Discussion of Results

In the reaction of 1,4- or 1,5-dihaloalkanes with diallylamine, it appears likely that the first attack would result in formation of the 4- or 5-bromoalkyl diallylamine hydrobromide. In the presence of an excess of diallylamine, the free bromoalkyl diallylamine should be liberated. The second step probably involves cyclic quaternary ammonium salt formation. It has been pointed out[5] that aliphatic bases containing amine and halogen in the 1,4-positions exist only as a salt and on liberation of the base condense to pyrrole derivatives. It has also been shown[6] that amines of the type $X(CH_2)_nNR_2$ yield $(CH_2)_n\overset{+}{N}R_2X^-$ when n has a value of 4, 5 or 6. Although disproportionation was not observed in the reaction of diallylamine with either 1,4-dibromobutane or 1.5-dibromopentane, probably because a large excess of diallylamine was not used, when diallylpyrrolidinium bromide was heated with a large excess of diallylamine, both allylpyrrolidine and triallylamine were isolated and identified. This disproportionation also occurred in attempting to use the method of preparation which involved use of the di-(arylsulfonoxy)-alkanes with a large excess of diallylamine. Although Laakso and Reynolds[2] reported a yield of 77.5% in the preparation of 1,4-bis-(dibutylamino)-butane, and 66.5% in the preparation of 2,5-bis-(dimorpholino)-hexane, the yield was only 10% in the preparation of 1,5-bis-(dibenzylamino)-pentane. It has been shown by von Braun, Kuhn and Goll[7] that the relative firmness of attachment of hydrocarbon residues to heterocyclic nitrogen in quaternary ammonium salts increases in the following order: allyl, benzyl, methyl, ethyl, propyl, etc. These authors also pointed out that methyl groups were lost in presence of primary or secondary amines from quaternary ammonium salts of heterocyclic nitrogen compounds, even piperazine, the least stable heterocyclic nitrogen compound studied, without rupture of the ring. The fact that the partial ionic character of carbon bond attachments in allyl and benzyl compounds is greater than in alkyl compounds due to resonance resulting in increased stability of the resulting ions, probably accounts for the poor yield of 1,5-bis-(dibenzylamino)-pentane and tends to support the carbonium ion[3] as an intermediate in the disproportionation reaction. The fact that furfuryltrimethylammonium iodide reacts with piperidine[3] to give a 48% yield of N-furfurylpiperidine is evidence that relative firmness of attachment, as discussed by von Braun, Kuhn and Goll,[7] of furfuryl is less than that of methyl. The fact that this reaction proceeds to 48% completion in three hours at reflux (approximately 100°) while after 36 hours at 109°, diallylpyrrolidinium bromide had shown no signs of reaction, would indicate that the C–N bond in furfuryltrimethylammonium iodide has a greater degree of ionic character than the allyl-N bond in diallylpyrrolidinium bromide. This is also supported by the fact that the number of resonance forms of the furfurylcarbonium ion is greater than that of the allylcarbonium ion.

Acknowledgment.—The authors are indebted to the Atomic Energy Commission for support of this work under Contract No. AT-(40-1)-1353.

GAINESVILLE, FLORIDA

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[5] C. Hollins. "The Synthesis of Nitrogen Ring Compounds," Ernest Benn, Ltd., London, 1924, p. 63.

[6] M. R. Lehman, C. D. Thompson and C. S. Marvel, THIS JOURNAL, **55**, 1977 (1933).

[7] J. von Braun, M. Kuhn and O. Goll, *Ber.*, **59**, 2330 (1926).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Arylation of Unsaturated Systems by Free Radicals. I. Arylation of Alkylbenzenes

BY CHRISTIAN S. RONDESTVEDT, JR., AND HARRY S. BLANCHARD[1,2]

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When toluene, cumene and *t*-butylbenzene are attacked by phenyl radicals, mixtures of alkylbiphenyls are produced. For each hydrocarbon, the ratios of *ortho*, *meta* and *para* substitution are the same, regardless of whether the radical was generated from benzoyl peroxide, N-nitrosoacetanilide or 1-phenyl-3,3-dimethyltriazene. The percentage *para* substitution is roughly constant (20); the percentage *ortho* substitution decreases from toluene (60) to cumene (27) to *t*-butylbenzene (15). A substantial amount of bibenzyl is formed from toluene, together with a minor impurity which may be biphenyl (or diphenylmethane); cumene gives a much larger quantity of 2,3-dimethyl-2,3-diphenylbutane. Syntheses of the pure alkylbiphenyls are reported, together with improved methods for 3-bromobiphenyl and indazole.

At the inception of this work, the orienting influence of a substituent on an aromatic ring toward an incoming aryl "free radical" was incompletely understood. As a result of the early work summarized by Bachmann and Hoffman,[3] it appeared that almost any substituent was a *para* director. However, this conclusion was based upon isolation of the *p*-substituted biphenyl and the inability of the earlier workers to isolate the pure *o*- and *m*-isomers in most cases. Since 1950, several workers[4–8] have been active in showing that each of the three isomers is formed. In fact, their results indicate that usually *ortho* substitution is predominant (50–60%) and that the *meta* and *para* isomers are formed in

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[1] Abstracted from a portion of the Ph.D. Dissertation of Harry S. Blanchard, University of Michigan, 1954.

[2] Allied Chemical and Dye Corporation Fellow, 1953–1954.

