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ARYNE CHEMISTRY—XI[1]

TRAPPING AGENTS FOR ARYNES PRODUCED FROM GRIGNARD- AND ORGANOLITHIUM REAGENTS

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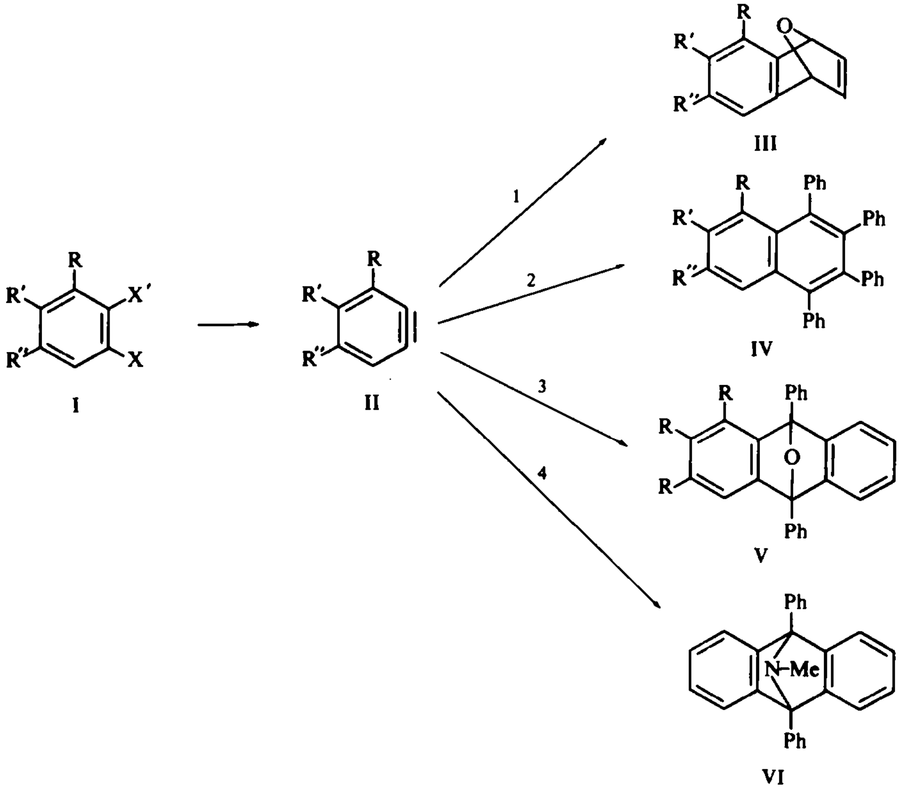
Abstract—A number of arynes, generated from Grignard and organolithium reagents have been trapped with furan and 1,3-diphenylisobenzofuran. Benzyne is efficiently trapped by N-methyl-1,3-diphenylisoindole.

THE synthesis of substituted triphenylenes in reactions involving arynes generated from organolithium and Grignard reagents has been reported.[1,2] The yields of substituted triphenylenes obtained were, however, lower than the yield of triphenylene in for example the reaction of *o*-fluorobromobenzene with magnesium in tetrahydrofuran,[2] or in the reaction of *o*-iodochlorobenzene with lithium.[3] We therefore undertook an assessment of the production of arynes in our reactions by using conventional trapping agents. It was also of interest to assess the merits of various trapping agents.

Furan was the first diene to be used in Diels-Alder type reactions with arynes.[4] Tetraphenylcyclopentadienone has been used extensively in reactions in which arynes are generated, for example, from *o*-iodophenylmercuric iodide,[5] from diphenyliodonium-2-carboxylate,[6] and from 1-aminobenzotriazole.[7] Tetraphenylcyclopentadienone is known to react with aliphatic Grignard reagents,[8] and we have found that n-butyl-lithium reacts very rapidly at −70°. Any attempt to trap arynes, formed from organolithium or Grignard reagents, with tetraphenylcyclopentadienone will therefore depend on the relative rate of elimination of metal halide from the precursor *versus* the rate of the addition of the precursor to the CO group in the trapping agent.

