SYNTHESIS OF 2-ALKYL- AND 2-ARYL-BIPHENYLS

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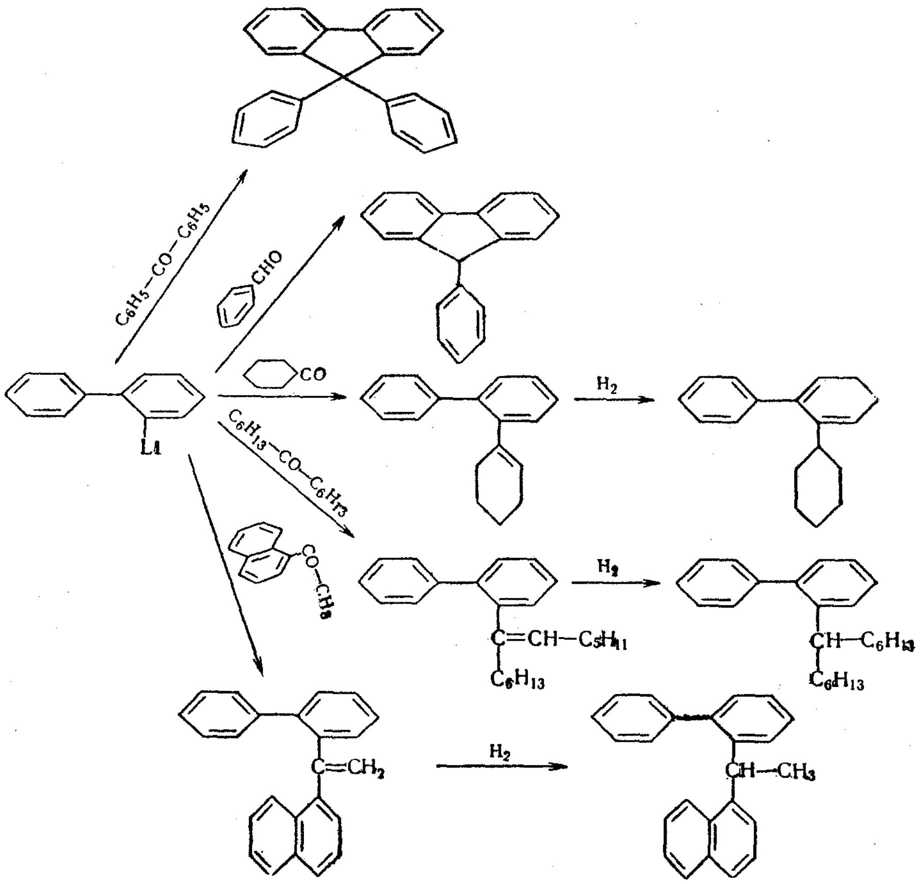
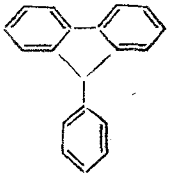
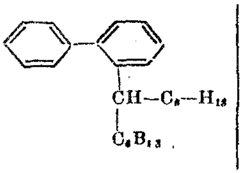
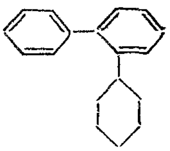
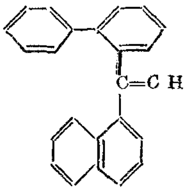
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 1,
pp. 161-166, January, 1963
Original article submitted April 25, 1962

It is known that of the three isomeric monosubstituted biphenyls the 2-isomer has the lowest freezing point. However, the synthesis of 2-derivatives of biphenyl presents certain difficulties because of their ready isomerization into the 3- and 4-isomers or into fluorene derivatives. Thus, an attempt to prepare 2-t-butylbiphenyl [1] by the Grignard reaction was unsuccessful because of the migration of the t-butyl group into the 3- and 4-positions. The reaction of 1,2-dichloro- and 1,2-dibromo-cyclohexenes with benzene and $AlCl_3$ [2], followed by dehydrogenation of the product with sulfur, gives not o-terphenyl, but m- and p-terphenyls.