[3] W. E. Bachmann and R. A. Hoffman in Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, Chapter 6.

[4] D. F. DeTar and H. J. Scheifele, Jr., THIS JOURNAL, **73**, 1442 (1951).

[5] R. L. Dannley and E. C. Gregg, Jr., *ibid.*, **76**, 2997 (1954), and previous papers.

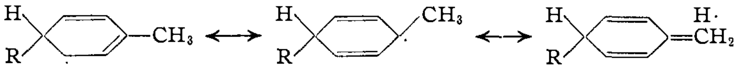
[6] J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 794 (1954), and previous papers.

[7] R. Huisgen and G. Sorge, *Ann.*, **566**, 162 (1950).

[8] O. Simamura, T. Inukai and M. Kurata, *Bull. Chem. Soc. Japan*, **25**, 76 (1952).

amounts roughly two-thirds and one-third of the remainder.

No complete explanation for the observed orientations has been advanced, particularly for the preponderance of *ortho* substitution. Wheland[9] performed quantum-mechanical calculations and predicted that *ortho-para* substitution should predominate when a substituted benzene is attacked by a free radical. Qualitatively, his method amounts to a statement that resonance should stabilize the transition states for *ortho* and *para* substitution far more than for *meta*. We attempted a semi-quantitative test of his conclusion by studying the phenylation of toluene, cumene and *t*-butylbenzene, in which the ability of the alkyl group to hyperconjugate with the ring decreases in the order given.



We also sought to compare quantitatively the phenylations by three different radical generators.

Results

Phenyl "radicals" were generated from benzoyl peroxide, N-nitrosoacetanilide and 1-phenyl-3,3-dimethyltriazene in each of the hydrocarbons as solvents, and the mixtures were worked up by careful distillation and analyzed by infrared spectroscopy. In the toluene case, the results demonstrated clearly that substantial amounts of other materials were present. Hey[10a] had stated that *no* bibenzyl was found when toluene was phenylated by benzoyl peroxide. Dannley and Zaremsky[10b,c] detected the presence of diphenylmethane by oxidation of the methylbiphenyl fraction and isolation of benzophenone as its phenylhydrazone. However, on careful examination of each methylbiphenyl fraction, we isolated substantial amounts of pure bibenzyl, the percentage being largest when benzoyl peroxide was the phenylating agent. In one experiment with nitrosoacetanilide, the temperature during the decomposition was maintained below 25°. There was no detectable amount of bibenzyl and the shoulder at 13.6 μ in the infrared spectrum (see below) was almost absent. The difference between our results and those of Dannley and Zaremsky[10b,c] and Hey[10a] may reflect different experimental conditions, particularly different concentrations and temperatures.

The spectrum of the methylbiphenyl fraction after partial removal of bibenzyl could be duplicated by an artificial mixture of the three methylbiphenyls, except for a shoulder at 13.6 μ. This feature could be reproduced by addition either of diphenylmethane or biphenyl (but not bibenzyl) though neither could be isolated or detected positively. Oxidation of the mixture as Dannley and Zaremsky had done[10c] did not lead to benzophenone. When the bibenzyl had not been removed, oxidation led to an oil which formed an impure dinitrophenylhydrazone, m.p. 222–230°, whose melting point was depressed upon admixture of benzophenone dinitrophenylhydrazone (m.p. 236°). The presence of biphenyl could not be positively proved.

When cumene was phenylated, substantially larger amounts of the coupled product, 1,2-diphenyl-1,2-dimethylbutane, were isolated. In both the cumene and toluene experiments, the figures for coupled product are based upon isolation and, hence, represent only *minimum* values. 2,2-Diphenylpropane was not observed, but small amounts might have escaped detection. *t*-Butylbenzene, having no α-hydrogens, gave no detectable coupling product.

Although phenylations by the several reagents occur at different temperatures, there appears to be little or no effect of temperature upon the isomer ratios (Table I). In this respect, radical substitution differs markedly from ionic substitution. The temperature effect seems to appear only in the reactions at the side chain (see above).

TABLE I

ISOMER COMPOSITION OF THE BIARYLS FROM THE PHENYLATION OF ALKYLBENZENES BY N-NITROSOACETANILIDE (NNA). BENZOYL PEROXIDE (BP). AND 1-PHENYL-3.3-DIMETHYLTRIAZENE (PDT)

	Toluene			Ethylbenzene[a]	Cumene			*t*-Butylbenzene[b]		
%	BP	NNA	PDT	BP	BP	NNA	PDT	BP	NNA	PDT
o	64	62	58	50	29	26	25	(17)	(15)	(14)
m	20	20	27	25	50	53	48	(61)	(63)	(63)
p	16	18	15	25	21	21	27	(22)	(22)	(23)

[a] Data from Dannley and Zaremsky.[10b] [b] Results in parentheses are assumed to be of somewhat lower accuracy.

