TABLE I

CHOLESTERYLAMIDES

Amine used	Formula	M. p., °C.	$[\alpha]^{24}D$	Concn. chloroform	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Ammonia	$C_{28}H_{47}NO$	227–228	−26	2.45	81.34	81.59	11.46	11.46	..	..
Diethyl	$C_{32}H_{55}NO$	146–147	−16	1.85	81.80	81.70	11.80	11.98	..	..
Dipropyl	$C_{34}H_{59}NO$	108–109	−14	3.30	82.01	81.52	11.96	12.01	2.81	2.95
Piperidine	$C_{33}H_{55}NO$	175–176	−20	1.47	82.26	82.04	11.51	11.33	..	..
Aniline	$C_{34}H_{51}NO$	229–231	+ 0.5	7.55	83.38	83.20	10.50	10.70	2.86	2.93
			DIHYDROCHLOLESTERYLAMIDES							
Aniline	$C_{34}H_{53}NO$	236–237	+17	1.50	83.01	83.54	10.86	10.78	2.84	2.83
Dipropyl	$C_{34}H_{61}NO$	101–102	+23	1.90	81.70	81.17	12.33	12.08	2.80	2.96

rapidly takes up two molecules of bromine or two equivalents of oxygen.

The amides were prepared by reaction of an excess of the appropriate amine with the acid chloride. Refluxing of the amine solutions with 3-carbomethyl-5-cholestene for twenty-four hours failed to bring about ammonolysis.

Experimental[6]

Cholesteryl-3-carboxylic Acid.—This was prepared as previously described[1] and crystallized very slowly from benzene, m. p. 227–228° with softening at 224° and noticeable sublimation at 215°, $[\alpha]^{24}D$ −14, *c.* 0.95 in chloroform.

Bromination.—A solution of 0.414 g. (1.00×10^{-3} mole) of the acid in 75 ml. of chloroform was titrated with a standard solution of bromine in chloroform requiring 9.93 $\times 10^{-4}$ mole.

Oxidations.—The acid, 0.0100 g. (2.42×10^{-5} mole) was dissolved in 4 ml. of a chloroform solution containing 3.34×10^{-5} mole of perbenzoic acid. After standing sixty hours at 0°, iodometric titration showed the consumption of 2.50×10^{-5} equivalent of oxygen.

5-Cholesteryl-3-cholestene (Bicholesteryl).—Extensive crystallization produced a compound of slightly higher m. p., 272–273°, than previously encountered[1] but having the same rotation. Perbenzoic oxidation of 0.0100 g. (1.35×10^{-5} mole) in a manner similar to the acid showed the consumption of 2.7×10^{-2} equivalent of oxygen.

3-Cholesterylcarbonyl Chloride.—The crude compound previously described[1] was crystallized from benzene, m. p. 119–120°. Micro carbon and hydrogen analyses corresponded more closely to the acid, probably due to hydrolysis during handling. A macro sample was hydrolyzed and the halogen determined volumetrically.

Anal. Calcd. for $C_{28}H_{45}ClO$: Cl, 8.18. Found: Cl, 8.08.

Preparation of the Amides.—The compounds shown in Table I were prepared with slight variations as follows. 3-Cholesterylcarbonyl chloride, 0.2 g. (4.6×10^{-4} mole) was dissolved in 2 ml. of the amine at room temperature. After standing one day the amide had crystallized. The excess amine was removed *in vacuo* and the amide crystallized from ethanol; yield, 80–98%. Analytical samples were crystallized three to five times without greatly affecting the m. p.

Hydrogenations.—Two of the amides were reduced in acetic acid–acetic anhydride solution using platinum oxide and one atmosphere of hydrogen.

(6) Microanalyses by Patricia Craig, Margaret Hines and Virginia Hobbs.

Summary

A series of cholesterylcarboxamides has been prepared. The structure and configurations of derivatives made from 3-cholesterylmagnesium halides are discussed.

