58. *Alkylation of the Aromatic Nucleus. Part IX.* Cyclopentylation and Cycloheptylation.*

By K. M. Davies and W. J. Hickinbottom.

Thermal decomposition of cycloheptyl toluene-*p*-sulphonate in phenol gives a mixture of *o*- and *p*-cycloheptylphenol. In anisole, *o*- and *p*-methoxyphenylcycloheptane are formed: no rearrangement of the cycloheptyl group could be detected. In benzene, however, alkylation gives a product of which only ~70% is phenylcycloheptane; the remainder is methylphenylcyclohexane. Alkylation of benzene by cycloheptene and cycloheptanol with suitable condensing agents has also been studied, and the extent of the isomerisation of the cycloheptyl group during the reaction has been determined.

The isomer distribution in the cycloheptylation of toluene has been determined, and compared with that from cyclopentylation and cyclohexylation.

The course of these alkylations is discussed.

In earlier papers in this series it has been shown that n-butyl,[1] isobutyl,[2] cyclohexylmethyl,[3] and 2- and 4-methylcyclohexyl groups[3] rearrange to a greater or less extent

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* Part VIII, preceding paper.

[1] Grant and Hickinbottom, *J.*, 1959, 2513.

[2] Hickinbottom and Rogers, unpublished work.

[3] Blackwell and Hickinbottom, preceding paper.

when introduced into aromatic systems by thermal decomposition of their sulphonic esters. A study of the behaviour of the cycloheptyl group in such alkylations is reported in the present paper since there is abundant evidence[4] that this ring system readily isomerises to methylcyclohexyl.

Thermal decomposition of cycloheptyl toluene-*p*-sulphonate in phenol gives a product which consists entirely of *o*- and *p*-cycloheptylphenol; there is no recognisable amount of *meta*-substitution or isomerisation of the cycloheptyl group. Anisole similarly gives *o*- and *p*-cycloheptyl derivatives. In benzene, however, there is some isomerisation, the product containing about 30% of methylcyclohexylbenzene and the remainder phenylcycloheptane. In *p*-xylene, isomerisation of the cycloalkyl group also occurs to the extent of about 30%. For comparison, the cycloheptylation of benzene by other methods was examined to determine how much of the cycloheptyl group survives, and the results are summarised in Table 1.

TABLE 1.

Cycloheptylation of benzene.

Reagent	$C_7H_{13}\cdot O\cdot SO_2\cdot C_6H_4Me$	p-$C_6H_4Me\cdot SO_3H$–C_7H_{12}	$AlCl_3$–$C_7H_{13}\cdot OH$	H_2SO_4–C_7H_{12}	BF_3–C_7H_{12}
Yield (%)	32	29	41	27	29
Cycloheptylbenzene (%) in product	68	69	15	88	95

There are two probable routes for alkylation by thermal decomposition: (*a*) bimolecular displacement, $AlkO\cdot SO_2\cdot R + ArH \longrightarrow Alk\cdot Ar + R\cdot SO_2\cdot OH$, and (*b*) a carbonium ion mechanism which was postulated in a general form in an earlier paper and can be represented as: $[AlkO\cdot SO_2\cdot RH]^+ \longrightarrow [Alk^+ + R\cdot SO_2\cdot OH] \xrightarrow{ArH} Alk\cdot Ar + R\cdot SO_2\cdot OH + H^+$. Bimolecular displacement alone cannot account for all our observations on this alkylation. If it were the sole reaction, isomerisation of the alkyl group would not be expected to occur and there would be no reason to suppose that such a reaction would be proton-catalysed or autocatalytic. Further, a bimolecular displacement should permit the introduction of optically active alkyl groups such as s-butyl or s-octyl: yet all attempts to do so have failed.[1,5] Although these considerations apply to most thermal alkylations, phenethyl toluene-*p*-sulphonate is an exception. This ester is particularly stable and is not noticeably sensitive to acids: it is unchanged after being boiled in toluene with 1 mol. of toluene-*p*-sulphonic acid. Yet it can alkylate mesitylene or phenol to give $Ph\cdot CH_2\cdot CH_2R$ ($R = C_6H_2Me_3$ or $C_6H_4\cdot OH$) in good yield and without detectable isomerisation of the phenethyl group.[3] It is possible that benzylation also falls into this category since the pattern of substitution differs from that of saturated alkyl groups in giving no *meta*-substitution and the halogenobenzenes can be benzylated smoothly and in good yield although the esters of alkanols and cycloalkanols react sluggishly and in poor yield.