Synthesis of Alkylbiphenyls.—4-Methyl-, 3-*t*-butyl- and 4-*t*-butylbiphenyl were synthesized by decomposing the corresponding nitrosoacetanilides in benzene. The three isopropylbiphenyls were all prepared by hydrogenolysis of the xenyldimethylcarbinols over copper chromite. 2-Methylbiphenyl was prepared by addition of *o*-tolylmagnesium bromide to cyclohexanone, followed by dehydration and dehydrogenation of the product. This latter procedure was not successful with 3- and 4-*t*-butylbiphenyls, since sulfur dehydrogenation led to some migration of the *t*-butyl group. 3-Methylbiphenyl was prepared by the alkaline decomposition of *m*-toluenediazonium chloride in benzene. When N-nitrosoaceto-*o*-toluidide was decomposed in benzene, a 42% yield of pure indazole was obtained, but no 2-methylbiphenyl. Indeed, this procedure constitutes the best available method for the preparation of indazole.[11] 3-Phenylindazole has been prepared previously in this way.[12a] In general, the nitrosoacetanilide and alkaline diazonium salt reactions fail or are very poor with substituents *ortho* to the diazo function.

All attempts to prepare 2-*t*-butylbiphenyl were unsuccessful. N-Nitroso-2-*t*-butylacetanilide, when decomposed in benzene, gave 2-*t*-butylphenyl acetate contaminated by what may have been 2-*t*-butylbiphenyl, but the latter could not be isolated. Addition of phenylmagnesium bromide to 2-*t*-

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(9) G. W. Wheland, THIS JOURNAL, **64**, 900 (1942).

(10) (a) D. H. Hey, *et al.*, *Research*, **4**, 386 (1951); (b) R. L. Dannley and B. Zaremsky, Abst. Am. Chem. Soc. Meeting, September, 1953, p. 36-O; B. Zaremsky, Ph.D. Thesis, Western Reserve University, 1954; (c) R. L. Dannley, private communication.

(11) *Cf.* E. F. M. Stephenson, *Org. Syntheses*, **29**, 54 (1949).

(12) (a) D. H. Hey and R. D. Mulley, *J. Chem. Soc.*, 2276 (1952); (b) D. H. Hey, A. Nechvatal and T. S. Robinson, *ibid.*, 2892 (1951).

butylcyclohexanone formed a product which could not be converted to 2-*t*-butylbiphenyl, and 2-(α-chloroisopropyl)-biphenyl could not be methylated by methylmagnesium iodide. Lacking the *ortho* isomer as a reference standard, we were forced to analyze for the *ortho* isomer in the *t*-butylbiphenyl mixture by a difference method, which, though theoretically correct, would lead to a slightly higher experimental error than in the other examples. Such a difference method has been used by Dannley[13] and Hey[12b] in cases where the *ortho* isomers possess no unique bonds.

Discussion

Table I makes clear that substituents are not invariably *ortho–para* directing toward homolytic substitution. As the alkyl group becomes more highly branched, the percentage of *ortho* substitution decreases. This may reflect either decreasing hyperconjugation or steric hindrance[10b,c] to *ortho* substitution by the larger groups. A discussion of the relative importance of these two factors will be deferred to a subsequent paper of this series, pending completion of experiments now in progress. Dannley[13] has noted with the halobenzenes that the percentage of *meta* substitution is almost exactly twice the *para* substitution, the distribution to be expected if attack in these two positions were purely statistical. Clearly this relationship does not hold with alkylbenzenes; our data indicate rather that the percentage of *para* isomer is roughly constant (15–23%, except for one experiment) and that the phenyl groups diverted from the *ortho* position by the effect of the larger alkyl substituents go almost entirely to the *meta* position. It is difficult to imagine some intrinsic tendency for *meta* substitution; it cannot be the result of a resonance effect of an alkyl group. However, the inductive effect of a substituent acts most strongly upon the *ortho* position, and more strongly upon the *meta* than *para* so it is reasonable at present to ascribe a substantial portion of the orienting influence of an alkyl group to its inductive effect.

The influence of other groups, where quantitative data are available,[4–8,13] does not appear to depend markedly upon the inductive effect. This may merely reflect the fact that the resonance effect, which would lead to *ortho–para* substitution according to Wheland,[9] is normally much stronger than the inductive effect for most groups. The inductive effect may be responsible for the preponderance of *ortho* over *para* observed with groups such as halogen, nitro and cyano. A case in point is benzotrichloride, where the resonance effect of a trichloromethyl group is not particularly strong and the inductive effect is great. Dannley and Sternfeld[14] found no *ortho* substitution (steric hindrance?), and *meta* substitution was much greater than *para*. Further discussion of the influence of the inductive effect must await additional experimental data on relative rates; Cadogan, Hey, Pangilly and Williams[15] observed rates (relative to benzene) of 2.1 and 0.75 for phenylation of isopropyl- and *t*-butylbenzene, respectively, but interpretation must await publication of their complete data and corresponding results for toluene and ethylbenzene.

The relative extents of α-attack by the radicals, as reflected in the percentages of bibenzyls isolated from the toluene and cumene arylations, is about as expected from the known susceptibilities of the α-hydrogens toward free-radical attack.[16] There appears to be no particular steric hindrance to the dimerization of the $PhCMe_2$ radical. Indeed, when cumene reacts with diacetyl peroxide, the dimer is formed quantitatively.[17]

NOTE ADDED IN PROOF.—J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 3352 (1954), have just published their study of the phenylation of *t*-butylbenzene. They were able to prepare 2-*t*-butylbiphenyl in very low yield, hence their isomer ratio *o*:*m*:*p*::24:49:27 may be slightly more accurate than ours.

Experimental

Materials.—Toluene (Reagent Grade) was dried over sodium; the Dolin modification[18] of the butanone test showed the absence of benzene.

