SYNTHESIS AND PROPERTIES OF DI- AND TRIPHENYLALKANES

COMMUNICATION 4. SELECTIVE HYDROGENATION OF DI- AND TRIPHENYLALKANES OVER PtO_2

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In previous work [1-3] we prepared some mixed tricyclic hydrocarbons of the type $(C_6H_{11})_2(C_6H_5)CR$, where $R = C_4$, C_4-g , C_7, $-C-(C)_6$, $-C-(C)_4$, by selective hydrogenation of the corresponding triphenylalkylmethanes over Raney nickel, under a pressure of H_2, at temperatures of 100-140°. No hydrocarbons of the series $(C_6H_5)_2(C_6H_{11})CR$ or $(C_6H_{11})_3CR$ were formed under these conditions. The presence of two cyclohexyl rings at one carbon atom in the molecule apparently creates definite steric hindrance to the hydrogenation of the third ring. In the present investigation we continued the synthesis of di- and triphenyl alkanes, but mainly of a different type with the phenyl rings distributed along the chain, and platinum oxide was used as the hydrogenation catalyst. We prepared 1,7-diphenyl-4-(3-phenylpropyl)heptane, 1,1,1-tritolylheptane, and 1,7-diphenyl-4-(2-cyclohexylethyl)heptane by organomagnesium synthesis. The properties of all the hydrocarbons are given in the table.

The hydrogenation of the first two hydrocarbons over Raney nickel at 170-180° under a pressure of H_2 yielded 1,7-dicyclohexyl-4-(3-cyclohexylpropyl)-heptane and 1,1,1-trimethylcyclohexylheptane, which have not been described in the literature. Under the same conditions, 1,1,4,4-tetraphenylbutane and 1,1,6,6-tetraphenylhexane yielded 1,1,4,4-tetracyclohexylbutane and 1,1,6,6-tetracyclohexylhexane, respectively, which have not been described in the literature previously. The following hydrocarbons, some of which were synthesized for the first time and others previously, were hydrogenated over platinum oxide prepared by Adams' method [4]: 1,1,1-triphenylheptane, 1-phenyl-3-(2-phenylethyl)tridecane, 1,7-diphenyl-4-(2-phenylethyl)heptane, 1,5-diphenyl-3-(2-phenylethyl)pentane, 1,7-diphenyl-4-cyclohexylheptane, 1-phenyl-4-(3-phenylpropyl)decane, 1,1,4,4-tetraphenylbutane, and 1,1,6,6-tetraphenylhexane. It was found that 1,1,1-triphenylheptane, 1,1,1-tritolylheptane, 1,1,4,4-tetraphenylbutane, and 1,1,6,6-tetraphenylhexane do not add hydrogen at room temperature over platinum oxide. The other hydrocarbons added sufficient hydrogen for the hydrogenation of one ring and we obtained the following hydrocarbons with cyclohexyl and phenyl rings in the molecule which have not been described in the literature previously: 1,7-diphenyl-4-(3-cyclohexylpropyl)heptane, 1,5-diphenyl-3-(2-cyclohexylethyl)pentane, 1-phenyl-4,7-dicyclohexylheptane, 1-phenyl-4-(3-cyclohexylpropyl)decane, 1-cyclohexyl-4-(3-cyclohexylpropyl)decane, 1-phenyl-3-(2-cyclohexylethyl)tridecane, 1-phenyl-4-(2-phenylethyl)-7-cyclohexylheptane.

Most of these hydrocarbons were purified by chromatography on a two-stage column with a lower section 56.5 cm in height and 1.0 in diameter and an upper section 42.0 cm in height and 2.2 cm in diameter. The column was packed with 150 g of ASM grade silica gel. On comparing the properties of the hydrocarbons given in the table both with each other and with the properties of hydrocarbons prepared previously [1-3], one finds a series of new examples of changes in the properties of hydrocarbons as a result of changes in their structures. 1,1,1-Triphenylheptane, which was obtained previously, melted at 76.5°, while 1,1,1-tritolylheptane melted at 23°. 1,1,1-Triphenyldecane, which has the same molecular weight as the latter hydrocarbon, melted at 30°. The viscosity of 1,1,1-tritolylheptane was considerably greater than the viscosities of the other two hydrocarbons given. The product of complete hydrogenation of 1,1,1-tritolylheptane had a lower viscosity than the starting aromatic hydrocarbon. This is the first case of a fall in viscosity with a change from aromatic hydrocarbons to naphthenes among three-ring alkanes. The change to naphthenes is normally accompanied by a considerable increase in viscosity.