Wittig favours the use of 1,3-diphenylisobenzofuran as a trapping agent for arynes and cycloalkynes,[9] because of the resonance stabilization on converting the *o*-quinonoid structure in the trapping agent to a benzenoid system after reaction. 1,3-Diphenylisobenzothiophen, and N-methylisoindole were also reported to act as aryne trapping agents.[9] The recent report of the preparation of 1,3-diphenylisoindoles,[10] prompted our assessment of these compounds. We decided to concentrate on N-methyl-1,3-diphenylisoindole in this connection. Since our studies were completed Lwowski published the full details of his studies including the use of 1,3-diphenylisoindole as a benzyne trapping agent.[11]



Our results with furan (1), 1,3-diphenylisobenzofuran (3), and tetraphenylcyclopentadienone (2) are summarized in Tables 1, 2, and 3, respectively. N-Methyl-1,3-diphenylisoindole (4) was used as a trapping agent for benzyne generated from *o*-fluorophenylmagnesium bromide, *o*-fluorophenyl-lithium, and benzenediazonium-2-carboxylate, in each case 9,10-dihydro-9,10-diphenyl-N-methyl-9,10-endoamino-

TABLE 1. REACTIONS OF ARYNES WITH FURAN

Precursor I	Adduct III	Yield %
1. R = R'' = H; R' = Me; X = I; X' = Cl	R = R'' = H; R' = Me	51·0
2. R' = R'' = H; R = Me; X = I; X' = Cl	R' = R'' = H; R = Me	43·0
3. R' = H; R = R'' = Me; X = F; X' = Br	R' = H; R = R'' = Me	40·0
4. R = H; R' = R'' = Me; X = F; X' = Br	R = H; R' = R'' = Me	40·0
5. R = R'' = H; R' = OMe; X = I; X' = Cl	R = R'' = H; R' = OMe	54·0
6. R = H; R' = R'' = OMe; X = I; X' = Br	R = H; R' = R'' = OMe	56·0
7. R = R'' = H; R' = CF_3; X = I; X' = Cl	R = R'' = H; R' = CF_3	54·0

TABLE 2. REACTIONS OF ARYNES WITH 1,3-DIPHENYLISOBENZOFURAN

Precursor	Adduct V	Yield %
1. *o*-fluorophenylmagnesium bromide	R = R′ = R″ = H	66
2. *o*-fluorophenyl lithium	R = R′ = R″ = H	55
3. 3,5-dimethyl-2-fluorophenyl lithium	R = R″ = Me; R′ = H	48
4. 4,5-dimethyl-2-fluorophenyl lithium	R′ = R″ = Me; R = H	56
5. 4,5-dimethoxy-2-bromophenyl lithium	R′ = R″ = OMe; R = H	25

TABLE 3. REACTIONS OF ARYNES WITH TETRAPHENYLCYCLOPENTADIENONE

Precursor	Adduct IV	Yield
1. R = Me; R′ = R″ = H; X = Cl; X′ = I	R = Me; R′ = R″ = H	7·5
2. R = R″=H; R′ = Me; X = Cl; X′ = I	R′ = Me; R = R″ = H	0·4
3. R = R″ = Me; R′ = H; X = Br; X′ = F	R = R″ = Me; R′ = H	22·0

anthracene was isolated in good yield. The reagent cannot be used, however, in the presence of lead tetraacetate, which oxidizes it at −70° to *o*-dibenzoylbenzene.

Cadogan,[12] has recently pointed out that the production of adducts identical to those obtained with authentic arynes need not necessarily confirm the intermediacy of arynes and this suggests that a wide variety of trapping agents should be employed. Similarly in novel reactions of arynes identity of reaction using arynes generated from different precursors should be sought in order to authenticate the intermediacy of an aryne.