Cumene (Eastern Chemical Corporation) was dried over sodium and fractionated (b.p. 151.8° (740 mm.), $n^{25}\text{D}$ 1.4891). ***t*-Butylbenzene** (Phillips Pure Grade, 99.6 mole %) was used directly in most of the work. **Biphenyl** (Eastman Kodak Co.) was recrystallized from methanol; m.p. 70.8–71.4°. **Diphenylmethane** (Eastman Practical) was fractionated (b.p. 262–263° (745 mm.)). **Bibenzyl** (Eastman), m.p. 53.6–54.6°, was used directly. **1,2-Dimethyl-1,2-diphenylbutane** was prepared by the method of Klages[19]; m.p. 118–119°. **Benzoyl peroxide** (Eastman) was used directly; analysis[20] showed it to be at least 98% pure. **N-Nitrosoacetanilide** was prepared by the method of DeTar.[21] **1-Phenyl-3,3-dimethyltriazene** was prepared by the method of Elks and Hey.[22]

Phenylation by Benzoyl Peroxide. General Procedure.—A solution of benzoyl peroxide in an excess of the aromatic hydrocarbon was heated at 80–110° until the evolution of carbon dioxide ceased. The cooled yellow solution was washed free of benzoic acid with sodium bicarbonate, washed with water, then dried and distilled. After removal of excess hydrocarbon, the residue was vacuum distilled. Since the crude distillate boiling in the alkylbiphenyl range invariably contained esters (infrared), these were removed by passing a petroleum ether solution of the distillate through a column of Fisher Chromatographic alumina. The redistilled material consisted solely of hydrocarbons (microanalysis and infrared); the spectra in the 12–13 μ region were unaffected by the chromatographic step.

Phenylation by N-Nitrosoacetanilide.—The air-dried nitrosoacetanilide was dissolved in excess hydrocarbon and the mixture was allowed to stand until no further gas evolution was apparent; if necessary, the flask was cooled to keep the temperature below 60–80°. It was then refluxed for several hours. The dark mixture was washed with bicarbonate, dilute acid and water, then dried and distilled. The biaryl mixture was invariably orange-red (azo compounds), and the color was removed by washing with cold, concd. sulfuric acid. However, the infrared spectra (12–13 μ) of samples before and after the acid wash were identical.

Phenylation by 1-Phenyl-3,3-dimethyltriazene.—A solution of triazene in hydrocarbon was maintained at 100–110° while excess glacial acetic acid was dropped in, then heated at the same temperature until evolution of nitrogen ceased. The mixture was washed with dilute acid, dilute alkali, and water, dried and distilled. The colored distillate

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(13) R. L. Dannley, E. C. Gregg, Jr., R. E. Phelps and C. B. Coleman, THIS JOURNAL, **76**, 445 (1954).

(14) R. L. Dannley and M. Sternfeld, *ibid.*, **76**, 4543 (1954).

(15) Quoted by D. Bryce-Smith, *J. Chem. Soc.*, 1085 (1954).

(16) R. A. Gregg and F. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947).

(17) M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

(18) B. H. Dolin, *Ind. Eng. Chem., Anal. Ed.*, **15**, 242 (1943).

(19) A. Klages, *Ber.*, **35**, 2638 (1902).

(20) V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1941).

(21) D. F. DeTar, *ibid.*, **73**, 1448 (1951).

(22) J. Elks and D. H. Hey, *J. Chem. Soc.*, 441 (1943).

was washed with sulfuric acid, though this treatment did not alter the infrared spectrum (12–13 μ).

The results of the experiments are presented in Table II, and additional details on isolation follow.

TABLE II

PRODUCT COMPOSITION FROM THE PHENYLATION OF THE ALKYLBENZENES

Moles of phenylating agent (molar ratio)[a]	Boiling range,[b] °C.	Mm.	Hydrocarbon fraction,[c] g.	Percentage mixed biaryls[d]	Mixed biaryls,[e] yield	Yield of coupling product[h]
			Toluene			
0.33 BP (20)	73–83	0.35	48.6	85 (62)[f]	37	(16)
.062 BP (23)	70–85	.30	4.4	86 (63)[f]	36	(7.8)
.38 NNA (19)	60–107	1.20	19.0	90	27	(3.9)
.066 NNA (14)	67–80	.25	1.0	100[g]	9	
.21 PDT (9)	80–100	.50	7.0	88	18	(3.1)
.10 PDT (19)	65–83	.20	3.9	85	20	(3.4)
			Cumene			
0.062 BP (23)	110–130	0.5	7.9	42 (41)[f]	27	(62.3)
.062 BP (36)	90–115	.8	8.4	40	28	(68.4)
.092 NNA (16)	78–140	1.0	9.0	48	24	(42.5)
.142 NNA (54)	82–135	.9	11.9	51	22	(34.5)
.067 PDT (22)	108–134	.40	5.0	52	20	(32.3)
			t-Butylbenzene			
0.066 BP (13)	70–135	0.25	5.0	100 (53)[f]	36	
.062 BP (21)	80–120	.20	4.5	100 (49)[f]	35	
.079 NNA (12)	110–125	.50	3.6	100	22	
.10 NNA (13)	99–110	.20	5.3	100	25	
.10 PDT (10)	110–135	.90	4.6	100	22	

[a] Moles of alkylbenzene/moles of arylating agent. [b] Prior to removal of the esters. [c] Following chromatography step. [d] Actual percentage of the hydrocarbon fraction found to be biaryls; the remainder arises from side chain attack and was determined by isolation or estimated from the infrared analyses. [e] Based on one mole of biaryl formed per mole of arylating agent. [f] Yield of benzoic acid based on one mole of acid per mole of peroxide. [g] Temperature of the decomposition was maintained below 25° throughout. [h] Yield of the coupling product based on one mole formed per 2 moles of phenylating agent; two radicals couple.