Bradscher and co-workers [3-6] and some other authors [7, 8] prepared 2-(alkenyl)- and 2-alkyl-biphenyls from 2-bromobiphenyl and magnesium, but the yields were low. Gilman and Gorsich [9] replaced magnesium by lithium and ether by tetrahydrofuran, and they obtained an 84% yield of (2-biphenylyl)diphenylmethanol. We made use of this procedure, and from 2-biphenylyllithium and the appropriate carbonyl compounds we obtained, after dehydration and hydrogenation, various 2-alkyl- and 2-aryl-biphenyls.



We did not succeed in isolating the intermediate tertiary alcohols, because they were partially dehydrated in the course of the synthesis so that we obtained a mixture of an alcohol and an olefin. In experiments with benzaldehyde and with benzophenone cyclodehydration occurred during fractionation, as a result of which we obtained 9-phenyl- and 9,9-diphenyl-fluorenes. The hydrogenation of the aryl olefins over platinum oxide was extremely slow. To prove the structures of the hydrocarbons obtained we determined their ultraviolet and infrared spectra. Ultraviolet spectra were determined with an SF-4 quartz spectrograph. Infrared spectra were determined with an IKS-12 apparatus in the 2800-3000 cm^{-1} region (LiF prism) and with a UR-10 apparatus in the 400-2000 cm^{-1} region (NaCl prism). The results are presented in the table.

Hydrocarbon	Ultraviolet spectrum	Infrared spectrum in 2800-3100 cm^{-1} region	No. of groups	
			CH_2	CH_3
	$\lambda_{max} = 264$ mμ $\varepsilon = 17\,000$ units $\lambda_{max} = 292$ mμ $\lambda_{max} = 304$ mμ	3062, 3026 2920 (w), 2870 (w)	—	—
	$\lambda_{max} = 232$ mμ $\varepsilon = 15\,000$units	3073, 3057, 3020 2955 (200 units), 2927 (700 units), 2870, 2850 cm^{-1}	10	2
	$\lambda_{max} = 234$mμ $\varepsilon = 520$ units	3080, 3062, 3024 2927 (450 units), 2857 cm^{-1}	5	—
	$\lambda_{max} = 235$mμ $\varepsilon = 43\,500$ units $\lambda_{max} = 250$ mμ $\varepsilon = 28\,000$ units	3080, 3064, 3032 cm^{-1}	—	—

As will be seen from the table, for compound (2), (3), and (4) characteristic bands for the fluorene ring system with wavelengths of 265, 292, and 304 mμ were not found. In the ultraviolet all three substances show considerable absorption with a not very prominent maximum at 233-235 mμ (Fig. 1). It is known that such aromatic compounds as 2-phenylbiphenyl and 2,3-diphenylbiphenyl give no strong maxima in the 260-280 mμ region. 2-Monosubstituted biphenyls usually give a small absorption maximum at 233-235 mμ [10]. Our compounds had very weak absorption maxima at 233-235 mμ, which indicates that the hydrocarbons obtained were substituted biphenyls. The infrared spectra of the compounds investigated (Fig. 2) were also different from the infrared spectrum of fluorene. To determine the numbers of the CH_2 and CH_3 groups in the alkyl substituents we determined the infrared spectra in the 2800-3100 cm^{-1} region. By a procedure developed earlier [11] we determined molecular absorption coefficients (ε) for the 2927 and 2955 cm^{-1} bands, which are characteristic for the CH_2 and CH_3 groups respectively. The results of the determinations are given in the table.

EXPERIMENTAL

2-Chloro- and 2-bromo-biphenyls were prepared from 2-phenylphenol [12]. 2-Biphenylyllithium was prepared by Gilman and Olta's method [13]. The yields of 2-biphenylyllithium obtained from 2-chloro- and 2-bromo-biphenyls ranged from 75 to 80%.

