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).

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[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

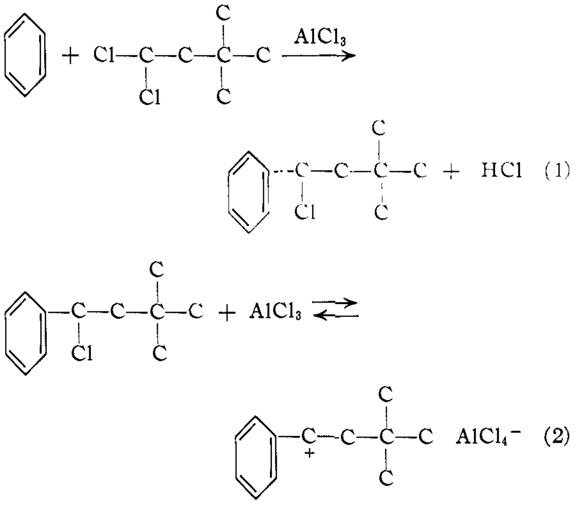
The reaction of 1,1-dichloro-3,3-dimethylbutane with benzene in the presence of aluminum chloride yields 1,1-diphenyl-3,3-dimethylbutane (II) together with a primary alkylbenzene, 1-phenyl-3,3-dimethylbutane ("neohexylbenzene," III). The yield of III is increased markedly at the expense of II by carrying 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



I

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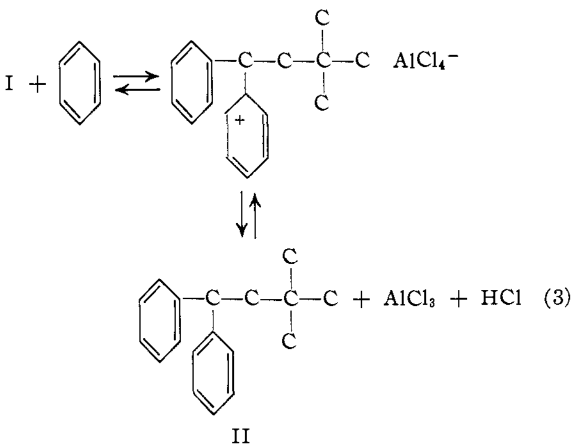
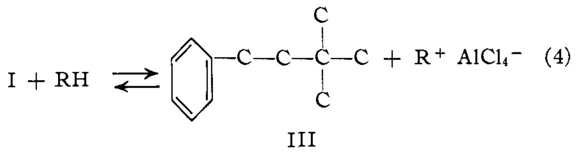
[1] Presented before the Division of Organic Chemistry of the American Chemical Society at the New York meeting, September, 1954.

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

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

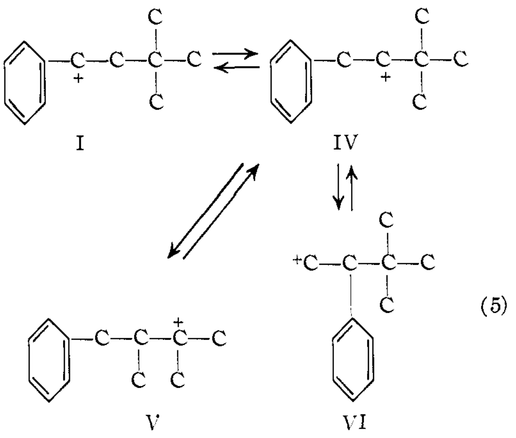
[4] H. C. Brown, *ibid.*, **45**, 1462 (1953).





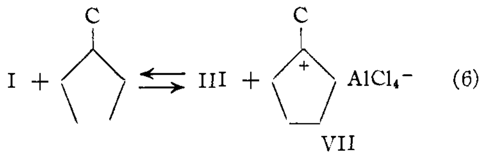
RH represents hydrogen donor which may be alkylated benzene, chloroalkane, polymer or other compounds present in the reaction mixture.

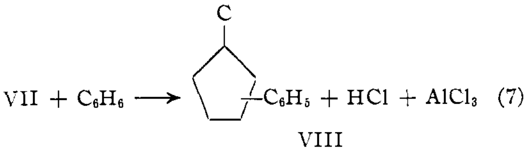
Rearrangement of the cation of I to IV (and thence to V or VI) does not occur because it (a benzyl cation) is more stable, being stabilized by resonance involving the benzene ring.



When the reaction of benzene with 1,1-dichloro-3,3-dimethylbutane was carried out in the presence of zirconium chloride at 27° or of aluminum chloride monomethanolate at 84°, the yield of monohexylbenzene (chiefly III) was only 5–6% while that of II was 20%. Less hydrogen transfer occurred in the presence of these milder catalysts.

The yield of III may be increased markedly at the expense of II by carrying out the reaction in the presence of a larger amount of an active hydrogen donor. For example, the addition of 1,1-dichloro-3,3-dimethylbutane to a mixture of benzene, methylcyclopentane and aluminum chloride (expt. 3) resulted in a 60% yield of III and only 6% of II. There was also isolated a (methylcyclopentyl)-benzene in 48% yield based on equation 8.