By-products in Phenylations of Toluene. Isolation of Bibenzyl.—Bibenzyl was isolated and identified positively by infrared comparison and by melting point and mixed melting point. Samples of the hydrocarbon fractions were dissolved in small amounts of petroleum ether (60–75°) and the solution was cooled to −50° with scratching. Bibenzyl crystallized and was washed by centrifuging with petroleum ether at −78°. The infrared analyses to determine isomer ratios were performed on samples from which the bulk of the bibenzyl had been thus removed; these still exhibited the shoulder at 13.6 μ.

Oxidation. Search for Diphenylmethane.—A 10-g. sample (from a benzoyl peroxide in toluene run) in 60 ml. of glacial acetic acid was treated dropwise with a solution of 14.9 g. (0.15 mole) of chromium trioxide in 35 ml. of water, 60 ml. of acetic acid and 13 ml. of concentrated sulfuric acid at such a rate that reflux was maintained. After being refluxed with stirring for an additional 2 hours, the mixture was poured into water and steam distilled. The pale green oil in the distillate did not crystallize. The derivative formed with dinitrophenylhydrazine melted, after repeated crystallizations, over the range 222–230° which was depressed to 215–225° when authentic benzophenone dinitrophenylhydrazone (m.p. 235.5–236°) was admixed. The phenylhydrazone was oily.

An identical experiment was performed with a sample which had been freed of bibenzyl by the treatment described above. The oil did not appear to react with phenylhydrazine or dinitrophenylhydrazine, and its infrared spectrum indicated that it was largely 2-methylbiphenyl which had escaped oxidation. In a third experiment, the oxidation was conducted with sodium dichromate in aqueous sulfuric acid, but no carbonyl compounds could be detected by infrared or chemical means.

Effect of Temperature upon Bibenzyl Formation.—In one run with nitrosoacetanilide, the reaction temperature was maintained below 25° by cooling as necessary. The methylbiphenyl fraction from this run did not contain detectable quantities of bibenzyl and the shoulder at 13.6 μ was almost absent from the infrared spectrum. Thus the formation of bibenzyl and the other by-product appears to require the higher temperatures which must be employed with benzoyl peroxide and phenyldimethyltriazene, and the autogenous temperatures usually found in larger-scale nitrosoacetanilide runs.

By-products in Phenylations of Cumene. 2,3-Diphenyl-2,3-dimethylbutane.—After the excess cumene had been removed by distillation, the residue was solid. It was taken up in petroleum ether (40–60°) and the insoluble diphenyldimethylbutane was removed by filtration. The filtrate was distilled and the semi-solid distillate was again taken up in petroleum ether (40–60°). Successive crops of diphenyldimethylbutane were taken by concentrating and chilling to −10°. After no more could be obtained, the filtrate was again distilled, and the liquid distillate was shown to be essentially free of diphenyldimethylbutane by its infrared spectrum.

Preparation of Pure Alkylbiphenyls. 2-Methylbiphenyl was prepared by the method of Sherwood, Short and Stansfield.[23] Its physical properties, as well as those of the other alkylbiphenyls employed in this work, are given in Table IV.

3-Methylbiphenyl was prepared by the Gomberg-Bachmann procedure.[24]

4-Methylbiphenyl was prepared by nitrosating aceto-*p*-toluidide by the method of DeTar[21] and decomposing the N-nitroso compound in benzene.

2-Isopropylbiphenyl.—A solution of 29.4 g. (0.14 mole) of *o*-xenyldimethylcarbinol[25] in 29 ml. of ethanol was refluxed with 1 g. of Raney nickel for one hour to remove impurities. The filtered solution was diluted to 60 ml. with ethanol and shaken with 6 g. of copper chromite catalyst at an initial gage pressure of 1200 p.s.i. for 12 hours at 225°.[26] The catalyst was removed by filtration and the alcohol was evaporated. The residue was distilled, giving 16.3 g. (59%) of 2-isopropylbiphenyl, which was redistilled from sodium.

Anal. Calcd. for $C_{15}H_{16}$: C, 91.72; H, 8.22. Found: C, 91.51; H, 8.24.

3-Isopropylbiphenyl.—3-Bromobiphenyl was prepared most conveniently by the nitrosoacetanilide method, rather than by the four-step process previously described.[27] *m*-Bromoacetanilide (182 g., 0.85 mole) was nitrosated by the procedure of DeTar.[21] The wet nitroso compound was dissolved in 1.5 l. of ice-cold benzene in a separatory funnel, the water was separated, and the cold solution was shaken briefly with 10 g. each of anhydrous sodium sulfate and potassium carbonate. The mixture, which had darkened, was filtered and allowed to warm to room temperature, then diluted to 3 l. with benzene and allowed to stand overnight. The opaque solution was washed with bicarbonate and water, the benzene was evaporated, and the residue was distilled, giving 124 g. of yellow to orange liquid, b.p. 146–190° (9 mm.). This was dissolved in benzene and shaken with concd. sulfuric acid until no more color was removed. The organic layer was washed, dried, and distilled. There was obtained after a small forerun, 111.1 g. (56%) of a pale yellow liquid, b.p. 152–153.5° (8 mm.), reported[27] 158–167° (11 mm.). This yield is one of the highest ever reported for a nitrosoacetanilide synthesis.