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[CONTRIBUTION FROM BATTELLE MEMORIAL INSTITUTE]

Studies in the Methylcyclopentane Series. I. Preparation and Reactions of Methylcyclopentyl Monochlorides[1]

BY GARSON A. LUTZ, ARTHUR E. BEARSE, JOHN E. LEONARD[2] AND FRANK C. CROXTON

For several years there has been in progress in this Laboratory a study of methylcyclopentane and its derivatives. This hydrocarbon is one of the constituents of petroleum, and methods for its isolation have been developed.[3] This paper deals with the preparation and reactions of methylcyclopentyl chlorides.

Markownikoff[4] chlorinated methylcyclopentane but the products were not identified with certainty. The preparation of 1-chloro-1-methylcyclopentane from 1-methylcyclopentanol has been described by several investigators.[4,5]

Yarnall and Wallis[6] synthesized 1-chloro-2-methylcyclopentane, but 1-chloro-3-methylcyclopentane has, apparently, not been reported.

The chlorination of methylcyclopentane has been re-investigated, and methods of synthesizing

(1) Presented before the Division of Organic Chemistry at the 113th Meeting of the American Chemical Society, Chicago, Illinois, April, 1948.

(2) Present address: Charles F. Kettering Foundation for the Study of Chlorophyll and Photosynthesis, Antioch College, Yellow Springs, Ohio.

(3) (a) Bruun, *Bur. Standards, J. Research*, **7**, 799 (1931); (b) Tooke, U. S. Patent 2,368,050.

(4) Markownikoff, *Ann.*, **307**, 360 (1899).

(5) (a) Meerwein, *ibid.*, **405**, 171 (1914); (b) Chavanne, Miller and Cornet, *Bull. Soc. Chim. Belg.*, **40**, 673 (1931); (c) Hönel and Zinke, U. S. Patent 2,162,172.

(6) Yarnall and Wallis, *J. Org. Chem.*, **4**, 284 (1939).

the isomeric methylcyclopentyl chlorides have been worked out. Chlorination with sulfuryl chloride in the presence of lauroyl peroxide[7] gave 64 and 27% yields of monochlorides and dichlorides, respectively.

When chlorine was passed into methylcyclopentane at reflux, 74 and 9% yields of monochlorides and dichlorides, respectively, were obtained. The monochlorides fraction was about 93% secondary chlorides.

1-Chloro-2-methylcyclopentane and 1-chloro-3-methylcyclopentane were synthesized by reaction of the corresponding alcohols with phosphorus pentachloride. Addition of hydrogen chloride to 1-methylcyclopentene[8] gave quantitative yields of 1-chloro-1-methylcyclopentane. Physical properties of the methylcyclopentyl chlorides are recorded in Table I. The properties of cyclopentyl methyl chloride[9] are included for comparison.

TABLE I

MONOCHLORIDES OF METHYLCYCLOPENTANE

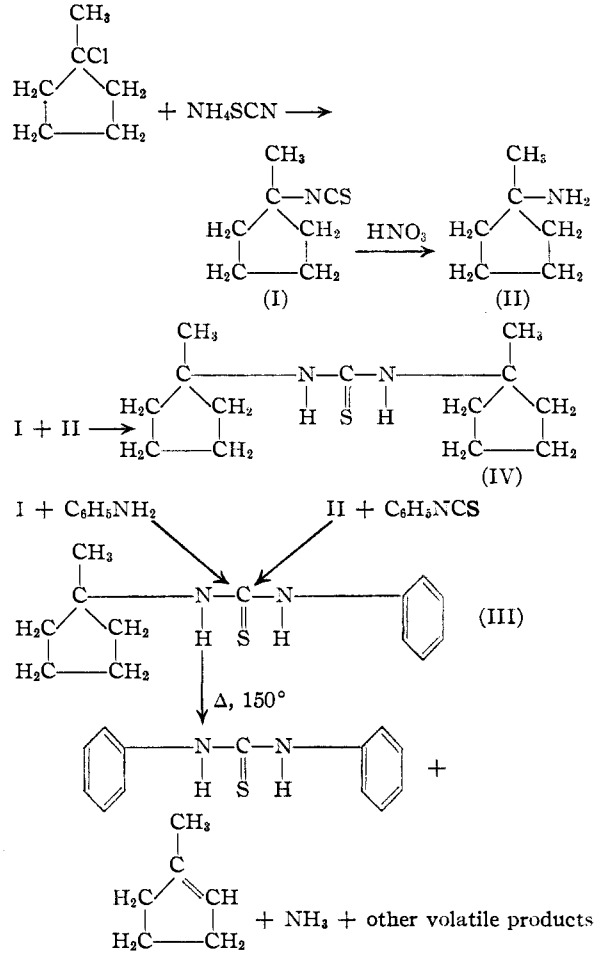
	B. p., °C. (125 mm.)	$n^{20}D$	d^{20}_4	MR_D Calcd.	MR_D Found
1-Chloro-1-methylcyclopentane	67	1.4477	0.968	32.62	32.77
1-Chloro-2-methylcyclopentane	70–72	1.4477	.966	32.62	32.81
1-Chloro-3-methylcyclopentane	74–76	1.4469	.966	32.62	32.74
Cyclopentylmethyl chloride[9]	76–78	1.4611	.993	32.62	32.76