Our results indicate that arynes generated from Grignard and organolithium reagents are in general best trapped with furan or 1,3-diphenylisobenzofuran. It should be noted, however, that the cleavage of furan by organolithium compounds at elevated temperatures,[4b] makes the use of furan impossible with organolithium compounds which are stable at temperatures much above 0°. We have found, for example, that tetrachlorobenzyne, generated from pentachlorophenyl-lithium cannot be trapped with furan while the aryne can be trapped with 1,3-diphenylisobenzofuran.[13]

The structures of the products reported in this paper have been proved by analytical and spectroscopic methods and in certain cases by chemical transformations. The IR spectra of the 1,4-dihydro-1,4-epoxynaphthalenes all contain three strong and characteristic bands whose positions change by no more than 10 cm^{-1}. The band assigned to C—O—C appears in most cases at 1285 cm^{-1}, and in none of the compounds studied higher than 1290 cm^{-1}. A band at 850–860 cm^{-1} which appears in all the spectra may be tentatively ascribed to epoxide ring vibrations.[14] The third characteristic band appears at 700 cm^{-1} in all except one compound and may be assigned to C—H out of plane bending of the vinylic hydrogens. Data for the IR spectra of other compounds are recorded in the Experimental section.

The PMR spectra of the adducts reported show certain interesting features. In particular the spectra of the adducts of certain Me substituted benzynes with tetraphenylcyclopentadienone and with 1,3-diphenylisobenzofuran allows deductions to be made concerning the conformations of these compounds. Thus in the spectrum of 9,10-dihydro-1,3-dimethyl-9,10-diphenyl-9,10-epoxyanthracene the C_1 and C_3 Me resonances occur at τ 8·1 and τ 7·8 respectively. The 2,3-dimethyl isomer shows its Me signal as a sharp singlet at τ 7·9. Similarly, the Me resonance of 5-methyl-1,2,3,4-tetraphenylnaphthalene appears at τ 8·18 whereas the Me resonance of 6-methyl-1,2,3,4-tetraphenylnapthalene appears at τ 7·68. It is of interest to compare these resonance positions with those of the Me protons in 1- and 2-methylnaphthalene which appear at τ 7·25 and τ 7·6 respectively.[15] The upfield shift of 0·93 ppm experienced by the Me resonance in 5-methyl-1,2,3,4-tetraphenylnaphthalene compared with the Me resonance of 1-methylnaphthalene, must be due to the Ph group at the 4-position being considerably out of the plane of the naphthalene nucleus. Thus the Me group in the 5-position would experience strong diamagnetic shielding. The same effect clearly operates in 5,7-dimethyl-1,2,3,4-tetraphenylnaphthalene which shows resonances at τ 8·2 and 7·76 for the 5- and 7-Me groups.

EXPERIMENTAL

Adducts of arynes with furan

Reaction of 4-chloro-3-iodotoluene with n-butyl-lithium. n-Bu-Li (25 ml, 0·05 mole) was slowly added to a soln of 4-chloro-3-iodotoluene (12·5 g, 0·05 mole) in ether (50 ml) and furan (50 ml) at −70°. The mixture was stirred at −70° for 2 hr and then allowed to warm to 10° over 3 hr, at which temp the mixture was added to solid CO_2 (50 g). After the CO_2 had disappeared water (50 ml) was added, the organic layer separated, washed with NaOH aq, water, and dried (Na_2SO_4). Removal of the solvents gave an oil which on distillation yielded 1,4-dihydro-6-methyl-1,4-epoxynaphthalene, (3·22 g, 51·0%), b.p. 59–61°/0·5 mm, n_D^{20} 1·5651, (lit.[16] b.p. 58–60°/0·4 mm); τ 2·4–3·5 (m, 3 aromatic and 2 vinylic protons), τ 4·64 (m, 2 bridgehead protons) and τ 7·82 (s, 3 Me protons); γ_{max}, 3050, 3012, 2960, 2925, 2875, 2860, 1615, 1470, 1370, 1285, 853, 700 cm^{-1}. (Found: C, 83·55; H, 6·4. Calc. for $C_{11}H_{10}O$: C, 83·55; H, 6·3%).