The over-all reaction may be written

$$(CH_3)_3CCH_2CHCl_2 + CH_3C_5H_9 + 2C_6H_6 \longrightarrow (CH_3)_3CCH_2CH_2C_6H_5 + C_6H_5C_5H_8CH_3 + 2HCl \quad (8)$$

Infrared analysis showed that VIII was not (1-methylcyclopentyl)-benzene, indicating that aluminum chloride yields secondary rather than tertiary cycloalkylbenzenes, presumably for the same reason that it tends to form secondary alkylbenzenes. Alkylation of benzene with 1-chloro-1-methylcyclohexane in the presence of aluminum chloride produced what was apparently 3- or 4-phenyl-1-methylcyclohexane or a mixture of these rather than the tertiary cycloalkylbenzene, 1-phenyl-1-methylcyclohexane.[5]

The reaction of benzene with 1,1-dichloro-3,3-dialkylalkanes (which may be obtained readily by the condensation of *t*-alkyl chlorides with vinyl chloride[6]) in the presence of aluminum chloride and a saturated hydrocarbon (particularly one containing a tertiary carbon atom) thus offers a simple means for obtaining III and other primary alkylbenzenes containing a *gem*-dialkyl group.

## Experimental

**Procedures.**—Two general procedures were used, resulting in the data summarized in Table I.

**Method A.**—A solution of the dichlorohexane in about 30% of the total amount of benzene used was added during about 1–2 hours to a stirred mixture of the catalyst and the remainder of the benzene (and methylcyclopentane, when used). Stirring was continued for an additional hour, the catalyst layer was permitted to settle out, and the upper layer was separated, washed with dilute alkali and water, dried over potassium carbonate, and distilled.

**Method R.**—The mixture of dichlorohexane, benzene and aluminum chloride monomethanolate was heated under reflux for 8 hours. The liquid product was decanted from the solid catalyst on the wall of the flask, washed with dilute alkali and water, dried and distilled.

**Identification of Products. 1-Phenyl-3,3-dimethylbutane.**—The hexylbenzene boiled chiefly at 103–104° at 24 mm. (211–212° at 760 mm.[7]); $n^{20}D$ 1.4835. It was characterized as 1-phenyl-3,3-dimethylbutane by comparison of its infrared spectrum[8] with that of an authentic sample[9] of the hydrocarbon and by determination of the "mixed melting point" (157–158°) of a mixture of its monoacetamido derivative (m.p. 157°) with that of the monoacetamido derivative[9] (m.p. 158°) of the authentic hydrocarbon.

The diacetamido derivative of the hexylbenzene melted at 236–237°.

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[5] L. Schmerling, unpublished results.

[6] L. Schmerling, THIS JOURNAL, **68**, 1650 (1946).

[7] As determined by means of the Lippincott nomograph, *Ind. Eng. Chem.*, **38**, 320 (1946).

[8] Infrared absorption analyses by Mr. Edmond Baclawski, Physics Division, Universal Oil Products Company.

[9] E. Berliner and F. Berliner, THIS JOURNAL, **72**, 222 (1950). We are indebted to Prof. Berliner for the sample of 1-phenyl-3,3-dimethylbutane and its monoacetamido derivative.

TABLE I

ALKYLATION OF BENZENE WITH 1,1-DICHLORO-3,3-DIMETHYLBUTANE

| Expt. | Method | Reactants, moles $C_6H_6$ | $C_6H_{12}Cl_2$[a] | Catalyst Kind | g. | Ave. temp., °C. | Chief products Formula | Yield, % |
|---|---|---|---|---|---|---|---|---|
| 1 | A | 4.15 | 0.55 | $AlCl_3$ | 8 | 3 | $Me_3CCH_2CH_2Ph$ | 26 |
| | | | | | | | $Me_3CCH_2CHPh_2$ | 19 |
| 2 | A | 4.15 | .55 | $AlCl_3$ | 20 | 3 | $Me_3CCH_2CH_2Ph$ | 28 |
| | | | | | | | $Me_2CCH_2CHPh_2$ | 20 |
| 3 | A | 4.15[b] | .55 | $AlCl_3$ | 20 | 3 | $Me_3CCH_2CH_2Ph$ | 60 |
| | | | | | | | $Me_3CCH_2CHPh_2$ | 6 |
| | | | | | | | $MeC_5H_8Ph$ | 48[c] |
| 4 | R | 1.53 | .19 | $AlCl_3 \cdot MeOH$[d] | 10 | 84 | $Me_3CCH_2CH_2Ph$ | 6 |
| | | | | | | | $Me_3CCH_2CHPh_2$ | 20 |
| 5 | A | 4.15 | .55 | $ZrCl_4$ | 5 | 27[e] | $Me_3CCH_2CH_2Ph$ | 5[f] |
| | | | | | | | $Me_3CCH_2CHPh_2$ | 20 |

[a] 1,1-Dichloro-3,3-dimethylbutane, b.p. 148° (6 mm.), prepared by the condensation of *t*-butyl chloride with vinyl chloride. [b] Also 1.8 moles methylcyclopentane. [c] Calculated on the basis of eq. 8. [d] L. Schmerling, THIS JOURNAL, 68, 280 (1946). [e] Stirring continued for ten hours after the addition of the dichlorohexane. [f] Presence of other monoalkylbenzene (not 2-phenyl-3,3-dimethylbutane, 2-phenyl-2,3-dimethylbutane, 2-phenyl-2-methylpentane, 3-phenyl-2-methylpentane, or 3-phenylhexane) was indicated by the infrared spectrum of the fraction boiling at 57–70° at 4 mm., chiefly 61–67° at 4 mm. (206–212° at 760 mm.).

