SYNTHESIS AND SELECTIVE HYDROGENATION OF DIBENZYLBENZENES AND α,α'-BIS(BENZYLPHENYL)XYLENES

(UDC 542.91)

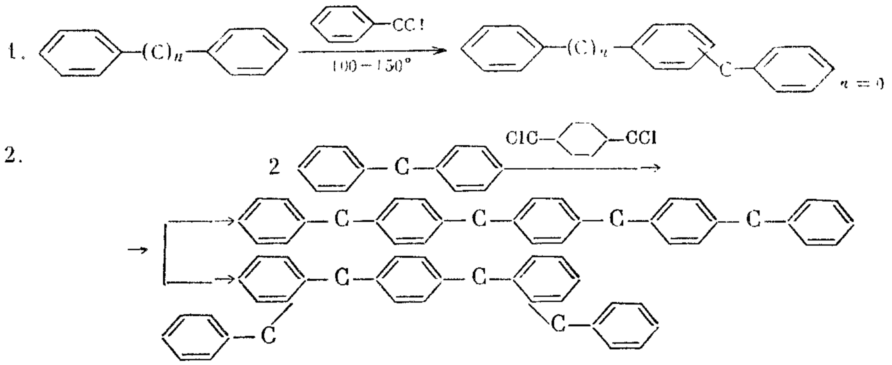
M. A. Chel'tsova, A. D. Petrov, E. D. Lubuzh, and T. E. Eremeeva

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

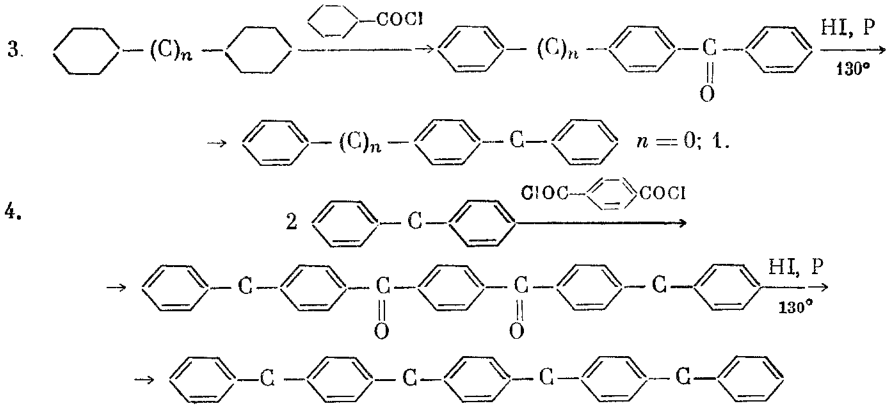
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1,
pp. 124-133, January, 1965
Original article submitted February 22, 1963

In previous investigations [1, 2] we studied the hydrogenation of a number of dibenzylbenzenes at various temperatures and over various catalysts. In the present investigation we have carried out the hydrogenation of dibenzylbenzenes and α,α'-bis(benzylphenyl)xylenes (compounds containing three and five benzene rings, respectively, linked through methylene groups) over nickel and platinum dioxide at various temperatures.

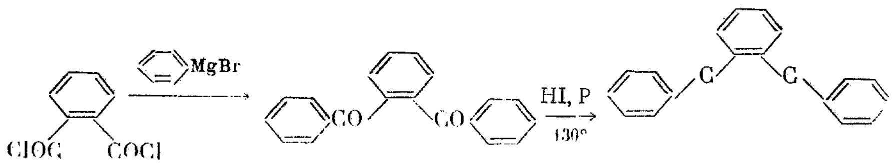
We synthesized the hydrocarbons by the following schemes:



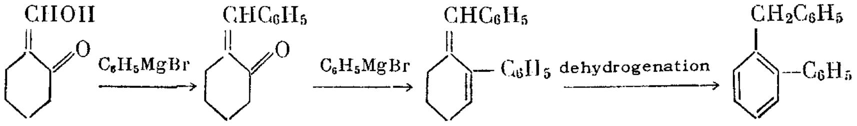
4-Benzylbiphenyl (I), p-dibenzylbenzene (II), and α,α'-bis-p-benzylphenyl-p-xylene (III) were also prepared by the acylation method in accordance with the following schemes:



o-Dibenzylbenzene (IV) was also prepared by organomagnesium synthesis by the scheme:



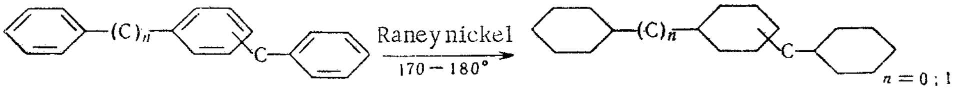
By alkylation of diphenylmethane with benzyl chloride we obtained (IV) and (II)—the latter in the larger amount. In the alkylation of biphenyl with benzyl chloride we obtained all three isomers—2-, 3-, and 4-benzylbiphenyls. The separation of the 2-, 3-, and 4-isomers was effected by fractional distillation and crystallization until a constant melting point was attained. One of these, m.p. 85°, was (I), for on oxidation it gave 4-phenylbenzophenone [3, 4]. This hydrocarbon was also obtained by the acylation method (m.p. 86°). The isomer of m.p. 54-56° has been regarded in the literature both as the 2-isomer [4] and the 3-isomer [5]. However, on the basis of the work of Freeman [6], who synthesized 2-benzylbiphenyl (m.p. 54-56°) as follows



it may be considered that the isomer of m.p. 54-56° is 2-benzylbiphenyl (V), which is confirmed by the ultraviolet spectra (Fig. 1), so that the isomer of m.p. 47° is 3-benzylbiphenyl (VI). The contradictory data on the melting points of (V) and (VI) is to be explained to a certain extent by the fact that their structures cannot be confirmed by the oxidation method [as was done in the case of (I)], for their oxidation goes in an extremely complex fashion [6].

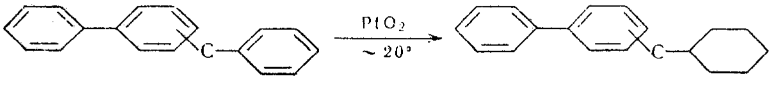
The structure of the 2-isomer of m.p. 56° is confirmed by the absence of an ultraviolet absorption maximum at about 252 mμ. Such a phenomenon is characteristic for ortho-substituted biphenyls and is explained by the disturbance of the coplanarity of the benzene rings of biphenyl [7]. In Fig. 1. we give the ultraviolet spectra of the isomers of m.p. 85 and 47°. The isomer of m.p. 85° gives strong absorption at about 252 mμ (ε 20,000), which indicates the presence of a highly conjugated system characteristic for para isomers of biphenyl derivatives. In the alkylation of α,α'-dichloro-p-xylene with diphenylmethane, in addition to (III) its ortho isomer (VII) is formed (Table 1).

The complete hydrogenation of the hydrocarbons was carried out under a pressure of hydrogen in accordance with the scheme:



The hydrogenation of hydrocarbons of this type goes in almost quantitative yield, and there is no splitting off of rings such as we observed earlier [8] for hydrocarbons of the alkyltriphenylmethane type, in the hydrogenation of which, under the conditions indicated above, a certain amount of alkyldicyclohexylmethanes is always formed. Whereas with the same catalyst but at 100-140° alkyltriphenylmethanes are hydrogenated to alkyldicyclohexylphenylmethanes, and 1-p-benzylphenyl-2-phenylethane to 1-p-(cyclohexylmethyl)phenyl-2-phenylethane in about 50% yield, (I) is not hydrogenated at all at 120°, but at 140° is hydrogenated to 4-(cyclohexylmethyl)biphenyl in 2-3% yield.

(III) is not hydrogenated either at 120° or at 140°, but at 170-180° all five rings are hydrogenated (bands characteristic for aromatic rings are absent from the ultraviolet spectrum). Interesting results were obtained in the hydrogenation of the hydrocarbons at identical temperature and in the same solvents over a platinum catalyst. In the case of (V), (VI), and (I) only one ring is hydrogenated in accordance with the scheme:



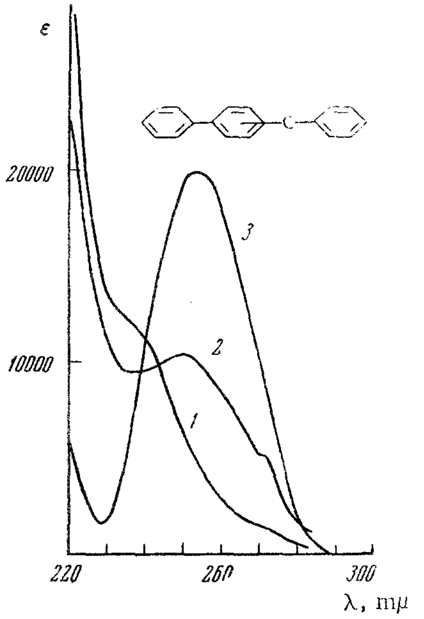


Fig. 1. Ultraviolet spectra: 1) 2-benzylbiphenyl; 2) 3-benzylbiphenyl; 3) 4-benzylbiphenyl.