Reaction of 3-chloro-2-iodotoluene with n-butyl-lithium gave 1,4-*dihydro-5-methyl*-1,4-*epoxynaphthalene*, (2·8 g, 43%), m.p. 21°, from pet. ether (at −70°); τ 2·76–3·52 (m, 3 aromatic protons and 2 vinylic protons [at τ 3·2]), τ 4·45 (m, 1 bridgehead proton [position 1]), τ 4·6 (m, 1 bridgehead proton [position 4], τ 7·8 (s, 3 Me protons); ν_{max} 3055, 3010, 2960, 2922, 2860, 1620, 1475, 1370, 1285, 860, 720 cm^{-1}. (Found: C, 83·4; H, 6·3. $C_{11}H_{10}O$ requires: C, 83·55; H, 6·3%).

Reaction of 4-chloro-3-iodoanisole with n-butyl-lithium gave 1,4-*dihydro-6-methoxy*-1,4-*epoxynaphthalene*, (4·8 g, 54%), m.p. 63–64°, from pet. ether; τ 3·12 (d, 1 proton [position 8], J_{8-7} = 8·5 c/s), τ 3·2 (m, 2 vinylic protons), τ 3·3 (d, 1 proton [position 5], J_{5-7} = 2·2 c/s), τ 3·75 (d of doublets, 1 proton [position 7], J_{7-5} = 2·2 c/s, J_{7-8} = 8·5 c/s); ν_{max} 3080, 3060, 3015, 2960, 2940, 2880, 2860, 2840, 1615, 1475, 1290, 1230, 850, 700 cm^{-1}. (Found: C, 76·1; H, 5·85. $C_{11}H_{10}O_2$ requires: C, 75·9; H, 5·75%).

Reaction of 4-chloro-3-iodobenzotrifluoride with n-butyl-lithium gave 1,4-*dihydro-6-trifluoromethyl*-1,4-*epoxynaphthalene*, (5·7 g, 54%), b.p. 69–70°/0·1 mm, n_D^{20} 1·4949; τ 2·3–3·2 (m, 3 aromatic protons and 2 vinylic protons), τ 4·46 (m, 2 bridgehead protons); ν_{max} 3080, 3020, 1635, 1435, 1330, 1280, 855, 700 cm^{-1}. (Found: C, 62·15; H, 3·20. $C_{11}H_7F_3O$ requires: C, 62·30; H, 3·30%).

Reaction of 3,5-dimethyl-2-fluorobromobenzene with n-butyl-lithium gave 1,4-*dihydro-5,7-dimethyl*-1,4-*epoxynaphthalene* (3·5 g, 40%), m.p. 42–43°, from pet. ether; τ 3·2 (m, 2 vinylic protons) τ 3·29 (d, 1 proton [position 8], J_{8-6} = 2 c/s), τ 3·65 (d, 1 proton [position 6], J_{6-8} = 2 c/s), τ 7·8 (s, 6 Me protons); ν_{max}: 3080, 3005, 2970, 2940, 2915, 2860, 1620, 1450, 1380, 1285, 850, 700 cm^{-1}. (Found: C, 83·50; H, 6·90. $C_{12}H_{12}O$ requires: C, 83·70; H, 7·0%).

Reaction of 4,5-dimethyl-2-fluorobromobenzene with n-butyl-lithium gave 1,4-*dihydro-6,7-dimethyl*-1,4-*epoxynaphthalene* (3·5 g, 40%), m.p. 68–69°, (lit.[17] m.p. 72·5–73°) from pet ether; τ 3·1 (s, 2 aromatic protons), τ 3·2 (m, 2 vinylic protons); τ 4·63 (m, 2 bridgehead protons); τ 7·9 (s, 6 Me protons); ν_{max}: 3080, 3020, 3005, 2975, 2940, 2920, 2890, 2870, 1625, 1465, 1395, 1283, 850, 700 cm^{-1}. (Found: C, 83·50; H, 7·10. Calc. for $C_{12}H_{12}O$: C, 83·70; H, 7·0%).

Reaction of 3-bromo-4-iodoveratrole with n-butyl-lithium gave *1,4-dihydro-6,7-dimethoxy-1,4-epoxynaphthalene* (5·7 g, 56%), m.p. 145° after recrystallization from EtOH; PMR ($CDCl_3$), τ 2·98 (m, 2 vinylic protons), τ 3·02 (s, 2 aromatic protons), τ 4·36 (m, 2 bridgehead protons), τ 6·20 (s, 6 MeO protons); ν_{max}: 3120, 3095, 3075, 3050, 3035, 3010, 2970, 2950, 2920, 2870, 2840, 1610, 1492, 1475, 1460, 1420, 1330, 1290, 1070, 860, 700 cm^{-1}. (Found: C, 70·45; H, 5·90. $C_{12}H_{12}O_3$ requires: C, 70·60; H, 5·90%).