*Anal.*[10] Calcd. for $C_{16}H_{29}N_2O_2$: N, 10.14. Found: N, 10.41.

A mixture of this diacetamido derivative with that[2] (m.p. 235°) of 2-phenyl-3,3-dimethylbutane melted at 205–210°.

**1,1-Diphenyl-3,3-dimethylbutane.**—The fraction boiling at 148–151° at 5 mm. (314–318° at 760 mm.) crystallized on standing; m.p. 33°.

*Anal.* Calcd. for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.85; H, 9.68.

Nitration of a pentane solution of the diphenylhexane with a 2:1 by volume mixture of sulfuric and nitric acids yield a dinitro compound; nacreous flakes (from ethanol), m.p. 156°.

*Anal.* Calcd. for $C_{18}H_{22}N_2O_4$: C, 65.84; H, 6.14. Found: C, 65.84; H, 5.98.

A mixture of 0.5 g. of the diphenylhexane and a solution of 3.5 g. of chromium trioxide in 5 cc. of concentrated sulfuric acid, 15 cc. of acetic acid and 15 cc. of water was heated under reflux for three hours. The cooled product was extracted with pentane and the extract was washed, dried and distilled. The residue was taken up in 5 cc. of ethanol and the solution was used for the preparation of crystalline derivatives: 2,4-dinitrophenylhydrazone, m.p. and "mixed m.p." with the 2,4-dinitrophenylhydrazone of benzophenone, 234–235°; semicarbazone, m.p. and "mixed m.p." with the semicarbazone of benzophenone, 46–47°.

**(*x*-Methylcyclopentyl)-benzene.**—The material boiled mainly at 149–153° at 87 mm. (226–231° at 760 mm.); $n^{20}D$ 1.5170.

*Anal.* Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 90.02; H, 10.21.

The infrared spectrum of this material indicated that no significant amount of (1-methylcyclopentyl)-benzene[11] was present.

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[10] Microanalyses byMr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois.

[11] H. Pines and J. D. LaZerte, unpublished results.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

# The Synthesis of 5-Dimethylamino-4,4-diphenyl-2-pentanol

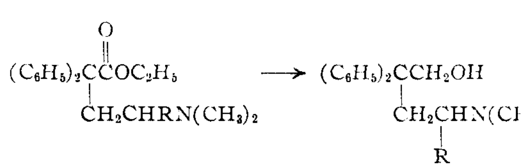
BY NELSON R. EASTON[1] AND VELMER B. FISH

RECEIVED SEPTEMBER 20, 1954

The synthesis of 5-dimethylamino-4,4-diphenyl-2-pentanol is described starting with 3,3-diphenyl-5-methyl-2-tetrahydrofuranoneimine. The formation of some derivatives and their reactions are reported.

The reduction of both methadone and isomethadone has been studied extensively.[2-5] The carbinols from these reductions either in the form of their acetoxy derivatives or the alcohols themselves generally exhibit considerable analgetic activity.

The reduction of esters of the general structure I to the amino carbinols (II) has also been reported.[4] Since compounds of this general structure usually show some analgetic activity the influence of interchanging the functional groups on the type and degree of analgetic activity should promise an interesting addition to the general study of analgesia. One of the compounds that has been prepared and found to have slight activity is 4-dimethylamino-2,2-diphenyl-1-pentanol (II, R = $CH_3$).[4] Interchanging the amino and hydroxy



$$\underset{\text{I}}{(C_6H_5)_2\overset{\overset{O}{\|}}{C}COC_2H_5 \atop |\;CH_2CHRN(CH_3)_2} \longrightarrow \underset{\text{II}}{(C_6H_5)_2CCH_2OH \atop |\;CH_2CHN(CH_3)_2 \atop \;\;\;\;\;\;\;|\;R}$$

I II

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[1] Lilly Research Laboratories, Eli Lilly and Company, Indianapolis 6, Indiana.

[2] (a) E. L. May and E. Mosettig, *J. Org. Chem.*, **13**, 459 (1948); (b) A. Pohland, F. J. Marshall and T. P. Carney, THIS JOURNAL, **71**, 460 (1949).

[3] E. L. May and N. B. Eddy, *J. Org. Chem.*, **17**, 1210 (1952).

[4] M. E. Speeter, W. M. Byrd, L. C. Cheney and S. B. Binkley, THIS JOURNAL, **71**, 57 (1949).

[5] N. B. Eddy, E. L. May and E. Mosettig, *J. Org. Chem.*, **17**, 321 (1952).