The 1,7-diphenyl-4-(3-phenylpropyl)heptane obtained in the present work melted at 5°, while a series of triphenylalkanes of similar structure, namely, 1,4,7-triphenylheptane, 1,7-diphenyl-4-benzylheptane, etc., [3] melted within the range of −25 to −35°. The viscosity of 1,7-diphenyl-4-(3-phenylpropyl)heptane was also greater than

Sample No.	Hydrocarbon	Formula	B.p. °C (p, mm Hg)	Solidification p., °C	$_{4}^{20}$	n_D^{20}	MR		Found, %		Calculated, %		Viscosity, centistokes			
							found	calc.	C	H	C	H	20°	50°	100°	150°
1	$(C_6H_5CH_2CH_2)_2CHCH_2CH_2C_6H_{11}$	$C_{25}H_{34}$	210—212(1)	—35, glass	0,9506	1,5300	108,63	108,25	89,30 89,25	10,80 10,70	89,74	10,26	107,75	21,55	9,6	2,12
2	$(C_6H_5CH_2CH_2CH_2)_3CH$	$C_{28}H_{34}$	260—262(5)	5, glass	1,0165	1,5710	119,7	120,7	90,70 90,72	9,13 9,23	90,74	9,26	—	173,74	13,47	3,98
3	$(C_6H_4CH_3)_3CC_6H_{13}$	$C_{28}H_{34}$	241—242(1)	23, glass	0,9932*	1,5710*	122,5	120,7	90,75 90,72	9,13 9,23	90,74	9,26	—	1454,6	30,15	5,45
4	$C_6H_5CH_2CH_2CH_2\underset{\substack{\vert\\ C_6H_{11}}}{CH}CH_2CH_2CH_2C_6H_{11}$	$C_{25}H_{40}$	193—194(1)	—32, glass	0,9357	1,5140	109,52	109,30	87,27 87,23	11,78 11,78	88,15	11,85	170,14	25,37	4,03	1,61
5	$C_6H_5CH_2CH_2CH_2\underset{\substack{\vert\\ C_6H_{13}}}{CH}CH_2CH_2CH_2C_6H_{11}$	$C_{25}H_{42}$	194—195(1)	—60, glass	0,8964	1,4970	111,77	111,85	87,90 87,73	12,11 12,11	87,61	12,39	68,46	10,47	2,58	1,21
6	$C_6H_5CH_2CH_2CH_2\underset{\substack{\vert\\ CH_2CH_2C_6H_5}}{CH}CH_2CH_2CH_2C_6H_{11}$	$C_{27}H_{38}$	225—227(2)	—30, glass	0,9577	1,5318	117,23	117,49	89,24 89,33	10,52 10,80	89,40	10,60	65,0	20,53	4,65	2,05
7	$C_6H_5CH_2CH_2CH_2\underset{\substack{\vert\\ CH_2CH_2C_6H_{11}}}{CH}—CH_2CH_2CH_2C_6H_5$	$C_{27}H_{38}$	185(0,5)	—23, glass	0,9685	1,5395	117,31	117,49	89,58 89,85	10,33 10,21	89,40	10,60	488,78	49,88	6,55	2,52
8	$C_6H_5CH_2CH_2\underset{\substack{\vert\\ C_{10}H_{21}}}{CH}CH_2CH_2C_6H_{11}$	$C_{27}H_{46}$	207—208(1)	—50, glass	0,8885	1,4930	121,18	121,09	87,77 87,63	12,58 12,47	87,45	12,54	26,78	7,85	2,42	1,17
9	$(C_6H_{10}CH_3)_3C\cdot C_6H_{13}$**	$C_{28}H_{52}$	160—162(0,5)	—5, glass	0,9223	1,5080	125,57	124,90	87,35 87,59	12,30 12,10	86,50	13,50	3910,8	131,54	9,00	2,79
10	$(C_6H_{11}CH_2CH_2CH_2)_3CH$	$C_{28}H_{52}$	244(2)	0, glass	0,9251	1,5020	124,0	124,9	86,95 87,12	13,18 13,19	86,49	13,51	8750,0	945,38	20,91	5,35
11	$(C_6H_5CH_2CH_2CH_2)_2CHCH_2CH_2CH_2C_6H_{11}$	$C_{28}H_{40}$	213—215(0,5)	—10, glass	0,9651	1,5380	122,37	122,10	88,49 88,67	11,38 11,56	89,27	10,73	2660,6	167,47	13,60	4,03
12	$C_6H_{11}CH_2CH_2CH_2\underset{\substack{\vert\\ C_6H_{13}}}{CH}CH_2CH_2CH_2C_6H_{11}$	$C_{25}H_{48}$	192(1)	—55, glass	0,8682	1,4760	113,24	113,25	86,10 86,13	13,83 13,91	86,01	13,92	46,31	11,68	5,22	2,07
13	$(C_6H_{11})_2CHCH_2CH_2CH(C_6H_{11})_2$	$C_{28}H_{50}$	—	—80, crystals	—	—	—	—	86,93 86,97	13,03 12,96	86,93	13,07	—	—	—	—
14	$(C_6H_{11})_2CHCH_2CH_2CH_2CH_2CH(C_6H_{11})_2$	$C_{30}H_{54}$	—	—127, crystals	—	—	—	—	86,80 86,79	12,94 12,90	86,85	13,15	—	—	—	—