Adducts of arynes with 1,3-diphenylisobenzofuran

(a) *Benzyne generated via Grignard reagent.* 2 Fluro-bromobenzene (1·75 g) in dry THF (10 ml) was added to dry Mg turnings (0·24 g) in an atmosphere of dry N_2. Reaction was initiated by addition of a crystal of I_2 and 1,3-diphenylisobenzofuran (2·7 g) in hot THF (6 ml) immediately added. After 40 min gently warming and stirring no Mg remained. The reaction mixture was boiled under reflux for a further hr and then concentrated under reduced press to a syrup. This residue was dissolved in benzene, washed with NH_4Cl aq water, and dried ($MgSO_4$). Concentration under reduced press yielded a partially crystalline mass (4·6 g) which appeared by TLC to be essentially homogeneous. Preparative chromatography on an alumina column gave a syrup (3·1 g) which was recrystallized from benzene–EtOH to give 9,10-dihydro-9,10, diphenyl-9,10-epoxyanthracene, m.p. 184–186° (2·1 g, 66%). Recrystallization from benzene–EtOH gave m.p. 186–188°. Wittig gives m.p. 188°; ν_{max} 3050, 3030, 1600, 1320, 995, 985, 890, 770, 740, 700, 670 cm^{-1}. (Nujol mull).

(b) *Benzyne generated via fluorophenyl lithium.* 2-Fluorobromobenzene (1·75 g) and 1,3-diphenylisobenzofuran (2·7 g) in dry ether (20 ml) were stirred at −70° in an atmosphere of dry N_2. n-Bu-Li (4 ml, 2·54 N-soln in hexane) was added dropwise over 0·5 hr and the mixture stirred at −70° for a further 1 hr. The soln was allowed to warm to room temp overnight, well washed with water, dried ($MgSO_4$) and concentrated under reduced press to a semi-crystalline mass. Chromatography on alumina and recrystallization from benzene–EtOH gave 9,10-dihydro-9,10-diphenyl-9,10-epoxyanthracene, m.p. 186–188°, (1·75 g, 55%).

Trapping of 3,5-dimethylbenzyne with 1,3-diphenylisobenzofuran. 2-Fluoro-3,5-dimethyl-bromobenzene (2·03 g) was allowed to react with n-BuLi (4 ml, 2·54N-soln in hexane) in the presence of 1,3-diphenylisobenzofuran (2·7 g) as described for 2-fluoro-bromobenzene. Crystallization from MeOH gave *9,10-dihydro-1,3-dimethyl-9,10-diphenyl-9,10-epoxyanthracene*, m.p. 83–90° (unchanged by further recrystallization), (1·8 g, 48%); ν_{max} 3050, 3030, 1600, 1500, 1305, 1005, 850, 755, 745, 700, 675 cm^{-1}; (Nujol mull); PMR ($CDCl_3$) τ 1·9–3·4 (16 aromatic protons), τ 7·8 (3 protons, Me at position 3), τ 8·1 (3 protons, Me position 1). (Found: C, 89·75; H, 5·95. $C_{28}H_{22}O$ requires: C, 89·8; H, 5·9%).

Trapping of 3,4-dimethylbenzyne with 1,3-diphenylisobenzofuran. 2-Fluoro-4,5-dimethyl-bromobenzene (2·03 g) was allowed to react as described and yielded *9,10-dihydro-2,3-dimethyl-9,10-diphenyl-9,10-epoxyanthracene*, m.p. 80–87° (unchanged by further recrystallization from pet. ether) (2·1 g, 56%); ν_{max} 3050, 3030, 1600, 1495, 1490, 1355, 1315, 1145, 990, 980, 900, 865, 750, 740, 700, 690, 670 cm^{-1} (Nujol mull); PMR ($CDCl_3$) τ 1·95–3·12 (16 aromatic protons), τ 7·9 (6 protons Me groups at positions 2 and 3). (Found: C, 89·75; H, 6·0. $C_{28}H_{22}O$ requires: C, 89·8; H, 5·88%).