Hydrolysis of *t*-methylcyclopentyl chloride gave methylcyclopentanol and *t*-methycyclopentene. Maximum yields (70–75%) of the alcohol were obtained under alkaline conditions and maximum yields (75–78%) of olefin resulted under acid conditions.

t-Methylcyclopentyl chloride reacted with inorganic thiocyanates to give *t*-methylcyclopentyl isothiocyanate (I), from which *t*-methylcyclopentylamine (II) was obtained. Reaction of the methylcyclopentyl isothiocyanate with aniline gave N-phenyl-N'-*t*-methylcyclopentyl thiourea (III), and reaction of *t*-methylcyclopentylamine with *t*-methylcyclopentyl isothiocyanate gave N,N'-di-(*t*-methylcyclopentyl)-thiourea (IV). (III) also was obtained from *t*-methylcyclopentyl amine and phenyl isothiocyanate. However, when (III) was heated at 150°, *sym*-diphenyl thiourea, 1-methylcyclopentene, and ammonia were obtained.

s-Methylcyclopentyl chlorides reacted with sodium thiocyanate to give a 55% yield of *s*-methylcyclopentyl thiocyanates. Oxidation of the latter gave sulfonic acids.

S-Tertiary methylcyclopentylthiuronium chloride was obtained in 92% yield by treating *t*-



methylcyclopentyl chloride with thiourea. The structure was verified by alkaline hydrolysis[10] to give *t*-methylcyclopentyl thiol and cyanamide, isolated as dicyandiamide.

Reaction of *t*-methylcyclopentyl chloride with phenol at 150° in the absence of a catalyst gave a nearly quantitative yield of *p*-(*t*-methylcyclopentyl)-phenol. This compound has been obtained previously[5c] using aluminum chloride to catalyze the above reaction. It has also been prepared in 34% yield from *t*-methylcyclopentanol and phenol.[11] Condensation of the *t*-chloride with cresols gave 80–85% yields of *t*-methylcyclopentyl cresols.

A 68% yield of *t*-methylcyclopentyl sulfide was obtained from thiophenol and *t*-methylcyclopentyl chloride.

Benzene, toluene and xylene were successfully alkylated with the tertiary chloride, using ferric chloride as a catalyst.

Secondary methylcyclopentyl acetates were prepared in 37% yield by heating the secondary chlorides with anhydrous sodium acetate. Saponification of the acetates gave a 90% yield of secondary methylcyclopentanols.

(7) Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).
(8) Lutz, Bearse, Leonard and Croxton, *ibid.*, **70**, 4139 (1948).
(9) Turkiewicz, *Ber.*, **72**, 1062 (1939).
(10) Renfrew, THIS JOURNAL, **68**, 1433 (1946).
(11) McLellan and Edwards, *ibid.*, **66**, 409 (1944).

Experimental[12]

Synthesis of 1-Chloro-3-methylcyclopentane

β-Methyladipic Acid.—Using a procedure adapted from Vogel[13] and similar to the preparation of adipic acid,[14] this compound was prepared in 70 to 75% yields from 4-methylcyclohexanol.

