termination with a sample of *N*-nitrosodineopentylamine showed no depression of the decomposition point.

Hydrolysis of 2,2-dimethylpropylidene-2′,2′-dimethylpropylamine. To 10 ml. of 6*N* hydrochloric acid was added 500 mg. of the aldimine. An immediate reaction occurred between the aldimine and the acid. The acid phase was extracted with 10 ml. of ether. The ether extract was then poured into 5 ml. of ethanol which contained 400 mg. of 2,4-dinitrophenylhydrazine and 1 ml. of 6*N* hydrochloric acid. The resulting 2,4-dinitrophenylhydrazone, after two crystallizations from ethanol, melted at 205–206°, mixture melting point with an authentic sample of trimethylacetaldehyde, 205–206°.

The acid phase was evaporated to dryness and the resulting amine hydrochloride added to 3 ml. saturated sodium hydroxide. The amine was then separated from the sodium hydroxide solution and converted into the phenyl thiourethane, m.p. 133–134°. The phenyl thiourethane of neopentylamine was prepared, m.p. 134–135°; mixture melting point with the above sample, 134–135°.

Reduction of o-bromoanisole by lithium dineopentylamide. Lithium dineopentylamide was prepared by the reaction of 15.7 g. (0.10 mole) of *n*-butyl lithium[4] in 200 ml. of ether. After stirring for 1 hr., 18.7 (0.10 mole) of *o*-bromoanisole was added at once to the reaction mixture and it was allowed to reflux for 20 hr. As soon as the reaction mixture was decomposed with water, the ether layer was dried over anhydrous sodium sulfate and fractionally distilled. All the material that boiled between 138–158° was collected (14.1 g.). Since the unreacted dineopentylamine (b.p. 153–154°), 2,2-dimethylpropylidene-2′,2′-dimethylpropylamine (b.p. 89–90° at 104 mm.) and anisole (b.p. 155°) all boiled within ten degrees of each other, further separation was accomplished by means of gas-liquid partition chromatography. The aldimine, 115 mg. (n_D^{20} 1.4110), was separated from a total of 1.65 g. of the mixture (b.p. 138–158°) containing dineopentylamine and anusiole. This corresponds to a 7% yield of imine actually isolated. The infrared spectrum of the aldimine was identical to that of 2,2-dimethylpropylidene-2′,2′-dimethylpropylamine prepared from trimethylacetaldehyde and neopentylamine.

The remainder of the 138–158° fraction was then treated with 25 ml. of 6*N* hydrochloric acid and extracted with ether. The amount of anisole recovered was 3.0 g. (32% theoretical). After alkaline treatment of the acid solution and extraction with ether, 8.1 g. (49%) of unreacted dineopentylamine was recovered. Since the aldimine was decomposed by the acid hydrolysis, the remaining difference in weight, 1.3 g., corresponds to a 10% yield of the aldimine. From the distillation residue was recovered 6.3 g. (34%) of *o*-bromoanisole. A small amount of unidentified basic material, 1.2 g. (b.p. 200–215°) was obtained. A residue of dark purple, basic material (3.4 g.) remained which could not be identified.

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Some Derivatives of *p*-Terphenyl[1]

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Approaches to direct substitution in the *p*-terphenyl molecule in the past have invariably been complicated by the high order of reactivity of both terminal positions, and to a lesser extent the 2′-position.[2,3] Preparations involving the Gomberg synthesis lead to random mixtures of isomers which can only be separated by systematic fractional crystallization.[3,4]

We have found that 4-bromo-*p*-terphenyl is readily converted to the lithium reagent by the halogen-metal interconversion reaction[5] with *n*-butyllithium. Reported herein are a few examples of 4-substituted-*p*-terphenyl derivatives prepared from this lithium reagent. Also included are the 2- and 3-methyl derivatives, prepared by condensation of *p*-biphenylyllithium with the appropriately substituted cyclohexanones, followed by dehydration and aromatization.