Trapping of 4,5-dimethoxybenzyne with 1,3-diphenylisobenzofuran. 2-Iodo-4,5-dimethyl-bromobenzene (3·43 g) was allowed to react as described and crystallized directly, without prior chromatography, from benzene–pet. ether to give *9,10-dihydro-2,3-dimethoxy-9,10-diphenyl-9,10-epoxyanthracene*, m.p. 172–173° after recrystallization from benzene–pet. ether, (1·0 g, 25%) ν_{max} 3050, 3010, 1600, 1350, 1315, 1275, 1205, 1180, 1070, 995, 980, 850, 745, 705, 670 cm^{-1} (Nujol mull); PMR ($CDCl_3$) τ 1·9–3·02 (16 aromatic protons) τ 6·18 (6 protons, MeO groups at positions 2 and 3). (Found: C, 82·9; H, 5·6. $C_{28}H_{22}O_3$ requires: C, 82·75; H, 5·4%).

Reactions of benzyne with 1,3-diphenyl-N-methylisoindole

(a) *Benzyne generated from o-fluorophenylmagnesium bromide.* The reaction was carried out as for the reaction of benzene with 1,3-diphenylisobenzofuran using 1,3-diphenyl-N-methylisoindole (7·1 g), o-fluorobromobenzene (4·37 g) and Mg (0·6 g) and gave *9,10-dihydro-9,10-diphenyl-N-methyl-9,10-endoaminoanthracene*, (6·6 g, 73·5%), m.p. 167–168°, after recrystallization from hexane; τ 2·0–3·24 (18 aromatic protons), τ 8·24 (s, 3 N-Me protons); ν_{max} 3060, 2995, 2960, 2840, 2780, 1610, 1500, 1455, 760, 750, 675 cm^{-1}. (Found: C, 90·05; H, 5·85; N, 3·9. $C_{27}H_{21}N$ requires: C, 90·25; H, 5·85; N, 3·9%). The amine (500 mg) was dissolved in excess MeI (5 g) and MeOH (25 ml) and the mixture refluxed for 30 min. Addition of ether gave a ppt of the *quaternary methiodide*, (650 mg, 91%), m.p. 236–237°, after recrystallization from acetone. (Found: C, 70·1; H, 4·8; N, 3·0. $C_{28}H_{24}NI$ requires: C, 70·4; H, 5·0, N, 2·9%).

The amine (500 mg) in AcOH (25 ml) was heated under reflux with Zn powder (1 g) for 1 hr and gave 9,10-diphenylanthracene (460 mg, 100%), m.p. 245° (lit.[9a] m.p. 249–250°) after recrystallization from benzene–pet. ether. (Found: C, 94·5; H, 5·6; Calc. for $C_{26}H_{18}$: C, 94·6; H, 5·4%).

(b) *Benzyne generated from o-fluorophenyl-lithium*

Using *o*-fluorobromobenzene (1·75 g; 0·01 mole), n-Bu-Li (0·01 mole) and 1,3-diphenyl-N-methylisoindole (2·8 g, 0·01 mole) gave 9,10-dihydro-9,10-diphenyl-N-methyl-9,10-endoaminoanthracene, (2·9 g, 75%), m.p. 165–166°).

(c) *Benzyne generated from anthranilic acid.* A soln of anthranilic acid (2·74 g, 0·02 mole) in THF (50 ml) was added over 2 hr to a refluxing soln of amyl nitrite (3·0 g) and 1,3-diphenyl-N-methylisoindole (5·6 g, 0·02 mole) in THF (25 ml). After the addition was complete the mixture was heated under reflux for a further 1 hr. The solvents were removed under reduced press and the residue in benzene when dried. (Na_2SO_4) and chromatographed on alumina gave 9,10-dihydro-9,10-diphenyl-N-methyl-9,10-endoamino-anthracene, (4·2 g, 58%), m.p. 165–166°.