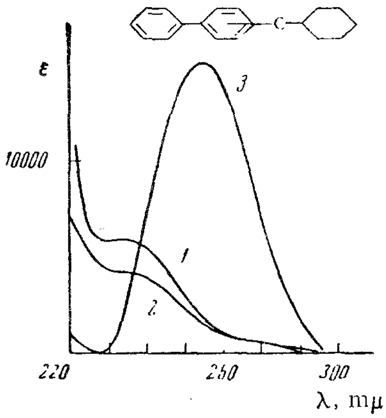
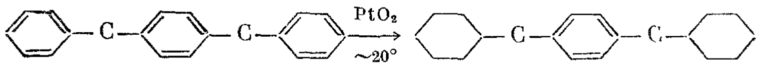


Fig. 2. Ultraviolet spectra: 1) 2-(cyclohexylmethyl)biphenyl; 2) 3-(cyclohexylmethyl)biphenyl; 3) 4-(cyclohexylmethyl)biphenyl.

The structures of the hydrogenation products were confirmed by their ultraviolet spectra. Thus, the hydrogenation product (I) (m.p. 58°) shows strong ultraviolet absorption characteristic for the conjugated system of biphenyl (Fig. 2, Curve 3), so that it may be assumed that it is the benzyl group that is hydrogenated. Figure 2 shows also the ultraviolet spectra of the hydrogenation products (V) and (VI), in which there is no strong absorption at about 252 mμ; this is indicative of the disturbance of the coplanarity of the system of these hydrocarbons. In the case of (II), two rings are hydrogenated as follows:



The number of CH_2 groups was determined by the method developed earlier [9]. In the case of the hydrogenation product (II) the infrared spectrum contains absorption bands characteristic for a p-disubstituted benzene ring (812 cm^{-1}). In the case of (III) all five rings are hydrogenated. Table 2 gives the numbers of CH_2 groups. The hydrogenation of all five rings in (III) is possibly the consequence of the conjugation in this molecule, which is to a certain extent confirmed by the magnitude of the conductivity of the hydrocarbon ($\sigma_{100} \sim 10^{-13}\ \Omega^{-1} \cdot cm^{-1}$, E_σ 3.5-4 eV).

The difference in melting point (Table 1) between the aromatic compounds (dibenzylbenzenes and bisbenzylphenylxylenes) and their full and partial hydrogenation products varies with the structures of the hydrocarbons. For example, in the transition from (III) to its full hydrogenation product the melting point falls by almost 60° (Nos. 7 and 17, Table 1). A particularly high fall (more than 100°) is found in the transition from (I) to 4-(cyclohexylmethyl)bicyclohexyl (Nos. 1 and 12, Table 1). An appreciable fall in melting point (more than 60°) is observed also in the transition from (V) to 2-(cyclohexylmethyl)biphenyl (Nos. 2 and 9, Table 1) and from (VI) to 3-(cyclohexylmethyl)biphenyl (50°, Nos. 3 and 10, Table 1). In a number of cases, however, hydrogenation, either full or partial, does not affect the melting points appreciably (Nos. 1 and 8 and Nos. 11 and 15, Table 1).

EXPERIMENTAL*

All fully and partially hydrogenated hydrocarbons were purified by adsorption chromatography in hexane solution on ASM silica gel (height of lower part of column 520 mm, diameter 12 mm; height of upper part of column 400 mm, diameter 22 mm). Elution was with hexane, benzene, and ethanol successively.

---

*Senior laboratory worker V. P. Yaroshenko took part in the experimental work.

