) in MeOH (200 ml) and aqueous solution of $Ti_2(SO_4)_3$ (15% w/v technical solution; the British Drug Houses ltd.; 130 ml; 0.05 mole); the temperature was maintained between -15 and -5°. At the end of the addition, the violet colour of the solution had turned to faint orange. Stirring was continued while the solution was allowed to reach room temperature. Then it was diluted with H_2O (1 liter) and extracted with three 100 ml portions of ethyl ether. The solvent was removed and the residue (11.5 g) distilled and the fraction boiling at 190-200°/3 mm collected to give 9.7 g (74% based on aniline).

Anal. Calcd. for $C_{20}H_{22}$: C,91.55; H,8.45. Found : C,91.37; H,8.53.

Gaschromatographic analysis (Fractovap GV C.Erba; flame detector; 2 mt x 4 mm i.d. glass column packed with SE 30 1% on Chromosorb P; temp : 168°; He at 40 ml/min flow rate) of the distillate revealed the presence of 4 products, in the order : 3.68, 5.4, 43.65 and 47.25 respectively.

By preparative gas-chromatography (Aerograph Autoprep 705; 2 mt x 4 mm i.d. glass column packed with SE 20% on Chromosorb P; temp : 150°; He at 100 ml/min flow rate) three fractions were separated : the first two peaks together (A) and the others individually (B and C).

The mass spectra of all the samples A, B and C (Hitachi-Perkin Elmer RMU 6D) showed the peak at m/e 262 (M^+) and significant fragments at m/e 171 $\left[M - (CH_2-C_6H_5)\right]$, 131 (M/2), 115 ($C_6H_5-CH_2-CH_2$), 91 (tropilium ion) and 77 (C_6H_5).

IR : bands at 700 and 745 cm^{-1} (monosubstituted phenyl) for A,B and C and, furthermore, for A bands at 915 and 995 cm^{-1} ($-CH=CH_2$), for C at 970 cm^{-1} (trans -CH=CH-) and for B at 915,970 and 995 cm^{-1} :therefore structure III (two diastereomers) was attributed to A, the structure II to B and the structure I to C.

This assignment was confirmed by the NMR spectra.NMR (CCl_4) : for fraction A, signals centered at 2.15-2.70 δ (m, 6 H, $Ph-\underline{CH_2}-\underline{CH}(CH=CH_2)_2$);

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4.60–5.00 δ (m,4 H, $\underline{CH_2}$=CH–), 5.30–5.80 δ (m,2 H, CH_2=$\underline{CH}$–), 6.80–7.30 (m, 10 H, aromatics); for fraction B, 2.15–2.70 δ (m,3 H, Ph-$\underline{CH_2}$-$\overset{|}{\underline{CH}}$-CH=$CH_2$), 3.25 δ (d,2 H, Ph-$\underline{CH_2}$-CH=CH–), 4.60–5.00 δ (m,2 H, $\underline{CH_2}$=CH–), 5.20–5.70 δ (m,3 H, CH_2=$\underline{CH}$–), 6.80–7.30 δ (m,10 H, aromatics); for fraction C, 1.90–2.20 δ (m,4 H, -CH=CH-$\underline{CH_2}$–), 3.25 δ (d,4 H, Ph-$\underline{CH_2}$-CH=CH–), 5.20–5.70 δ (m,4 H, -CH=CH–), 6.80–7.30 δ (m,10 H, aromatics).

Tetraphenylbutanes. An aqueous solution of benzenediazonium salt, obtained as above from 0.1 mole of aniline, and an aqueous solution of $Ti_2(SO_4)_3$(15% w/v technical solution British Drug Houses; 130 ml; 0.05 mole) were added dropwise, simultaneously, into a stirred solution of styrene (30 ml; 0.26 mole) in MeOH (300 ml) under a nitrogen atmosphere; the temperature was maintained at 0–5°. The reaction mixture was diluted with water (500 ml) and extracted with ether : the ethereal extract was washed with 10% NaOH, then with 10% H_2SO_4, finally with water and dried over Na_2SO_4. The solvent was removed and the residue distilled. After the excess styrene was removed, the fraction boiling at 180–220°/2 mm (9.7 g, 54% based on aniline) was collected. There remained a tarry residue (5.5 g). The distilled product, a semisolid at room temperature, was a mixture of practically equal quantities of *meso* and *d,l* isomers of 1,2,3,4-tetraphenylbutane, as shown by spectral analysis (IR, NMR and mass) and by comparison with authentic samples.[5] From this mixture, the *meso* form was easily isolated by three washings with petroleum ether : the solid (4.3 g) which remained undissolved was crystallized from MeOH and had m.p. 183–185°, lit.[5] 183–185°.

Tetraphenyldimethylbutanes. The reaction was carried out exactly as described above for styrene, using α-methylstyrene (35 ml). Dilution with water precipitated 2.6 g of a solid, m.p. 160°. The solution was extracted with ether and, after removal of the solvent from the ethereal extract, an additional amount of solid (2 g) separated on cooling. The liquid residue was distilled and, after α-methylstyrene, a fraction

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boiling at 130-140°/2 mm was collected. It was shown (chromatography on SiO_2, hexane : ethyl acetate = 9 : 1) to consist of 10% of an unidentified product and about equal quantities of 1,3-diphenyl-3-methoxy-propane and 1,3-diphenyl-3-oxy-propane.

The combined solid (total of 4.6 g, 23.6% based on the aniline) was shown to be 1,2,3,4-tetraphenyl-2,3-dimethylbutane by elemental analysis, mass and NMR spectra.

Anal. Calcd. for $C_{30}H_{30}$: C, 92.26; H, 7.74. Found : C, 92.15;H,7.90. The mass spectrum did not record the molecular ion, but significant fragments at m/e 195 (M/2), 91 (tropilium ion) and 77 (phenyl).

In an analogous preparation by diluting with less water the solid first separated was in lesser amount but showed higher m.p., 225-28°. The NMR spectrum (Varian A 60; TMS as internal reference; in $CDCl_3$) of this high melting compound showed signals centered at 1.28 δ (s,6 H, CH_3), 2.90 δ (d,2 H, one type of methylenic protons), 3.78 δ (d,2 H, the other type of methylenic protons) and 6.60-7.40 δ (m, 20 H, aromatics); the coupling constant between the two types of methylenic protons was ~13.5 c.p.s.; the compound appeared better than 95% (absence of other signals) and was attributed the meso form on the analogy of the behaviour of the corresponding tetraphenylbutanes (lower solubility and higher m.p.).[5] The NMR spectrum of the whole separated solid showed besides the above mentioned ones, other signals, attributed to the d,l form, centered at 1.20 δ (s,CH_3), 2.98 δ (d,one type of methylenic protons) and 3.45 δ (the other methylenic protons) : from the relative areas of the methyl peaks a ratio of meso : d,l forms = 53 : 47 was calculated.

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