3-Bromobiphenyl was converted to *m*-xenyldimethylcarbinol[25] which was hydrogenolyzed as described above for the 2-isomer in 61% yield. The 3-isopropylbiphenyl was redistilled from sodium.

Anal. Calcd. for $C_{15}H_{16}$: C, 91.72; H, 8.32. Found: C, 91.93; H, 8.31.

4-Isopropylbiphenyl.—Hydrogenolysis of *p*-xenyldimethylcarbinol[25] gave a 68% yield of 4-isopropylbiphenyl which was redistilled from sodium.

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[23] I. R. Sherwood, W. F. Short and R. Stansfield, *J. Chem. Soc.*, 1832 (1932).

[24] M. Gomberg and J. C. Pernert, THIS JOURNAL, **48**, 1372 (1926).

[25] D. T. Mowry, J. Dazzi, M. Renoll and R. W. Shortridge, *ibid.*, **70**, 1916 (1948).

[26] L. I. Smith and C.-P. Lo, *ibid.*, **70**, 2209 (1948).

[27] W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, *ibid.*, **68**, 1109 (1946).

Anal. Calcd. for $C_{15}H_{16}$: C, 91.72; H, 8.32. Found: C, 91.78; H, 8.30.

Attempted Synthesis of 2-*t*-Butylbiphenyl.—2-*t*-Butylacetanilide was nitrosated by the procedure of DeTar.[21] The air-dried nitroso compound (21 g., 0.11 mole) was dissolved in 400 ml. of dry benzene and allowed to stand until the very slow evolution of nitrogen was complete, then refluxed for 2.5 hours. The mixture was washed, dried and distilled, yielding a red liquid, b.p. 70–155° (0.6 mm.). Redistillation gave 8.5 g. of a pale yellow-green liquid, b.p. 76–78° (0.6 mm.), whose infrared spectrum showed a strong absorption at 5.72 μ (carbonyl). It was dissolved in petroleum ether and passed through an alumina column, giving 3.5 g. of pale yellow-green liquid, b.p. 55–57° (0.06 mm.), which again exhibited carbonyl absorption; the spectra before and after the alumina treatment were superimposable, and showed a broad band at 8.3–8.5 μ characteristic of esters. The infrared spectrum of an authentic sample of *o*-*t*-butylphenyl acetate was very similar, having a band at 5.72 μ and a doublet at 8.3–8.5 μ. The pale green liquid also had a band at 12.8 μ, which is in the region where the other *ortho*-substituted biphenyls absorb. Analysis of the pale green liquid indicated that it was mostly *o*-*t*-butylphenyl acetate contaminated with a little *o*-*t*-butylbiphenyl.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 75.20; H, 8.35. Calcd. for $C_{16}H_{18}$: C, 91.40; H, 8.63. Found: C, 77.30; H, 8.07.

3-*t*-Butylbiphenyl.—*m*-*t*-Butylacetanilide was prepared essentially by the procedure of Wepster.[28] When *p*-*t*-butylacetanilide was nitrated, the presumed 2-nitro-4-*t*-butylacetanilide proved to be extraordinarily difficult to hydrolyze by standard methods, and the amine when obtained was a remarkably weak base. These properties led us to suspect that the *t*-butyl group had migrated during the nitration reaction, to form instead 2-nitro-6-*t*-butylacetanilide; Bartlett, Roha and Stiles[29] showed that *o*-*t*-butylaniline was a very weak base compared to the *para* isomer. Wepster did not prove the structure of his intermediate, but this omission did not affect the validity of his synthesis of *m*-*t*-butylaniline because either intermediate would have given the same product upon deamination. Examination of ultraviolet absorption spectra, as shown in Table III, indicated quite conclusively that the *t*-butyl group had *not* migrated and confirmed the structure assigned by Wepster. The base-weakening effect of the nitro group in the position *ortho* to amino is therefore *enhanced* by a *t*-butyl group in the *para* position, possibly for solubility reasons.

TABLE III

ULTRAVIOLET SPECTRA IN ETHANOL OF COMPARISON COMPOUNDS

Compound	$\lambda_{max.}$ A.	Compound	$\lambda_{max,}$ A.
Acetanilide	2435	2-*t*-Butylacetanilide	<2100
2-Nitroacetanilide	2330	2-Nitro-4-*t*-butylacetanilide	2360
4-*t*-Butylacetanilide	2450		

The N-nitroso-*m*-*t*-butylacetanilide prepared from 10.2 g. (0.054 mole) of *m*-*t*-butylacetanilide by the procedure of DeTar[21] was decomposed in 150 ml. of reagent benzene, the mixture being refluxed for 12 hours after the evolution of nitrogen ceased. Workup by the general procedure and distillation gave a fraction, b.p. 105–106° (0.5 mm.), n^{20}D 1.5735, weighing 2.7 g., 24%. Chromatography on alumina, followed by Norit-Celite, did not remove the faint yellow color, nor did sulfuric acid.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.40; H, 8.63. Found: C, 91.33; H, 8.66.