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* At 40°.

** Mol. wt. 386.5; calculated 388.

the viscosities of the other hydrocarbons given. On the basis of the latter circumstance we first assumed that the dehydration of the corresponding alcohol, namely, 1,7-diphenyl-4-(3-phenylpropyl)heptanol-4 resulted in the formation of a hydrindan ring in the molecule, the more so as this alcohol required considerably more drastic conditions for dehydration than alcohols of similar structure. However, the ultraviolet spectrum of the hydrocarbon indicated that the molecule contained only benzene rings. The increase in viscosity and the rise in solidification point are apparently explained solely by the higher symmetry of the molecule $(C_6H_5-CH_2CH_2CH_2)_3CH$. The small rule holds for the products of complete hydrogenation of the hydrocarbons given. An increase in the side chain from C_6H_{11} to $CH_2CH_2C_6H_{11}$ lowered the solidification point from −20 to −25° and the viscosity from 423 to 279 centistokes at 20° and from 49 to 35 centistokes at 50°. A further increase in the side chain to $CH_2CH_2CH_2C_6H_{11}$ raised the solidification point to 0° and the viscosity to 8750 centistokes at 20° and 945 centistokes at 50° and this can also be explained by the higher symmetry of the molecule $(C_6H_{11}CH_2CH_2CH_2)_3CH$.

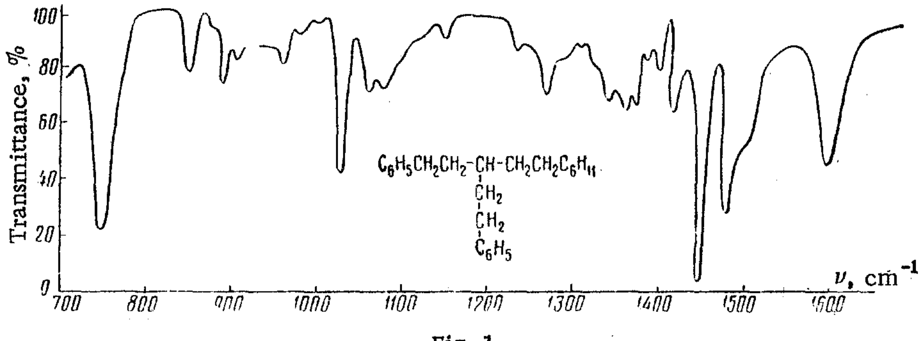

Fig. 1.