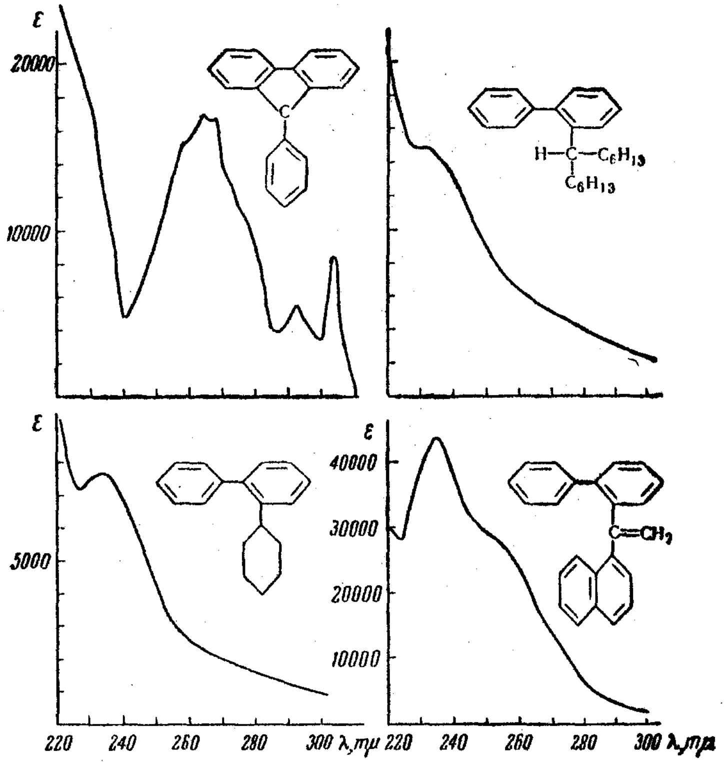


Fig. 1. Ultraviolet spectra of hydrocarbons.

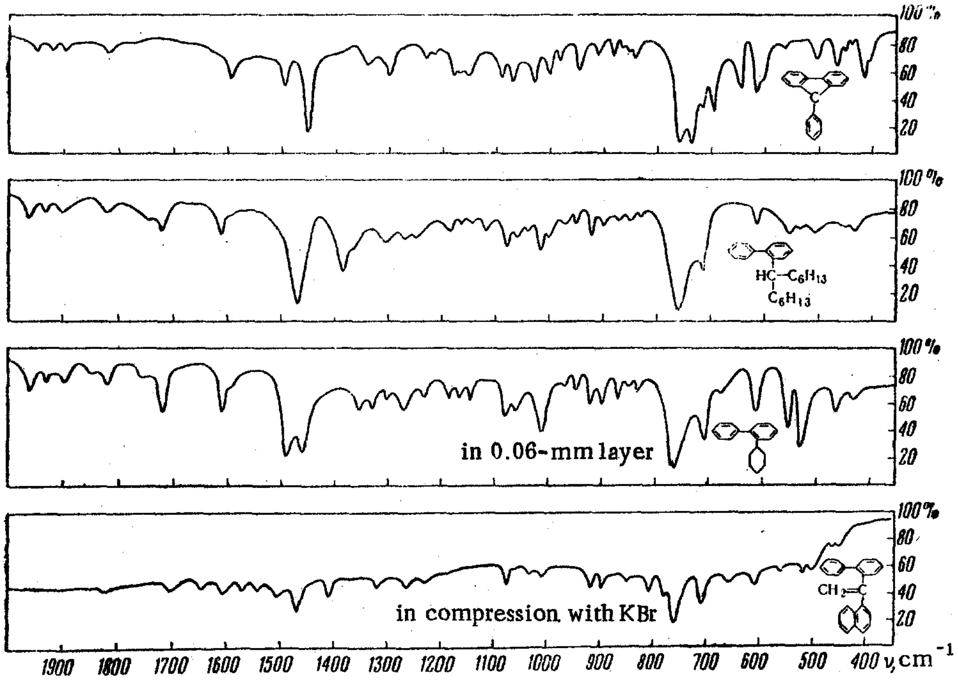


Fig. 2. Infrared spectra of hydrocarbons.

Reaction of 2-Biphenylyllithium with Benzaldehydehyde. The synthesis was carried out in a stream of nitrogen in a 500-ml flask fitted with a mercury-sealed stirrer, a reflux condenser, and a dropping funnel. For reaction we took 2.5 g of lithium, 50 ml of tetrahydrofuran (THF), and 23.5 g of 2-chlorobiphenyl. To the resulting 2-biphenylyllithium, 13.2 g of benzaldehyde in an equal volume of THF was added at 0° over a period of one hour. After the addition of the benzaldehyde the reaction mixture was stirred further for two hours. The product was decomposed with ammonium chloride solution. We obtained 8.5 g of a greasy mass, which was dehydrated over sodium hydrogen sulfate. After being crystallized from ethanol, the phenylfluorene obtained had m.p. 147°. The literature [14] gives m.p. 147-148°.