Apart from these exceptions, thermal alkylations find a satisfactory explanation on the carbonium hypothesis. It explains adequately why cyclopentylation and cyclohexylation of toluene by cyclopentanol or cyclohexanol with either sulphuric acid or boron trifluoride give the same proportions of *ortho*-, *meta*-, and *para*-isomers as does the thermal alkylation by the cycloalkyl toluene-*p*-sulphonate. A similar test of cycloheptylation shows some variation of the isomer ratio (Table 2). A possible explanation depends on the isomerisation of the cycloheptyl group, the extent of which depends on the nature of the alkylating reagent.

The carbonium ion mechanism for thermal alkylation in which a t-butyl or 1-methylcyclohexyl group is introduced is the only alternative, since sulphonic esters of the corresponding alcohols are unstable and as yet unknown. The carbonium ion hypothesis is

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[4] Turova-Pollak, *Doklady Akad. Nauk S.S.S.R.*, 1948, **60**, 807; Pines, Pavlik, and Ipatieff, *J. Amer. Chem. Soc.*, 1952, **74**, 5544.

[5] Nenitzescu, Ioan, and Teodorescu. *Chem. Ber.*, 1957, **90**, 585.

TABLE 2.

Cycloalkylation of toluene.

			Isomer distribn. (%) in product				
		Yield	I.R. analysis *			Gas–liquid chromatog.†	
No.	Reagents	(%)	*o*-	*m*-	*p*-	*o*-	*m*- + *p*-
1	$C_5H_9·O·SO_2·C_6H_4Me$ ...	90	43	21	36	45	55
2	$C_5H_9·OH–BF_3$	22	43	19	38	48	52
3	$C_5H_9·OH–H_2SO_4$	48	45	18	37	48	52
						o- + *m*-	*p*
4	$C_6H_{11}·O·SO_2·C_6H_4Me$...	65	30	17	53	46	54
5	$C_6H_{10}–C_6H_4Me·SO_3H$...	72	30	17	53	44	56
6	$C_6H_{11}·OH–BF_3$	67	33	16	51	42	58
7	$C_6H_{11}·OH–H_2SO_4$	23	36	12	52	42	58
8	$C_7H_{13}·O·SO_2·C_6H_4Me$...	57	53	16	31	‡	
9	$C_7H_{13}·OH–BF_3$	51	46	22	32	—	—
10	$C_7H_{13}·OH–H_2SO_4$	30	41	15	44	—	—

* The following infrared bands were used for determination (±3%) of the isomer distribution. Nos. 1—3: *o*-, 13·3, 13·85; *m*-, 12·8, 14·3; *p*-, 12·35. Nos. 4—7: *o*-, 13·35, 13·8; *m*-, 12·8, 14·25; *p*-, 12·3. Nos. 8—10: *o*-, 13·3, 13·8; *m*-, 12·85, 14·2; *p*-, 12·4 μ. † Chromatography was on a 4-ft. column at 150—200° with (nos. 1—3) 10% of Reoplex on Celite (60—70 mesh) or (nos. 4—7) 10% of Apiezon on Celite (100—120 mesh). ‡ At least 5 components were indicated.

further supported by the isomerisation of some groups during the alkylation, although the occasional formation of olefins makes it probable that the classical rearrangement of a carbonium ion does not present a complete picture. The last conjecture is made more probable by the observation[5,6] that there is an equilibrium between the olefin, the sulphonic acid, and the sulphonic ester, a conclusion confirmed by the finding that the same proportions of isomers are formed by reaction of cyclohexene with toluene in presence of toluene-*p*-sulphonic acid as on thermal decomposition of cyclohexyl toluene-*p*-sulphonate in an excess of toluene.[7]

EXPERIMENTAL

Cyclopentylation of Toluene.—(*a*) Cyclopentyl toluene-*p*-sulphonate, m. p. 30·5—31° (lit.,[8] m. p. 28·5—29°) (0·25 mole), was heated in boiling toluene (1·25 moles) for 5 hr. The product was a mixture of cyclopentyltoluenes, b. p. 101—102°/12 mm., n_D^{20} 1·5260 (21·8 g., 70%) [Found: C, 90·1; H, 10·0. Calc. for $C_{12}H_{16}$: C, 90·0; H, 10·0%).