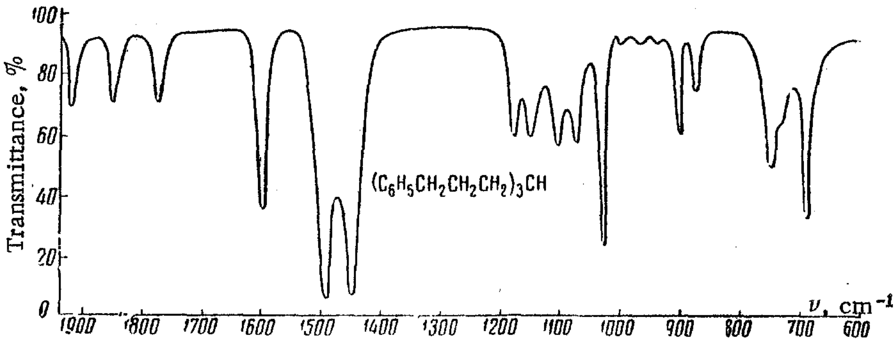

Fig. 2.

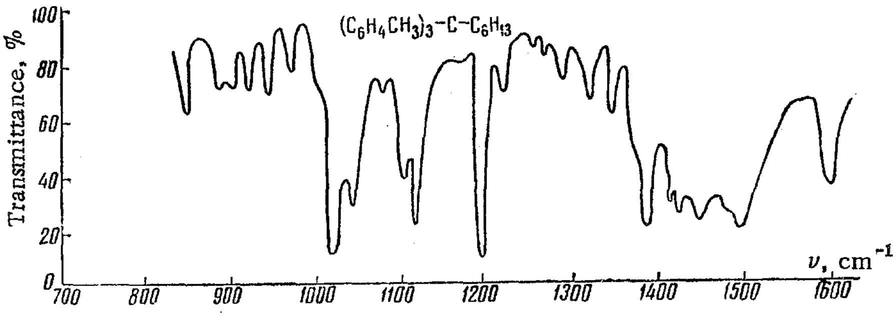

Fig. 3.

With the naphthene–aromatic hydrocarbons we obtained, the solidification point was often lower and the viscosity higher than in the case of the starting aromatic hydrocarbons. The viscosities of the complete hydrogenation products were even higher. Thus, for example, 1,5-diphenyl-3-(2-phenylethyl)pentane solidified at −32° [5] and the corresponding naphthene melted at 41° [5], while 1,5-diphenyl-3-(2-cyclohexylethyl)pentane solidified at −35°. In exactly the same way, 1-phenyl-4,7-dicyclohexylheptane solidified at a lower temperature than 1,4,7-triphenyl- and 1,4,7-tricyclohexylheptanes [3].

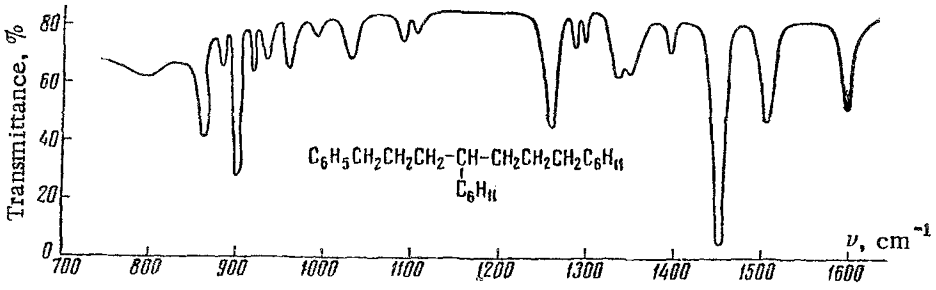

Fig. 4.

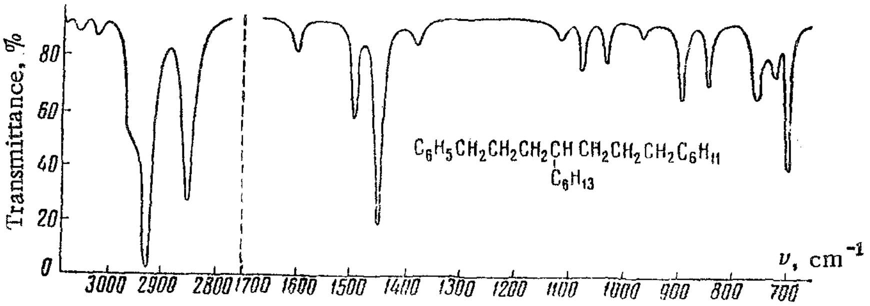

Fig. 5.