TABLE 1

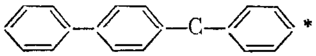
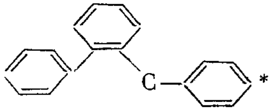
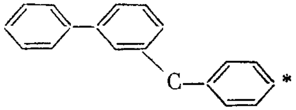
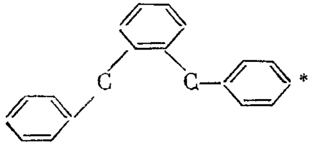
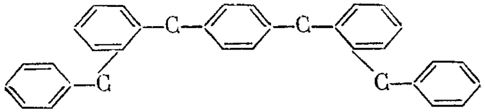
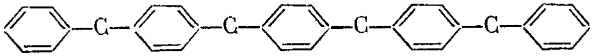
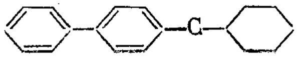
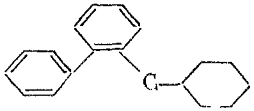
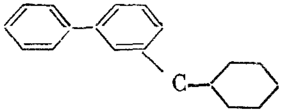
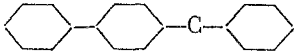
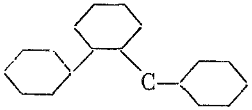
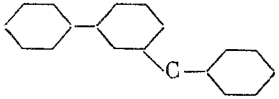
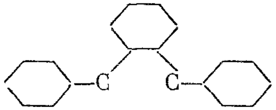
No.	Formula of substance	Molecular formula	B.p., °C (p, mm)	M.p., °C	n_D^{20}	d_4^{20}	MR found	MR calcd.
1		$C_{19}H_{16}$	—	86	—	—	—	—
2		$C_{19}H_{16}$	—	56	—	—	—	—
3		$C_{19}H_{16}$	—	47	—	—	—	—
4		$C_{20}H_{18}$	—	86	—	—	—	—
5		$C_{20}H_{18}$	—	66	—	—	—	—
6		$C_{34}H_{30}$	—	64	—	—	—	—
7		$C_{34}H_{30}$	—	121	—	—	—	—
8		$C_{19}H_{22}$	—	58	—	—	—	—

TABLE 1 (continuation)

No.	Formula of substance	Molecular formula	B.p., °C (p, mm)	M.p., °C	n_D^{20}	d_4^{20}	*MR*	
							found	calcd.
9		$C_{19}H_{22}$	140 (0,5)	—12	1,5594	0,9931	81,43	80,54
10		$C_{19}H_{22}$	148 (0,5)	—5	1,5572	0,9925	81,17	80,54
11		$C_{20}H_{30}$	—	85	—	—	—	—
12		$C_{19}H_{34}$	141 (0,5)	—32	1,4885	0,9240	83,26	83,34
13		$C_{19}H_{34}$	—	62	—	—	—	—
14		$C_{19}H_{34}$	—	65	—	—	—	—
15		$C_{20}H_{36}$	a) — b) 146—147 (0,5)	a) 86—87 b) —25	1,4950	0,9184	8749	87,96
16		$C_{20}H_{36}$	—	59—60	—	—	—	—
17		$C_{34}H_{60}$	—	63	—	—	—	—

---

*Nos. 1 and 2 [4], 3 [5], 4 [9], 5 [11], and 7 [14] have been prepared previously.

TABLE 2

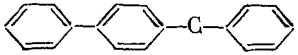
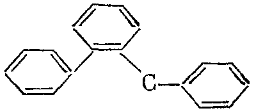
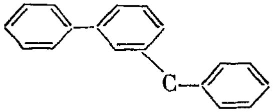
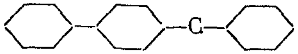
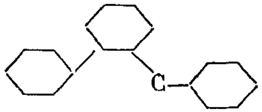
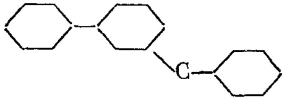
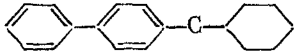
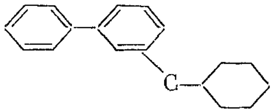
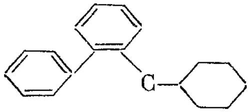
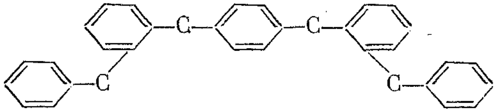
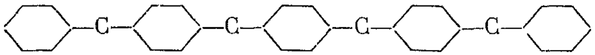
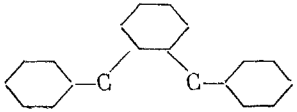
No.	Formula of substance	Ultraviolet spectrum	No. of CH_2 groups		
			calcd.	CH_2 2920	found
1		Strong maximum, λ 252 mμ, ε 20,000	1	33 units	1
2		Stong absorption without maximum λ 250 mμ, ε 6500	1	24 units	1
3		Strong absorption, weak maximum, λ 250 mμ, ε 10,400	1	22 units	1
4		No absorption (no aromatics)	15	1140 units	15,2
5		The same	15	1260 units	16,8
6		»	15	1180 units	15,8
7		λ 252 mμ, ε 15,000	6	485 units	6,5