By coupling of *N*-nitroso-4-acetamidobiphenyl with toluene only small amounts of any particular isomeric methyl-*p*-terphenyl could be recovered by earlier workers. The direct preparation of the 4-methyl isomer from the corresponding lithium reagent is clearly the ideal approach to this isomer in view of the yield obtained (67%). Although the three-step preparation of the other two isomers results in considerably lower yields, this method has the advantages of wide scope, direct approach, and the apparent lack of need for isolation and purification of the intermediate carbinol or olefin. The purification of the final product from this series of reactions can surely be simplified by application of a more suitable dehydrogenating agent. Although the use of selenium by von Braun, Irmisch, and Nelles[2] gave poor results, dehydrogenation by chloranil in xylene according to Arnold, Collins, and Zenk[6] appears promising with this type of compound.

The compounds described at this time were prepared incidental to a study concerned with organic liquid solution scintillators. Evaluation of the compounds for this purpose is being made by Drs. Wright H. Langham, F. N. Hayes, and D. G. Ott of the Los Alamos Laboratories who will report the results later.

EXPERIMENTAL[7]

4-Carboxy-p-terphenyl. Into a three necked flask, fitted with stirrer, dropping funnel, and condenser, were placed

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[1] This work was supported by the United States Atomic Energy Commission under Contract No. AT(11-1)-59.

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[7] All melting points are uncorrected. Reactions involving organolithium reagents were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium dried solvents.

4.64 g. (0.015 mole) of 4-bromo-*p*-terphenyl (m.p. 228–230°) and 75 ml. of ether. This suspension was stirred slowly at room temperature while 12.5 ml. (0.016 mole) of *n*-butyllithium solution[8] was added dropwise. After stirring 10 min. the reaction mixture became pink, though not quite clear, and the insoluble bromide was no longer evident. At this point Color Test II[9] was negative and Color Test I[10] was positive. The solution was poured jetwise into a stirred Dry Ice–ether slurry and stirring was continued until the ether had evaporated. The residual lithium salt was insoluble in water and had to be moistened with glacial acetic acid and stirred 1 hr. with 100 ml. of 10% hydrochloric acid in order to convert it to the free acid. This product was filtered and recrystallized from glacial acetic acid to give 2.18 g. (53%) of clear plates, m.p. 315–317°; reported[1] m.p. 315°.

Diphenyl-p-terphenyl-4-ylcarbinol. To a stirred solution of *p*-terphenyl-4-yllithium prepared as above was added 2.91 g. (0.016 mole) of benzophenone in 50 ml. of ether. After stirring for 5 min. Color Test I was negative, and the mixture was hydrolyzed with 30 ml. of saturated ammonium chloride solution. One hundred ml. of benzene was added and the layers were separated. The organic layer was evaporated to a gummy residue which was sucked dry on a Büchner funnel; yield 4.95 g. (80.1%); m.p. 213–216°. Two recrystallizations from 1:1 benzene–petroleum ether (b.p. 60–70°) raised the m.p. to 216–217°; yield 4.42 g. (72%).

Anal. Calcd. for $C_{31}H_{24}O$: C, 90.25; H, 5.87. Found: C, 90.10, 90.27; H, 6.04, 5.80.

4-Benzoyl-p-terphenyl. Upon addition of 1.65 g. (0.016 mole) of benzonitrile in 50 ml. of ether to 0.015 mole of *p*-terphenyl-4-yllithium solution, the mixture turned to a bright red-orange suspension, and Color Test I was negative after stirring for 5 min. The mixture was hydrolyzed with 30 ml. of 10% hydrochloric acid and worked up in the same fashion as the benzophenone adduct to give 2.95 g. (88.3%) of pale yellow material having a melting range of 192–195°. After four recrystallizations from 1:2 benzene–petroleum ether (b.p. 60–70°) the product melted at 196–197°.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.80; H, 5.42. Found: C, 90.14, 90.23; H, 5.61, 5.58.