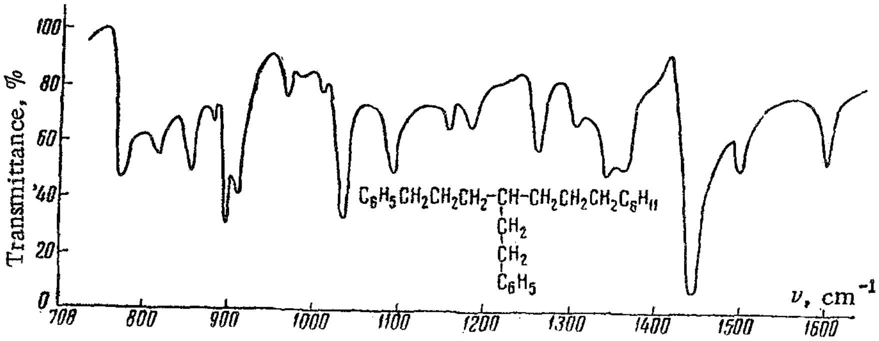

Fig. 6.

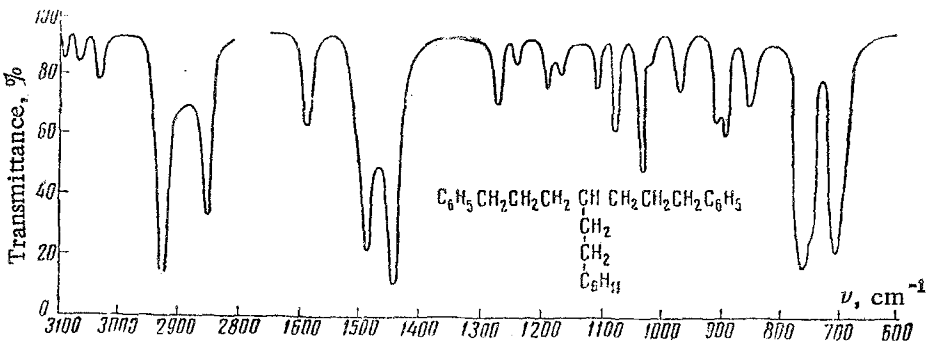

Fig. 7.

We consider that in the hydrogenation of 1,7-diphenyl-(2-phenylethyl)heptane, the ring farthest from the center of the molecule was hydrogenated. This was confirmed to some extent by the difference in the properties of this hydrocarbon and those of 1,7-diphenyl-4-(2-cyclohexylethyl)heptane, which we synthesized (Table No. 6 and 7).

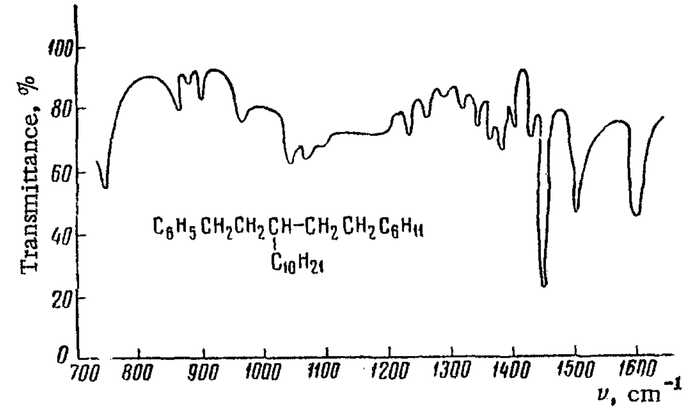

Fig. 8.

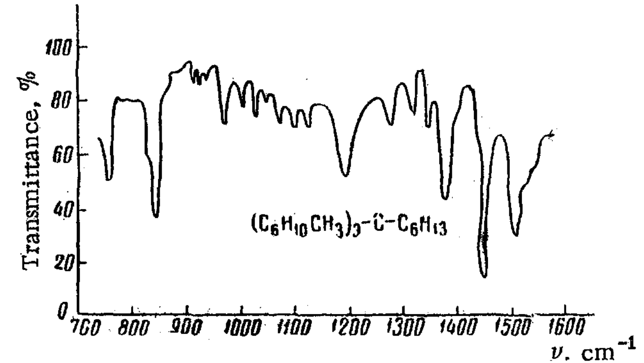

Fig. 9.