TABLE 2 (continuation)

No.	Formula of substance	Ultraviolet spectrum	No. of CH_2 groups		
			calcd.	**CH_2 2920**	found
8		Weak maximum, λ 235 mμ, ε 4,200	6	550 units	7,3
9		Weak maximum, λ 235 mμ	6	550 units	7,3
10		λ 260 mμ 266, 276, ε 204, 202, 141	4	108 units	4
11		No absorption (no aromatics)	26	1950 units	26
12		λ 254 mμ 260, 266, 264, ε 474, 484,	12	860 units	11,5
13		No absorption (no aromatics)	16	1215 units	16,2
14		The same	16	1260 units	16,8

The ultraviolet spectra were run on a Soviet SF-4 spectrograph in hexane solution. Infrared spectra were determined on an IKS-12 spectrograph with an LiF prism in the range 800-3100 cm^{-1} and on an IKS-14 spectrograph with an NaCl prism in the range 700-2000 cm^{-1}. The number of CH_2 groups was determined from the molecular absorption coefficient ε for the band due to the antisymmetrical stretching CH vibrations of CH_2 groups. The measuring procedure was described earlier. Ultraviolet and infrared data are given in Table 2.

In the alkylation of biphenyl (100 g) with benzyl chloride (150 g) at 100° in presence of small amounts of zinc dust we obtained 65 g of a crystalline mixture of benzylbiphenyl isomers. After numerous crystallizations we isolated: (I), m.p. 85°, yield 25%; (VI), m.p. 47°, yield 12%; and (V), m.p. 56°, yield 25%. In addition, (I) was prepared by the acylation of biphenyl with benzoyl chloride and the reduction of the product. From 200 g of benzoic acid and 120 g of thionyl chloride we obtained 209 g (91%) of benzoyl chloride; b.p. 197-198°; n_D^{20} 1.5520; d_4^{20} 1.2101. From 200 g of biphenyl and 100 g of benzoyl chloride (with the gradual addition of 100 g of aluminum chloride at 20°) we obtained 78 g (43%) of 4-phenylbenzophenone, m.p. 100-101° (the literature [10] gives m.p. 102°). 26 g of the ketone was reduced with HI (47 g) in presence of red phosphorus (9.5 g) at 130-150° for 20 h. The mixture was poured into water, the crystalline product was dissolved in ether, and red phosphorus was filtered off from the ethereal solution, which was then evaporated. The residue was dissolved in acetone, and the solution was poured into sodium bisulfite solution (20 g in 500 ml of water) to free it from iodine compounds. We obtained 22 g (90%) of a hydrocarbon of m.p. 85-86°. The experiment was repeated several times, and we obtained 65 g of the hydrocarbon. 15 g of (I) was hydrogenated over 5 g of Raney nickel in 100 ml of cyclohexane at 120° for 8 h. The melting point of the product was 85°, undepressed by admixture of the original hydrocarbon. The experiment was repeated with 12 g of the same hydrocarbon at 140°. The hydrogenation product was separated on silica gel. We obtained 0.3 g of 4-(cyclohexlmethyl)biphenyl, m.p. 57.5°, and 11 g of unchanged starting substance. In the hydrogenation of 9 g of (I) over 3 g of Raney nickel in 150 ml of cyclohexane at 170-180° under a pressure of hydrogen until no more hydrogen was absorbed we obtained a product from which, after purification on silica gel and vacuum distillation, we obtained 6.5 g of 4-(cyclohexylmethyl)bicyclohexyl, b.p. 141° (0.5 mm) (see Table 1). In the hydrogenation of 1 g of (I) in 50 ml of glacial acetic acid over 0.1 g of PtO_2 we obtained, after purification on silica gel, 0.5 g of a hydrocarbon of m.p. 58°, undepressed by admixture of the 4-(cyclohexylmethyl)biphenyl prepared above.