The alternative synthesis from 3-bromo-*t*-butylbenzene and cyclohexanone gave a product, after sulfur dehydrogenation, whose infrared spectrum indicated contamination by isomers.

4-*t*-Butylbiphenyl.—This compound was prepared in the same manner as the 3-isomer and was purified by recrystallization from ethanol; yield 26%. Again, the alternate route gave an impure material contaminated with isomers, perhaps not surprising since sulfur dehydrogenation often causes migration of labile groups such as *t*-butyl.[30]

Anal. Calcd. for $C_{16}H_{18}$: C, 91.40; H, 8.63. Found: C, 91.36; H, 8.75.

TABLE IV

PHYSICAL PROPERTIES OF THE ALKYLBIPHENYLS

Biphenyl deriv.	B.p., °C.	Mm.	n^{20}D or m.p.
2-Methyl-[a]	131–135	19	1.5867
3-Methyl-[b]	156.3–157	31	1.6015
4-Methyl-[c]	140–150	20	47.8–48.8°[c]
2-Isopropyl-[d]	101–105	1.8	1.5688
3-Isopropyl-	110–115	1.3	1.5807
4-Isopropyl-	110–112	1	1.5831
3-*t*-Butyl-	105–106	0.5	1.5735
4-*t*-Butyl-[e]	104–110	0.2	52–53°[e]

[a] I. A. Goodman and P. H. Wise, THIS JOURNAL. **72**, 3077 (1950), report n^{20}D 1.5914; their sample is probably purer. Reference 23, reports b.p. 130–136° (27 mm.). [b] Reference 23 reports b.p. 148–150° (20 mm.); n^{22}D 1.5916. [c] Reference 23 reports b.p. 134–136° (15 mm.), m.p. 47.5°. [d] I. A. Goodman and P. H. Wise, THIS JOURNAL, **72**, 3077 (1950), report n^{20}D 1.5703. [e] A. V. Grosse, J. M. Mavity and V. N. Ipatieff, *J. Org. Chem.*, **3**, 448 (1939), report b.p. 122–125° (2 mm.), m.p. 51–52°. We could not repeat their synthesis, however.

Preparation of Indazole.—The N-nitroso derivative prepared[21] from 14.9 g. (0.1 mole) of aceto-*o*-toluidide was obtained as an oil which was dissolved in 200 ml. of benzene. The water was separated and the cloudy solution was dried by shaking with calcium chloride. There was little darkening when the solution stood at room temperature and nitrogen evolution was barely perceptible. The solution was refluxed for several hours, after which the benzene was evaporated. The red residue was dissolved in hot ethanol and treated several times with Norit. The pale solution was evaporated and the residue was crystallized from benzene, giving indazole as a white solid. Crystallization from aqueous ethanol gave white plates; 5 g. (42%), m.p. 146.0–146.2° (reported[11] 146°). Nitrogen analysis was satisfactory.

Preparation of 2,4,7-Trinitrofluorenone (TNF) Derivatives.—For further characterization of the biphenyls, attempts were made to prepare their TNF derivatives by the procedure of Orchin, Reggel and Woolfolk,[31] using 0.5 mole

TABLE V

COMPLEXES OF BIARYLS WITH 2,4,7-TRINITROFLUORENONE (TNF)

Biaryl[a,b]	M.p., °C.	Molecular formula	Nitrogen, % Calcd.	Nitrogen, % Found
Biphenyl (88)	132–133	$C_{25}H_{15}N_3O_7$	8.95	8.97
m-Methylbiphenyl[c]	140–141	....	..	..
p-Methylbiphenyl (85)[d]	138.5-139	$C_{26}H_{17}N_3O_7$	8.69	8.64
p-Isopropylbiphenyl[c]	145-150	....	..	..
p-*t*-Butylbiphenyl (67)[e]	141–142	$C_{29}H_{23}N_3O_7$	8.00	8.40
3,4-Dimethylbiphenyl (86)	137.2–138.2	$C_{27}H_{19}N_3O_7$	8.47	8.63

[a] Figures in parentheses are yields. [b] Diphenylmethane and *o*-methylbiphenyl gave nearly quantitative recoveries of TNF. [c] These complexes dissociated on crystallization from ethanol, acetic acid or ethanol–benzene. [d] Acetic acid was satisfactory, but no complex was formed in ethanol. [e] The analytical sample had been crystallized once from acetic acid. Further crystallization caused ultimately complete dissociation.

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[28] H. J. Biekert, H. B. Dessens, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **71**, 32 (1952).

[29] P. D. Bartlett, M. Roha and R. M. Stiles, THIS JOURNAL, **76**, 2349 (1954).

[30] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 454.

[31] M. Orchin, L. Reggel and E. O. Woolfolk, THIS JOURNAL, **69**, 1225 (1947).

of TNF per mole of biaryl. Details of the work and physical properties of the new compounds are given in Table V and the accompanying notes. Most of the complexes were too unstable to be satisfactory derivatives.