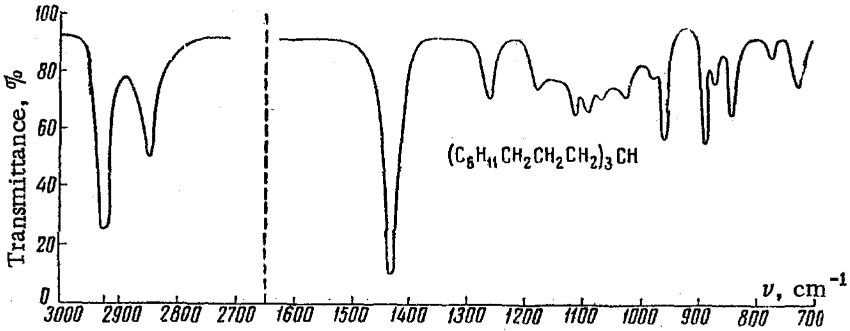

Fig. 10.

We plotted the infrared spectra of all the hydrocarbons we obtained and the ultraviolet spectrum of $(C_6H_5CH_2CH_2CH_2)_3CH$. The infrafred spectra of $(C_6H_4CH_3)_3C-C_6H_{13}$ and $(C_6H_{10}CH_3)_3C-C_6H_{13}$ contained bands with frequencies of 850, 1070, 1080, 1500, 1600, and 1110 cm^{-1} in the first case and 906 and 1250 cm^{-1} in the second case, which correspond to disubstituted aromatic and naphthene hydrocarbons. The spectral data are given as curves in Figs. 1-12.

EXPERIMENTAL*

1,7-Diphenyl-4-(3-phenylpropyl)heptane. From $C_6H_5CH_2CH_2CH_2MgBr$ (320 g of phenylpropyl bromide) and 118 g of ethyl phenylbutyrate we obtained 168 g (71% yield) of 1,7-diphenyl-4-(3-phenylpropyl)heptanol-4 with b. p. 233° (1 mm); d^{20}_4 1.0137; $n^{20}D$ 1.5660; MR found 123.68; MR calculated MR 123.26. Found: C 87.70; H 9.14; OH 4.83%. $C_{28}H_{34}O$. Calculated: C 86.98; H 8.88; OH 4.40%.

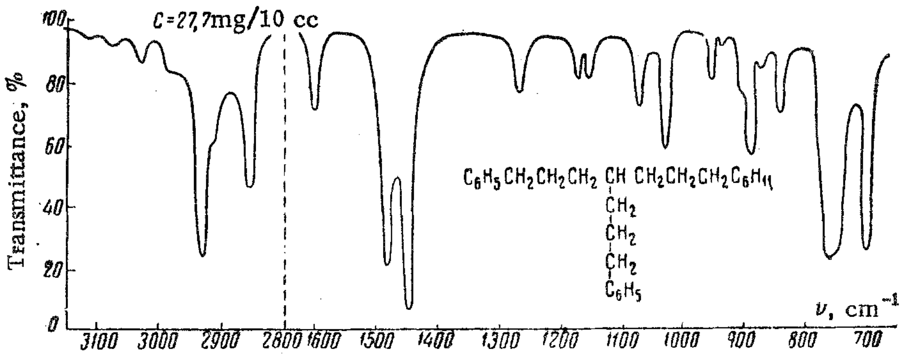

Fig. 11.

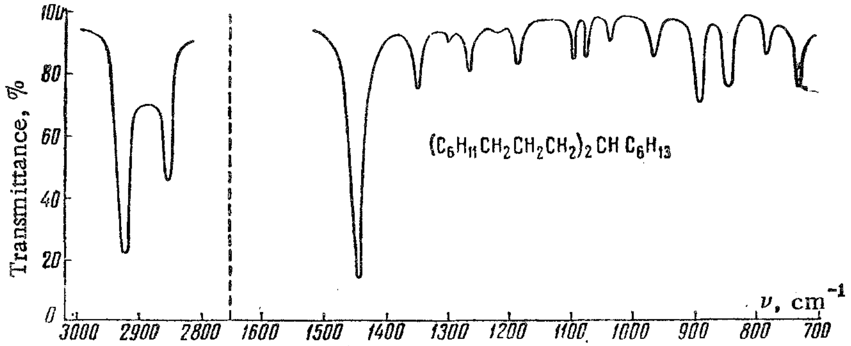

Fig. 12.