(*b*) A slow stream of boron trifluoride was passed into a stirred solution of cyclopentanol (0·35 mole) in toluene (2·35 moles) at 20° for $\frac{3}{4}$ hr., giving cyclopentyltoluenes, b. p. 122—127°/23 mm., n_D^{18} 1·5269 (10 g., 23%) (Found: C, 90·2; H, 9·8%).

(*c*) Toluene (2·72 moles), cyclopentanol (0·58 mole), and 98% sulphuric acid (150 g.), when stirred together for 3 hr. at 0°, gave cyclopentyltoluenes, b. p. 107—109°/15 mm., n_D^{16} 1·5290 (44·3 g., 48%) (Found: C, 90·0; H, 10·0%), and dicyclopentyltoluenes, b. p. 139—142°/0·3 mm., n_D^{19} 1·5420 (11·6 g., 9%) (Found: C, 89·6; H, 10·4. Calc. for $C_{17}H_{24}$: C, 89·4; H, 10·6%).

Cyclohexylation of Toluene.—(*a*) Cyclohexanol (50 g.) was stirred with toluene (215 g.) while boron trifluoride was passed in for 5 hr. at 15—60°; this gave cyclohexyltoluenes, b. p. 122—126°/15 mm., n_D^{20} 1·5242 (57·5 g., 67%) (Found: C, 89·6; H, 10·2. Calc. for $C_{13}H_{18}$: C, 89·6; H, 10·4%), and dicyclohexyltoluenes, b. p. 130—140°/0·15 mm., n_D^{20} 1·5366 (5·8 g., 3%) (Found: C, 89·0; H, 10·8. Calc. for $C_{19}H_{28}$: C, 89·0; H, 11·0%).

(*b*) Cyclohexanol (50 g.), toluene (216 g.), and 98% sulphuric acid (130 g.), when stirred together for 3 hr. at 0—10°, gave cyclohexyltoluenes, b. p. 117—119°/12 mm., n_D^{19} 1·5258 (20 g., 23%) (Found: C, 89·5; H, 10·6%).

Cycloheptylation of Benzene.—(*a*) Cycloheptyl toluene-*p*-sulphonate was obtained as a slightly yellow oil, n_D^{20} 1·5260, from cycloheptanol, b. p. 76—77°/13 mm., n_D^{20} 1·4761, which had been purified through its hydrogen phthalate, m. p. 96—101° (lit.,[9] 90—95°).

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[6] Johnson and Lion, U.S.P. 2,665,293/1954.

[7] Blackwell and Hickinbottom, following paper.

[8] Brown and Ham, *J. Amer. Chem. Soc.*, 1956, **78**, 2735.

[9] Smith, Baer, and Edge, *J. Amer. Chem. Soc.*, 1954, **76**, 4564.

The ester (0·46 mole) and benzene (2·46 moles) were refluxed together for 70 hr. The product, b. p. 68—70°/0·12 mm., n_D^{20} 1·5248 (Found: C, 89·5; H, 10·5. Calc. for $C_{13}H_{18}$: C, 89·6; H, 10·4%), consisted largely of phenylcycloheptane, identified by nitration and hydrogenation to an amine, the acetyl derivative of which melted at 173° and was identical (mixed m. p. and infrared spectrum) with authentic *p*-cycloheptylacetanilide.

(*b*) Cycloheptanol (0·15 mole), benzene (1·1 moles), and aluminium chloride (0·15 mole) were refluxed together for 2 hr., then kept at room temperature for 16 hr. The product had b. p. 122—132°/16 mm., n_D^{21} 1·5233 (Found: C, 89·6; H, 10·3%). With acetyl chloride and aluminium chloride in carbon disulphide this gave ketones whose 2,4-dinitrophenylhydrazones were a mixture, the m. p. being raised to 163—170° after several crystallisations from methanol–chloroform. The m. p. was raised to 169—175° on admixture with the 2,4-dinitrophenylhydrazone, m. p. 180—181°, of 1-*p*-acetylphenyl-1-methylcyclohexane. The main constituent of this product appears to be methylphenylcyclohexane.

(*c*) Cycloheptene, b. p. 114—115°, n_D^{20} 1·4575 (lit.,[10] b. p. 114·5—115, n_D^{20} 1·4574) (0·188 mole), in benzene (0·2 mole) was added regularly to a stirred mixture of benzene (0·2 mole) and 96% sulphuric acid (56 g.) at 5°. After ½ hr. the mixture was allowed to warm to room temperature. There was obtained a product, b. p. 131·5—133°/16 mm., n_D^{20} 1·5264 (Found: C, 98·4; H, 10·5%).