Reaction of 2-Biphenylyllithium with Cyclohexanone. For reaction we took 2.5 g of lithium, 60 ml of THF, and 30 g of 2-bromobiphenyl in 30 ml of THF. 12.5 g of cyclohexanone in an equal volume of THF was added at −20°. The treatment was as in the preceding experiment. We obtained 2-(cyclohexenyl)biphenyl; b.p. 150-154°/4 mm; n_D^{20} 1.5960; d_4^{20} 1.0535. Found: C 91.64; 91.70; H 7.92; 7.90%; MR 75.5. $C_{18}H_{18}$. Calculated: C 92.25; H 7.74%; MR 75.7.

The product was hydrogenated in glacial acetic acid solution over a platinum oxide catalyst for 25 hours. The reaction was carried out in a long-necked glass flask. 2-Cyclohexylbiphenyl had: b.p. 160-163° (4 mm); f.p. −13° (glass); n_D^{20} 1.5700; d_4^{20} 1.0189. Found: MR 75.15. $C_{18}H_{20}$. Calculated: MR 75.16.

Reaction of 2-Biphenylyllithium with 7-Tridecanone. For reaction we took 3.5 g of lithium, 100 ml of THF, and 47 g of 2-chlorobiphenyl. 49.6 g of 7-tridecanone was added at 0°. The further treatment was as usual. After dehydration over sodium hydrogen sulfate we obtained 2-(1-hexyl-1-heptenyl)biphenyl; b.p. 187-190° (2 mm); n_D^{20} 1.5410; d_4^{20} 0.9670. Found: C 89.71; 89.53; H 10.20; 10.50%; MR 108.7. $C_{25}H_{34}$. Calculated: C 89.75; H 10.24%; MR 108.6.

The double bond was hydrogenated over PtO_2, and we obtained 2-(1-hexylheptyl)biphenyl; b.p. 195-197° (4 mm), f.p. −28° (glass); n_D^{20} 1.5160; d_4^{20} 0.9227. Found: MR 110.3; calculated: MR 110.8.

Reaction of 2-Biphenylyllithium with 1'-Acetonaphthone. For reaction we took 3.5 g of lithium, 60 ml of THF, and 47 g of 2-chlorobiphenyl dissolved in 50 ml of THF. 42.5 g of 1'-acetonaphthone was added at 0°. We obtained 16 g of a glassy product, b.p. 170-200° (3 mm). After two weeks at 0° crystals of 1-(2-biphenylyl)-1-(1-naphthyl)ethylene formed; after being crystallized from hexane the product melted at 87°. Found: C 94.87; 93.88; H 6.04; 5.90%; $C_{24}H_{18}$. Calculated: C 94.07; H 5.92%.

After hydrogenation of the ethylenic bond we obtained 1-(2-biphenylyl)-1-(1-naphthyl)ethane, f.p. 14° (glass).

Reaction of 2-Biphenylyllithium with Benzophenone. For reaction we took 4 g of lithium, 50 g of 2-chlorobiphenyl, and 150 ml of THF. 46 g of benzophenone was added at 10°. We obtained 20 g of a glassy product, b.p. 160-180° (2 mm). On standing the mass crystallized. We obtained 9,9-diphenylfluorene, m.p. 220° (from alcohol). The literature [14] gives m.p. 222°.

SUMMARY

1. By the reaction of 2-biphenylyllithium with carbonyl compounds the following compounds were prepared: 2-cyclohexylbiphenyl, 9-phenylfluorene, 9,9-diphenylfluorene, 2-(1-hexylheptyl)biphenyl, and 1-(2-biphenylyl)-1-(1-naphthyl)ethane.

2. The structures of these hydrocarbons were proved with the aid of ultraviolet and infrared spectra.

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