The alcohol obtained was dehydrated by the method in [6] to yield 78 g (49%) of 1,7-diphenyl-4-(3-phenylpropyl)heptene-4 with b. p. 234° (1 mm), solidification p. −6°; d^{20}_4 1.0208; $n^{20}D$ 1.5750; MR found 119.23; MR calculated 120.23. Found: C 90.96; H 9.00%. Calculated: C 91.23; H 8.77%. Viscosity in centistokes: ν^{20} 1067.2; ν^{50}77.24; ν^{100} 9.30; ν^{150} 3.12.

The unsaturated hydrocarbon was hydrogenated under a pressure of H_2 in an autoclave at 40-50° with Raney nickel. We obtained 68 g of 1,7-diphenyl-4-(3-phenylpropyl)heptane. A 26-g sample of the latter was hydrogenated over 0.22 g of PtO_2 in 76 ml of acetic acid. The amount of hydrogen added was 4.1 liters (theoretical 4.7 liters). Chromatography twice yielded 5 g of $(C_6H_5CH_2CH_2CH_2)_2CHCH_2CH_2CH_2C_6H_{11}$.

1,1,1-Tritolylheptane. From $MgBrC_6H_{13}$ (83 g, 0.5 mole of hexyl bromide) and 75 g (0.23 mole) of $(C_6H_4CH_3)_3CCl$ we obtained 26 g of the hydrocarbon, whose properties are given in the table. An 11-g sample of 1,1,1-tritolylheptane was hydrogenated under a pressure of H_2 in an autoclave at 180-200° over Raney nickel (3 g) for 20 hr. We obtained 6 g of 1,1,1-trimethylcyclohexylheptane.

1,7-Diphenyl-4-(2-cyclohexylethyl)heptane. From $C_6H_5CH_2CH_2CH_2MgBr$ (42 g of $C_6H_5CH_2CH_2CH_2Br$) and 18.5 g of ethyl cyclohexylpropionate we obtained 17 g of a product with b. p. 200-235° (1 mm), which was a mixture of 1,7-diphenyl-4-(2-cyclohexylethyl)-heptanol-4 and the corresponding olefins and 3 g of pure alcohol with b. p. 245° (1 mm); d^{20}_4 0.9988; $n^{20}D$ 1.5410; MR found 119.05; MR calculated 119.01. Found: C 85.42; H 10.27; OH 5.85%. $C_{27}H_{38}O$. Calculated: C 85.62; H 10.15; OH 4.54%.

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* Laboratory assistant V. P. Krukhtanova helped with the experimental work.

Without preliminary separation, the mixture of alcohol and olefin was dehydrated by the method in [6]. The olefins obtained had b. p. 212-220° (1 mm); d^{20}_4 0.9826; $n^{20}D$ 1.5490; MR found 116.67; MR calculated 117.01. A 10.5 g sample of the mixture of olefins was hydrogenated in 20 ml of acetic acid over 0.08 g of PtO_2 at ~20°. The amount of hydrogen required for the hydrogenation of one double bond (620 ml) was added. The hydrocarbon, which had a bromine number of zero, was chromatographed.

1,5-Diphenyl-3-(2-cyclohexylethyl)pentane. From $C_6H_5CH_2CH_2MgBr$ (185 g of $C_6H_5CH_2CH_2Br$) and 89 g of ethyl hydrocinnamate we obtained 124 g of 1,5-diphenyl-3-(2-phenylethyl)pentanol-3; the latter was dehydrated by the method in [6] to yield 100 g of 1,5-diphenyl-3-(2-phenylethyl)pentene-3 with b. p. 205° (2 mm); $n^{20}D$ 1.5860. Literature data [5]: b. p. 210.5° (1 mm); d^{20}_4 1.0159; $n^{20}D$ 1.5816. A 29 g sample of the latter was hydrogenated in 70 ml of acetic acid over 0.23 g of PtO_2. The amount of hydrogen absorbed was 6.2 liters. The amount of hydrogen required for the hydrogenation of one phenyl ring and one double bond was 8.3 liters. Chromatography twice yielded 14 g of 1,5-diphenyl-3-(2-phenylethyl)pentane and 10 g of 1,5-diphenyl-3-(2-cyclohexylethyl)pentane.