Adducts of arynes with tetraphenylcyclopentadienone

Reaction of 3,5-*dimethyl*-2-*fluorobromobenzene with magnesium.* The reaction of Mg (0·26 g) and 3,5-dimethyl-2-fluorobromobenzene (1·0 g) in THF (10 ml) was started and tetraphenylcyclopentadienone (3·9 g, 2 moles) was added. The mixture was heated under reflux for 1½ hr prior to hydrolysis with sat NH_4Cl. The solvent was removed and the residue taken into benzene and dried (Na_2SO_4). Chromatography on alumina and elution with benzene gave 5,7-*dimethyl*-1,2,3,4-*tetraphenylnaphthalene*, (508 mg, 22%), m.p. 240–242°, after recrystallization from pet ether (b.p. 120–180°), m.p. 249°; τ 2·8–3·35 (22 aromatic protons), τ 7·76 (3 protons, Me at position 7), τ 8·2 (3 protons, Me at position 5); ν_{max} 3080, 3055, 3025, 2970, 2930, 2860, 1620, 1600, 1495, 1445, 730, 700 cm^{-1}. (Found: C, 93·95; H, 6·30. $C_{36}H_{28}$ requires: C, 93·90; H, 6·10%).

Reaction of 3-*chloro*-2-*iodotoluene with magnesium* gave 5-*methyl*-1,2,3,4-*tetraphenylnaphthalene* (7·5%), m.p. 227°, after recrystallization from pet. ether (b.p. 120–180°); τ 2·85–3·35 (23 aromatic protons), τ 8·18 (3 protons, Me at position 5); ν_{max} 3040, 3005, 2950, 2910, 2840, 1595, 1490, 1440, 730, 690 cm^{-1}. (*Found*: C, 94·75; H, 5·3. $C_{35}H_{26}$ requires: C, 94·25; H, 5·15%).

Reaction of 4-*chloro*-3-*iodotoluene with magnesium* gave 6-methyl-1,2,3,4-tetraphenylnaphthalene (0·4%), m.p. 221° (lit.[7] m.p. 222°). (Found: C, 94·75; H, 5·3. Calc. for $C_{35}H_{26}$: C, 94·85; H, 5·15%).

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REFERENCES

[1] Aryne Chemistry, Part X, H. Heaney and P. Lees, *Tetrahedron* **24**, 3717 (1968).

[2] [a] H. Heaney and P. Lees, *Tetrahedron Letters* 3049 (1964);
[b] K. D. Bartle, H. Heaney, D. W. Jones and P. Lees, *Tetrahedron* **21**, 3289 (1965).

[3] H. Heaney and P. Lees, unpublished results.

[4] [a] G. Wittig and L. Pohmer, *Angew. Chem.* **67**, 348 (1955);
[b] H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.* **79**, 2625 (1957).

[5] G. Wittig and H. F. Ebel, *Angew. Chem.* **72**, 564 (1960).

[6] E. Le Goff, *J. Am. Chem. Soc.* **84**, 3786 (1962);
F. M. Beringer and S. J. Huang, *J. Org. Chem.* **29**, 445; 1637 (1964).

[7] C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.* 296 (1964).

[8] A. G. Bonagura, M. B. Myers, S. J. Storfer and E. I. Becker, *J. Am. Chem. Soc.* **76**, 6122 (1954).

[9] [a] E. Knauss and K. Niettammer, *Liebigs Ann.* **630**, 10 (1960);
[b] G. Wittig, Personal communication.

[10] J. C. Emmet, D. F. Veber and W. Lwowski, *Chem. Comm.* 272 (1965).

[11] J. C. Emmett and W. Lwowski, *Tetrahedron* **22**, 1011 (1966).

[12] D. L. Brydon, J. I. G. Cadogan, D. M. Smith and J. B. Thomson, *Chem. Comm.* 727 (1967).

[13] H. Heaney and J. M. Jablonski, unpublished results.

[14] L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, p. 118. Methuen, London (1958).

[15] American Petroleum Research Project, Catalogue 44.

[16] E. Wolthuis, *J. Org. Chem.* **27**, 2215 (1961).