4-Methyl-p-terphenyl. Addition of 2.02 g. (0.016 mole) of methyl sulfate in 50 ml. of ether to the terphenylyllithium solution as prepared above caused vigorous reflux and precipitation of a white solid. Color Test I was negative after stirring 10 min., and the mixture was hydrolyzed with 30 ml. of water. The layers were separated and the organic layer washed with water, dried and evaporated to a gummy residue. After drying on a Büchner funnel there remained 2.46 g. (67%) of white solid; m.p. 205.5–207°. Recrystallization from 1:2 benzene-petroleum ether (b.p. 60–70°) gave glassy prisms; m.p. 207–208°, as reported by France, Heilbron, and Hey.[3]

3-Methyl-p-terphenyl. A solution of 0.077 mole of *p*-biphenylyllithium[11] in 200 ml. of ether was added over a period of 30 min. to a stirred solution of 8.96 g. (0.080 mole) of 3-methylcyclohexanone in 50 ml. of ether. Color Test I was negative after stirring for 30 min., and the mixture was hydrolyzed with 50 ml. of 10% hydrochloric acid. The layers were separated and the aqueous layer was extracted with 50 ml. of benzene. The organic layer was filtered from a small amount of solid and distilled to remove the solvents. The solid (0.45 g.) proved to be impure quaterphenyl having a melting range of 260–285°. Two recrystallizations from toluene raised the m.p. to 315–317°; reported[12] m.p. 320° The residual oil was stirred and heated at 90–100° with 20 ml. of 20% sulfuric acid for 1 hr. The mixture was cooled and diluted with 30 ml. of water and 30 ml. of benzene. The layers were separated and the organic layer washed three times with 30 ml. portions of water, then distilled to remove the benzene. The residual oily solid was distilled at reduced pressure and three fractions were collected:

Fraction I: 1.64 g.; b.p. 55–57°/22 mm.
Fraction II: 6.41 g.; b.p. 85–98°/0.15 mm.
Fraction III: 7.77 g.; b.p. 152–158°/0.10 mm.

Fraction I was unreacted 3-methylcyclohexanone. Fraction II was impure biphenyl; m.p. and mixed m.p. with pure biphenyl 67–69°. The product in fraction III (crude 1-*p*-biphenylyl-2-methylcyclohexene) was dehydrogenated by heating with 2.05 g. (0.064 g.-atom) of sulfur for 5 hours at 205–210°. The resulting reddish solid was distilled at 145–150°/0.04 mm., and the product recrystallized from ethanol to give 3.88 g. (21%, based on *p*-biphenylyllithium) of pale yellow needles, having a melting range of 110–117°. This material was sublimed at 100°/0.01 mm. to give 3.02 g. of white powder; m.p. 122–124°. After two recrystallizations from ethanol the product[13] melted at 125.5–126°.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.44; H, 6.56. Found: C, 93.44; H, 6.71.

2-Methyl-p-terphenyl. This material was prepared by condensation of 0.077 mole of *p*-biphenylyllithium with 8.96 g. (0.080 mole) of 2-methylcyclohexanone in the same manner as the 3-methyl isomer. After dehydration with 20% sulfuric acid, there was recovered 1.42 g. of unreacted 2-methylcyclohexanone and 4.92 g. of biphenyl before the main fraction: 7.64 g. of what is presumed to be a mixture of 1-(*p*-biphenylyl)-3-methylcyclohexene and 1-(*p*-biphenylyl)-5-methylcyclohexene; b.p. 138–151°/0.10 mm. This material was heated with 1.96 g. (0.061 g.-atom) of sulfur for 8 hr. at 200–210° and distilled to give 4.13 g. of pale yellow solid; b.p. 125–140°/0.05 mm. Three recrystallizations from ethanol removed all sulfur and left 1.92 g. (10.4%); m.p. 93–94°. France, Heilbron, and Hey[3] reported 91–92°.

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[13] The m.p. reported[3] was 169–170°. Information kindly supplied by Prof. D. H. Hey in a private communication said that their compound was 4-acetamidodiphenyl.

Coupling Reactions with Some Organolithium Compounds in Tetrahydrofuran

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Several investigations concerning the reactions of *n*-butyllithium with dihalobenzene compounds have been reported recently. Depending upon conditions and solvents used, a variety of products have been obtained from these reactions. One such investigation[1] described the reactions of *o*-diiodobenzene and *o*-dibromobenzene with magnesium, lithium and *n*-butyllithium in various solvents to yield a series of coupling products. The formation

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