1-Phenyl-4,7-dicyclohexylheptane. A 12-g sample of 1,7-diphenyl-4-cyclohexylheptene-4 was hydrogenated over 0.1 g of PtO_2 in 30 ml of acetic acid. The amount of hydrogen absorbed was 2.73 liters, while the amount of hydrogen required for the hydrogenation of one double bond and one ring was 3.17 liters. We obtained 8.3 g of a product. The experiment was repeated with 8 g of 1,7-diphenyl-4-cyclohexylheptane, 0.0949 g of PtO_2, and 23 ml of acetic acid. We obtained 5.5 g of product. The two incomplete hydrogenation products were mixed and chromatographed twice. We obtained 6.4 g of 1-phenyl-4,7-dicyclohexylheptane.

1-Phenyl-4-(3-cyclohexylpropyl)decane. A 20 g sample of 1-phenyl-4-(3-phenylpropyl)decane was hydrogenated in 50 ml of acetic acid over 0.18 g of PtO_2 at 20°. The amount of hydrogen required for the hydrogenation of one ring was 4.0 liters and 4.5 liters of hydrogen was actually absorbed. Chromatography twice yielded 8 g of 1-phenyl-4-(3-cyclohexylpropyl)decane and 4.7 g of 1-cyclohexyl-4-(3-cyclohexylpropyl)decane.

1-Phenyl-3-(2-cyclohexylethyl)tridecane. A 4-g sample of 1-phenyl-3-(2-phenylethyl)tridecane was hydrogenated in 10 ml of acetic acid over 0.03 g of PtO_2 at ~20°. The amount of hydrogen required for the hydrogenation of one ring was 0.73 liter and 0.71 liter of hydrogen was absorbed. We obtained 2.9 g of the hydrocarbon.

1-Phenyl-4-(2-phenylethyl)-7-cyclohexylheptane. An 8.5-g sample of 1,7-diphenyl-4-(2-phenylethyl)heptane was hydrogenated over 0.12 g of PtO_2 in 40 ml of acetic acid. The amount of hydrogen required for the hydrogenation of one ring was 0.73 liter and 0.71 liter was absorbed. Chromatography twice yielded 5.6 g of the hydrocarbon.

In conclusion, the authors would like to thank Yu. P. Egorov and E. Lubush for plotting the spectra.

SUMMARY

1. 1,7-Diphenyl-4-(3-phenylpropyl)heptane, 1,7-dicyclohexyl-4-(3-cyclohexylpropyl)heptane, 1,1,1-tritolylheptane, 1,1,1-tricyclohexylheptane, and 1,7-diphenyl-4-(2-cyclohexylethyl)heptane were prepared for the first time by organomagnesium synthesis.

2. The following hydrocarbons were obtained by selective hydrogenation of the corresponding triphenylalkanes over PtO_2: 1,7-diphenyl-4-(3-cyclohexylpropyl)heptane, 1,5-diphenyl-3-(2-cyclohexylethyl)pentane, 1-phenyl-4,7-dicyclohexylheptane, 1-phenyl-4-(2-cyclohexylpropyl)decane, 1-cyclohexyl-4-(3-cyclohexylpropyl)decane, 1-phenyl-3-(2-cyclohexylethyl)tridecane, and 1-phenyl-4-(2-phenylethyl)-7-cyclohexylheptane.

LITERATURE CITED

1. M. A. Chel'tsova and A. D. Petrov, Zh. obshch. Khimii 27, 600 (1957).
2. M. A. Chel'tsova, A. D. Petrov, and Yu. P. Egorov, Zh. obshch. khimii 28, 945 (1958).
3. M. A. Chel'tsova and A. D. Petrov, Zh. obshch. khimii 29, 820 (1959).
4. R. Adams, in the collection: Syntheses of Organic Preparations [Russian translation] (IL, 1949) Vol. 1, p. 357.
5. R. W. Schiessler, D. G. Clarke, C. S. Rowland, W. S. Sloatman, and C. H. Herr, Refiner 22, 390 (1943).
6. K. Ziegler, K. Richter, and B. Schnell, Liebigs Ann. Chem. 443, 171 (1925).