(*d*) Cycloheptene (0·21 mole), benzene (2·5 moles), and toluene-*p*-sulphonic acid (0·24 mole) were boiled together for 50 hr., giving a product, b. p. 130—134°/18 mm., n_D^{20} 1·5243 (Found: C, 98·4; H, 10·7%).

(*e*) Cycloheptene (0·15 mole) in benzene (1·6 moles) was saturated at 0° with boron trifluoride and kept at 0° for 2 hr., then allowed to warm to room temperature in 3 hr. The product had b. p. 135—138°/15 mm., n_D^{21} 1·5240 (Found: C, 89·6; H, 10·5%). The main constituent was shown to be phenylcycloheptane by nitration to the dinitro-compound and hydrogenation thereof to the diamine; the diacetyl derivative had m. p. 234—235° alone or mixed with 2,4-diacetamidophenylcycloheptane.

Isomerisation of Phenylcycloheptane.—Phenylcycloheptane (0·057 mole) in benzene (2 moles) was heated with aluminium chloride (0·15 mole) for 2 hr. The recovered product, b. p. 107—128°/17 mm., n_D^{21} 1·5350, contained six components according to its gas–liquid chromatogram; methylphenylcyclohexanes formed ~88% of the mixture.

No change was detected by infrared spectroscopy or gas–liquid chromatography when phenylcycloheptane was boiled in benzene with toluene-*p*-sulphonic acid for 50 hr.

The extent of the isomerisation of the cycloheptyl ring during these alkylations was determined most conveniently by gas–liquid chromatography.

Cycloheptylation of Toluene.—(*a*) Cycloheptyl toluene-*p*-sulphonate (0·194 mole) and toluene (1·94 moles) were heated together under reflux for 5 hr., giving a product, b. p. 125—130°/13 mm., n_D^{20} 1·5253 (Found: C, 89·4; H, 10·6. Calc. for $C_{14}H_{20}$: C, 89·3; H, 10·7%).

(*b*) Toluene (1·63 moles), cycloheptanol (0·22 mole), and 98% sulphuric acid (150 g.), when stirred together at 0° for 3 hr., gave monocycloalkyltoluenes, b. p. 147—151°/22 mm., n_D^{20} 1·5282 (Found: C, 89·5; H, 10·7%), and dicycloalkyltoluenes, b. p. 167—170°/0·15 mm., n_D^{20} 1·5424 (4%) (Found: C, 88·6; H, 11·1. Calc. for $C_{21}H_{32}$: C, 88·6; H, 11·4%). The gas–liquid chromatogram showed at least 5 isomeric monocycloalkyltoluenes.

(*c*) Boron trifluoride was passed into cycloheptanol (0·26 mole) in toluene (1·96 moles) at 15° for 5 hr. The product was a mixture of monocycloalkyltoluenes, b. p. 148—155°/22 mm., n_D^{19} 1·5272 (Found: C, 89·2; H, 10·8%), and dicycloalkyltoluenes, b. p. 152—158°/0·1 mm., n_D^{20} 1·5317 (Found: C, 88·6; H, 11·4%).

In these alkylations it was established by infrared spectra that tolylcycloheptanes are not altered in a boiling toluene solution of toluene-*p*-sulphonic acid. Similarly *p*-tolylcycloheptane is unchanged when kept in toluene, saturated with boron trifluoride, for 4 hr. at room temperature. *o*-Tolylcycloheptane is unchanged when stirred in toluene with concentrated sulphuric acid for 3 hr.

Cycloheptylation of p-*Xylene.*—From cycloheptyl toluene-*p*-sulphonate (0·075 mole) and *p*-xylene (1·55 moles), kept at 125° for 5 hr., 5·5 g. (36%) of product were obtained having b. p. 73—82°/0·15 mm., n_D^{20} 1·5237 (Found: C, 88·9; H, 10·9. $C_{15}H_{22}$ requires C, 89·0; H, 11·0%), estimated, from the gas–liquid chromatogram, to contain about 73% of *p*-xylylcycloheptane,

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[10] Vogel, *J.*, 1938, 1323.