Determination of Isomer Ratios in the Mixed Biphenyl Fractions.—The infrared spectrophotometric method of analysis was a simplification of the procedure of Heigl, Bell and White[32] for multicomponent hydrocarbon mixtures. The optical densities D_B at the analytical peaks selected (Table VI) were determined by their "base-line" method. Then working curves of D_B *vs.* composition were prepared from several artificial mixtures of the pure alkylbiphenyls; the plots for the *meta* isomers were straight lines, while those for *ortho* and *para* curved slightly. The compositions of the unknown mixtures were estimated from the working curves and the results were checked against artificial mixtures of the same percentage composition. Checks against other known mixtures indicated that the relative accuracy of the results was 4% for the *ortho*, 2% for the *meta*, and 5% for the *para;* the deviation from Beer's law was greatest for *para*, least for *meta*.

The original spectra may be consulted in Mr. Blanchard's thesis, available from the University of Michigan Library.

TABLE VI

ANALYTICAL PEAKS FOR THE ALKYLBIPHENYLS

Compound	Wave length, μ	Compound	Wave length, μ	Compound	Wave length, μ
Methylbiphenyls		Isopropylbiphenyls		*t*-Butylbiphenyls	
2	12.90	2	13.00	2	...
3	12.63	3	12.60	3	12.55
4	12.15	4	12.05	4	12.00

ANN ARBOR, MICHIGAN

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(32) J. J. Heigl, M. F. Bell and J. A. White, *Anal. Chem.*, **19**, 293 (1947).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Alkylation of Benzene with 1,1-Dichloro-3,3-dimethylbutane[1]

BY LOUIS SCHMERLING, J. P. LUVISI AND R. W. WELCH

RECEIVED OCTOBER 6, 1954

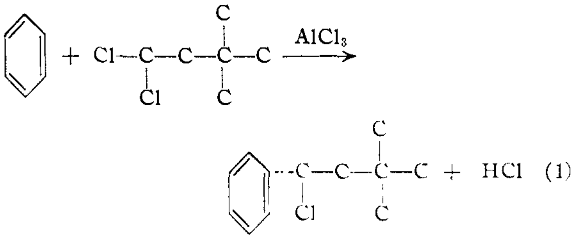
The reaction of 1,1-dichloro-3,3-dimethylbutane with benzene in the presence of aluminum chloride yields 1,1-diphenyl-3,3-dimethylbutane (II) together with a primary alkylbenzene, 1-phenyl-3,3-dimethylbutane ("neohexylbenzene," III). The yield of III is increased markedly at the expense of II by carrying out the reaction in the presence of methylcyclopentane which serves as a hydrogen donor and is converted to (methylcyclopentyl)-benzene. The alkylation mechanism which presumably involves a bimolecular displacement reaction followed by an intermolecular hydrogen transfer is discussed.

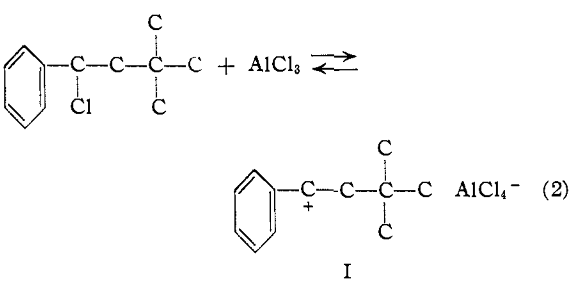
Alkylation of benzene with the primary hexyl chloride, 1-chloro-3,3-dimethylbutane in the presence of aluminum chloride has been shown[2] to yield the secondary alkylbenzene, 3-phenyl-2,2-dimethylbutane. The same isomer, rather than 2-phenyl-2,3-dimethylbutane, is also obtained by the aluminum chloride-catalyzed alkylation of benzene with the tertiary chloride, 2-chloro-2,3-dimethylbutane.[2] It may be concluded that contrary to general opinion alkylation in the presence of aluminum chloride tends to yield *s*-alkylbenzene rather than *t*-alkylbenzene as the major product.

It was of interest to determine what products would be formed by the reaction of 1,1-dichloro-3.3-dimethylbutane with benzene in the presence of aluminum chloride. Experiments carried out at ice temperature yielded 19–20% of a crystalline diphenylhexane and 26–28% of a monohexylbenzene. The latter apparently consisted exclusively of 1-phenyl-3,3-dimethylbutane ("neohexylbenzene," III), no evidence for the presence of 2-phenyl-2,3-dimethylbutane or 3-phenyl-2,2-dimethylbutane being found in the infrared spectrum of the material.

The structure of the diphenylhexane was not rigidly proved. That it was a 1,1-diphenylalkane rather than a 1,2- or 2,3-diphenylalkane was shown by the fact that it yielded benzophenone on oxidation with chromic acid. That it contained the *gem*-dimethylbutane structure seems probable in view of the structure of the monohexylbenzene.

The unexpected formation of III rather than rearrangement product may be explained by postulating that the first step of the alkylation mechanism involves a concerted bimolecular nucleophilic displacement reaction[3,4] to yield 1-chloro-1-phenyl-3,3-dimethylbutane (not isolated). Ionization of this secondary alkyl chloride in the presence of aluminum chloride yields I which reacts with either benzene to yield the diphenylhexane or a hydrogen donor to yield 1-phenyl-3,3-dimethylbutane by hydrogen transfer





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(1) Presented before the Division of Organic Chemistry of the American Chemical Society at the New York meeting, September, 1954.

(2) L. Schmerling and J. P. West, THIS JOURNAL, **76**, 1917 (1954).

(3) L. Schmerling, *Ind. Eng. Chem.*, **45**, 1447 (1953).

(4) H. C. Brown, *ibid.*, **45**, 1462 (1953).