(V) (3 g) was hydrogenated over 1 g of Raney nickel in 50 ml of cyclohexane at 170-180° under a pressure of hydrogen. After purification on silica gel we obtained 2 g of 2-(cyclohexylmethyl)bicyclohexyl, m.p. 62° (Table 1).

(V) (1 g) was hydrogenated in 50 ml of acetic acid over 0.1 g of PtO_2 at room temperature. After purification on silica gel we obtained 0.7 g of a product with n_D = 1.558 (which corresponds to hydrocarbons with two aromatic and one cyclohexane rings). The experiment was repeated with 2.4 g of the original hydrocarbon, and as a result we obtained 1.7 g of 2-(cyclohexymethyl)biphenyl (see Table 1). 6 g of (VI) was hydrogenated in 100 ml of cyclohexane over 2 g of Raney nickel under a pressure of hydrogen (until no more was absorbed). After purification on silica gel we obtained 4.2 g of 3-(cyclohexylmethyl)bicyclohexyl, m.p. 65° (see Table 1). (VI) (2 g) was hydrogenated in 100 ml of glacial acetic acid over 0.2 g of PtO_2 at room temperature. After purification on silica gel we obtained 3-(cyclohexylmethyl)biphenyl, b.p. 148° (0.5 mm) (see Table 1). In the alkylation of 100 g of diphenylmethane with benzyl chloride (75 g) at 140-150° in presence of small amounts of zinc dust we obtained, after unchanged diphenylmethane had been distilled off (50 g), 24 g (50%) of a product of b.p. 225-245° (1 mm) and m.p. 59°. After repeated fractional crystallization from ethanol we obtained 12 g (26%) of (II) with a constant m.p. of 86° and 8 g (17%) of (IV) with a constant m.p. of 66°.* For (II) the literature [10] gives m.p. 86°, and for (IV) it [11] gives m.p. 66°. (II) was also prepared from terephthaloyl chloride and benzene with reduction of the product. From 100 g of terephthalic acid and 350 g of thionyl chloride we obtained 105 g of terephthaloyl chloride, m.p. 78-79°. From 105 g of the latter, 156 g of benzene, and 150 g of $AlCl_3$ (added gradually at room temperature) after the usual treatment of the resulting mixture we isolated 99 g (67%) of p-dibenzoylbenzene, m.p. 160° (the literature [12] gives m.p. 159-160°). 100 g of p-dibenzoylbenzene was heated with 180 g of HI (47%) and 42 g of red phosphorus at 140-150° for 30 h. The mixture was then poured into water, and the crystalline product was dissolved in ether. After removal of red phosphorus the solution was evaporated, the residue was dissolved in acetone, and the resulting solution was poured into a solution of sodium bisulfite (20 g in 500 ml of water) to remove iodine. We obtained 81 g (89.8%) of (II), m.p. 86° (from alcohol). 7 g of (II) was hydrogenated over 2 g of Raney nickel in 50 ml of cyclohexane at 170-180° (until no more hydrogen was absorbed). We obtained 1,4-biscyclohexylmethylcyclohexane, which by

---

*Wu Chung-yü, a student of the Moscow Institute of Chemical Technology, took part in the synthesis and hydrogenation of (IV) and (II).