Cycloheptylation of Phenol.—The above ester (0·39 mole) and phenol (2·1 moles), when kept at 120° for 6 hr., gave a mixture of *o*- and *p*-cycloheptylphenol (59%), b. p. 170—188°/14 mm. (Found: C, 82·0; H, 9·7; active H, 0·55. Calc. for $C_{13}H_{18}O$: C, 82·0; H, 9·5; active H, 0·53%). A pure sample of the *para*-isomer, isolated by fractional crystallisation of the sodium salts, had m. p. and mixed m. p. 105—106° and gave a benzoate, m. p. and mixed m. p. 111—111·5°. A nearly pure sample of the *ortho*-isomer was obtained from the more soluble fractions of the sodium salts, and had b. p. 169—173°/14 mm., n_D^{21} 1·5500.

From a gas–liquid chromatogram of the entire alkylation product it was estimated with an accuracy of ±3% that it contained 72% of *ortho*- and 28% of *para*-isomer; no *meta*-isomer or isomerisation product was detected.

Cycloheptylation of Anisole.—The above ester (0·37 mole) and anisole (1·85 moles), kept at 125° for 7 hr., gave a mixture of methoxyphenylcycloheptanes, b. p. 86—91°/0·1 mm., n_D^{20} 1·5338 (81%) (Found: C, 82·1; H, 10·3. Calc. for $C_{14}H_{20}O$: C, 82·3; H, 9·9%), containing 63% of *ortho*- and 37% of *para*-isomer, which with hydrogen bromide in acetic acid gave mixed phenols, b. p. 172—184°/17 mm., from which *p*-cycloheptylphenol, m. p. and mixed m. p. 103—104° (benzoate, m. p. and mixed m. p. 110·5—111·5°), was isolated.

Preparation of Reference Compounds.—All the possible products of the alkylations described in this paper were prepared to serve as reference compounds for estimations by infrared spectroscopy or gas–liquid chromatography.

(*a*) *Arylcycloalkanes.* The standard method consisted in reaction of an arylmagnesium bromide with a cycloalkanone, followed by dehydration of the resulting alcohol with boiling aqueous oxalic acid for several hours. The olefins thus formed were hydrogenated in ethanol over palladium–charcoal. The physical constants of the products are recorded in Tables 3 and 4.

TABLE 3.

Arylcycloalkenes.

			Found (%) *		
	B. p./mm.	n_D^{20}	C	H	Note
o-Tolylcyclopentene	122—123°/25	1·5569	91·2	8·8	1
m-Tolylcyclopentene	127°/18	1·5668	91·3	8·6	2
p-Tolylcyclopentene	128—130°/20	—	90·8	9·1	3
Phenylcycloheptene	137—139°/15	1·5610	91·1	9·1	4
1-Methyl-2-phenylcyclohexene	117—120°/13	1·5521	90·4	9·4	5
1-Methyl-3-phenylcyclohexene	121°/13	1·5552	90·3	9·6	6
1-Methyl-4-phenylcyclohexene	131·5/15	1·5544	90·6	9·7	7
o-Tolylcycloheptene	78°/0·15	1·5432	90·2	9·9	8
m-Tolylcycloheptene	65—68°/0·1	1·5545	90·3	9·5	2
p-Tolylcycloheptene	68—70°/0·1	1·5571	89·9	9·6	9
p-Xylylcycloheptene	86—89°/0·1	1·5340	89·9	10·1	

Notes: (1) Addition of 2,4-dinitrobenzenesulphenyl chloride in acetic acid gave the *sulphide* m. p. 174° (from ethanol) (Found: C, 61·0; H, 4·4; N, 7·9; S, 91. $C_{18}H_{16}N_2O_4S$ requires C, 60·7; H, 4·5; N, 7·9; S, 9·0%). (2) *n* at 22°. (3) M. p. 54·5—55°. (4) Lit.,[11] b. p. 113—115°/8 mm., n_D^{20} 1·5624. (5) Lit.,[12] b. p. 86—87°/1·5 mm., n_D^{20} 1·5539. (6) Lit.,[13] b. p. 87—88°/1·5 mm., n_D^{20} 1·5581. (7) Lit.,[14] b. p. 137°/16 mm., n_D^{20} 1·5558. (8) *n* at 21°. (9) *n* at 19°.

* Theoretical figures are given in the text.

1-Methyl-1-phenylcyclohexane, b. p. 110—111°/12 mm., n_D^{20} 1·5228 (Found: C, 89·55; H, 10·6%), was prepared by reaction of 1-methylcyclohexanol with benzene in presence of aluminium chloride (Linsk [12] gives b. p. 103°/9·5 mm., n_D^{20} 1·5278).

Benzylcyclohexane, obtained by Wolff–Kishner reduction of benzoylcyclohexane, had b. p. 118—119°/14 mm., n_D^{20} 1·5191 (Found: C, 89·5; H, 10·4%). Siderova and Tsukervanik [13] give b. p. 137°/20 mm., n_D^{17} 1·5255. The ketone, m. p. 56—57°, was obtained by oxidation of the corresponding alcohol, m. p. 49—50°, which was prepared from cyclohexylmagnesium chloride and (lit., ketone,[13] m. p. 54°; alcohol,[14] 48—49°).

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[11] Pines, Edeleanu, and Ipatieff, *J. Amer. Chem. Soc.*, 1945, **67**, 2193.
[12] Linsk, *J. Amer. Chem. Soc.*, 1950, **72**, 4257.
[13] Siderova and Tsukervanik, *J. Gen. Chem.* (*U.S.S.R.*), 1940, **10**, 2013.
[14] Godchot and Cauquil, *Compt. rend.*, 1928, **186**, 2193.

TABLE 4.

Arylcycloalkanes.

			Found (%) *		
	B. p./mm.	n_D^{20}	C	H	Notes
o-Tolylcyclopentane	126°/27	1·5303	89·8	9·9	
m-Tolylcyclopentane	124°/25	1·5244	89·9	10·0	
p-Tolylcyclopentane	126°/27	1·5240	90·0	10·0	
Phenylcycloheptane	131—132°/17	1·5340	89·7	10·2	1, 2
1-Methyl-2-phenylcyclohexane	115—117·5°/12	1·5283	89·6	10·2	3
1-Methyl-3-phenylcyclohexane	110°/12	1·5203	89·6	10·2	4
1-Methyl-4-phenylcyclohexane	124°/16	1·5209	89·6	10·6	5
o-Tolylcycloheptane	66—69°/0·1	1·5340	89·7	10·4	
m-Tolylcycloheptane	60°/0·1	1·5287	89·4	10·6	1
p-Tolylcycloheptane	82—83°/0·4	1·5280	89·4	10·6	1
p-Xylylcycloheptane	98—100°/0·3	1·5275	89·0	10·9	

Notes: (1) n at 19°. (2) Lit.,[11] b. p. 108°/7 mm., n_D^{20} 1·5309. (3) Lit.,[12] b. p. 62—63°/0·4 mm., n_D^{20} 1·5285. (4) Lit.,[12] b. p. 78—79°/1·3 mm., n_D^{20} 1·5232. (5) Lit.,[11] b. p. 120°/12 mm., n_D^{20} 1·5210.

* Theoretical values are given in the text.

(*b*) *Methoxyphenylcycloheptanes and cycloheptylphenols.* By reaction of *o*- or *p*-methoxyphenylmagnesium bromide with cycloheptanone and dehydration of the resulting alcohol with boiling aqueous oxalic acid, *o*- and *p*-methoxyphenylcycloheptene were formed. These were hydrogenated over palladium–charcoal in ethanol to the saturated compounds. Demethylation with hydrogen bromide in acetic acid gave the corresponding hydroxyphenyl-cycloheptanes. These products are recorded in Table 5.

TABLE 5.

			Found (%) *	
	B. p./mm.	n_D^{20}	C	H
o-Methoxyphenylcycloheptene	155—156°/16	1·5534	83·2	9·2
p-Methoxyphenylcycloheptene	89—91°/0·2	1·5631	82·9	9·0
o-Methoxyphenylcycloheptane	159°/14	1·5361	82·3	9·6
p-Methoxyphenylcycloheptane	84—93°/0·2	1·5322	82·5	9·9
o-Cycloheptylphenol †	172—174°/14	1·5496	82·0	9·4
p-Cycloheptylphenol ‡	M. p. 105—106°	—	81·6	9·4

* Theoretical values are given in the text. † Active H, 0·53 atom. ‡ Active H, 0·55 atom; *benzoate*, m. p. 111—111·5° (Found: C, 81·4; H, 7·4. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%).

p-1′-Methylcyclohexylphenol, m. p. 110—111° (Found: C, 82·3; H, 9·5. Calc. for $C_{13}H_{18}O$: C, 82·0; H, 9·5%), obtained from 1-methylcyclohexanol, phenol, and phosphoric acid at 110° (3 hr.), gave a benzoate, m. p. 80·5—81° (lit.,[15] phenol, m. p. 108°; benzoate, m. p. 80—81°).

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[15] Siderova, *J. Gen. Chem.* (*U.S.S.R.*), 1951, **21**, 869.