absorption chromatography on silica gel we separated into two forms. One of these had m.p. 86-87°, and the other froze at −25° (see Table 1). There was no difference between the infrared spectra of the two forms. 1 g of (II) was hydrogenated in 50 ml of glacial acetic acid over 0.05 g of PtO_2 at about 20°. After purification on silica gel we obtained 0.5 g of p-biscyclohexylmethylbenzene, m.p. 85°. A mixture with the original (II) melted at 63°, and the depression in melting point was 22°. For data on the ultraviolet and infrared spectra see Table 2. Since the preparation of (IV) by the acylation method was difficult, we prepared this hydrocarbon by organomagnesium synthesis [3]. Phenylmagnesium bromide (from 32 g of magnesium and 212 g of bromobenzene) was added with cooling to −15° to a solution of 115 g of phthaloyl chloride in a mixture of benzene and ether, and the mixture was heated in a water bath for 30 min and then decomposed with ice and HCl. After the usual treatment and the removal of solvent we obtained 20 g of the corresponding diketone, m.p. 145-147° (the literature [13] gives m.p. 145-146°). In the reduction of 20 g of the diketone under the conditions stated above for p-dibenzoylbenzene we obtained a crystalline product, from which by fractional crystallization we isolated (IV), m.p. 64°. 7 g of (IV) was hydrogenated over 2 g of Raney nickel in 50 ml of cyclohexane at 170-180° (until no more hydrogen was absorbed). After purification on silica gel we obtained 1,2-biscyclohexylmethylcyclohexane, m.p. 59-60° (see Table 1). For data on the ultraviolet and infrared spectra see Table 2. In the alkylation of 114 g of diphenylmethane with 20 g of α,α'-dichloro-p-xylene at 150° in presence of a little zinc dust we obtained the alkylation product. The experiment was repeated with 20 and 36 g of α,α'-dichloro-p-xylene, and in all we obtained 32 g of alkylation product, from which by fractional distillations and fractional crystallizations we isolated 12 g of (III) [14], m.p. 121°, and 6 g of (VII), m.p. 63-64° (see Table 1). For data on the ultraviolet and infrared spectra see Table 2. 18 g of (III) was hydrogenated over 6 g of Raney nickel at 170-180° (until no more hydrogen was absorbed). After purification on silica gel we obtained 15 g of fully hydrogenated product, m.p. 63° (see Table 1). For the ultraviolet and infrared spectra see Table 2.

The conductivity determinations were made by A. A. Dulov, whom we thank.

SUMMARY

1. The following previously undescribed hydrocarbons were prepared: 2-(cyclohexylmethyl)biphenyl, 3-(cyclohexylmethyl)biphenyl, 4-(cyclohexylmethyl)biphenyl, p-biscyclohexylmethylbenzene, 2-(cyclohexylmethyl)bicyclohexyl, 3-(cyclohexylmethyl)bicyclohexyl, 4-(cyclohexylmethyl)bicyclohexyl, 1,2-biscyclohexylmethylcyclohexane, 1,4-biscyclohexylmethylcyclohexane, α,α'-bis-o-benzylphenylxylene, and 1,4-bis[[4-(cyclohexylmethyl)cyclohexyl]methyl] cyclohexane.

2. The hydrogenation of dibenzylbenzenes and α,α'-bisbenzylphenylxylenes of various structure goes in various ways. Thus, under identical conditions of hydrogenation over PtO_2 in 2-, 3-, and 4-benzylbiphenyls only one ring is hydrogenated, in p-dibenzylbenzene two rings are hydrogenated, and in α,α'-bis-p-benzylphenyl-p-xylene all five rings are hydrogenated. The selective hydrogenation of α,α'-bis-p-benzylphenyl-p-xylene could not be effected, either over PtO_2 or over Raney nickel.

LITERATURE CITED

1. M. A. Chel'tsova, A. D. Petrov, and V. I. Grigos, Izv. AN SSSR. Otd. khim. n., 1961, 294.
2. M. A. Chel'tsova and A. D. Petrov, Izv. AN SSSR. Otd. khim. n., 1961, 2209.
3. E. Clar, Fr. John, and B. Hawran, Ber. Chem., 62, 940 (1929).
4. G. Goldschmiedt, Monatschefte chem., 2, 432 (1881).
5. G. Igloff, Physical Constants of Hydrocarbons, 3 (1946), p. 486.
6. I. P. Freeman, J. Amer. Chem. Soc., 80, 1929 (1958).
7. E. A. Braude and W. F. Forbes, J. Chem. Soc., 1955, 3776; B. Williamson and W. H. Rodebush, J. Amer. Chem. Soc., 63, 3018 (1957).
8. M. A. Chel'tsova and A. D. Petrov, Zh. obshch. khimii, 27, 600 (1957).
9. Yu. P. Egorov and E. D. Lubuzh, Dokl. AN SSSR, 136, 342 (1961).
10. S. S. Nametkin and D. N. Kursanov, Zh. obshch. khimii, 60, 919 (1928).
11. N. Sharma and S. Dumt, J. Indian Chem. Soc., 12, 774 (1935).
12. I. Munchmeyer, Ber. Chem., 19, 1847 (1886).
13. F. Seidel, Ber. Chem., 61, 2267 (1928).
14. M. A. Chel'tsova, Wu Chung-yü, and E. D. Lubuzh, Izv. AN SSSR. Otd. khim. n., 1962, 1470.