3-Methylcyclopentanone was prepared in 70–75% yields by pyrolyzing β-methyladipic acid in 200-g. (1.25 moles) portions at 285° in the presence of 10 g. of barium carbonate.

3-Methylcyclopentanol.—Hydrogenation of 3-methylcyclopentanone at 100° and 1700 p.s.i. of hydrogen in the presence of Raney nickel gave 3-methylcyclopentanol in almost quantitative yield. The ketone-free alcohol distilled at 149–150° (750 mm.).[15]

1-Chloro-3-methylcyclopentane.—To a solution of 100 g. (1.0 mole) of 3-methylcyclopentanol in 1.5 liters of dry ether, 208.3 g. (1.0 mole) of phosphorus pentachloride was added. After standing overnight, the reaction mixture was washed with water, dried and distilled. The yield of 3-methylcyclopentyl chloride was 71 g. (60%), b. p. 74–76° (125 mm.), $n^{20}D$ 1.4469, d^{20}_4 0.966, MR_D found 32.74, MR_D calcd. 32.62.

Anal. Calcd. for $C_6H_{11}Cl$: Cl, 29.9. Found: Cl, 29.5.

Synthesis of 1-Chloro-2-methylcyclopentane

2-Carbethoxycyclopentanone was prepared in 80% yield as described in "Organic Syntheses."[16]

2-Carbethoxy-2-methylcyclopentanone, b. p. 97–100° (7 mm.), $n^{20}D$ 1.4464, was obtained in 77% yield by alkylating the sodio-complex of 2-carbethoxycyclopentanone in benzene with methyl iodide.[17]

2-Methylcyclopentanone, b. p. 139–142°, $n^{20}D$ 1.4344, was prepared in 82% yield by refluxing 2-carbethoxy-2-methylcyclopentanone with 4*N* hydrochloric acid.[18]

2-Methylcyclopentanol, b. p. 147–148°, $n^{20}D$ 1.4510, was obtained in almost quantitative yield by hydrogenating 2-methylcyclopentanone in the presence of Raney nickel.

1-Chloro-2-methylcyclopentane was prepared in 34% yield by the reaction of phosphorus pentachloride with 2-methylcyclopentanol in dry ether. The purified product gave b. p. 70–72° (125 mm.)[6], $n^{20}D$ 1.4477, d^{20}_4 0.966; MR_D found 32.81, MR_D calcd. 32.62.

Chlorination of Methylcyclopentane with Sulfuryl Chloride.[7]—In a flask were placed 756 g. (9 moles) of methylcyclopentane (Phillips Petroleum Company), 405 g. (3.0 moles) of sulfuryl chloride, and 6 g. (0.015 mole) of lauroyl peroxide. Vigorous evolution of sulfur dioxide and hydrogen chloride occurred during five hours of refluxing (50–80°). Fractionation gave 457 g. of recovered hydrocarbon, 227 g. of methylcyclopentyl monochlorides, and 62 g. of dichlorides. The yields of monochloride and of dichloride (based on sulfuryl chloride) were 64 and 27%, respectively.

Chlorination of Methylcyclopentane with Chlorine.—Chlorine was passed into refluxing methylcyclopentane (1515 g., 18.0 moles) until the temperature rose to 122° (12 hours). Fractionation of the mixture gave 176 g. (11.7%) of methylcyclopentane, 1573 g. (73.7%) of methylcyclopentyl monochlorides, and 249 g. (9%) of dichlorides.

Anal. Calcd. for $C_6H_{11}Cl$: Cl, 29.9. Found: Cl, 29.7.

Preparation of 1-Chloro-1-methylcyclopentane.—Twenty-eight grams (0.34 mole) of 1-methylcyclopentene cooled to 0° was saturated with gaseous hydrogen chloride. Distillation gave 40 g. (0.34 mole) of 1-chloro-1-methylcyclopentane, b. p. 67° (125 mm.), $n^{20}D$ 1.4477, d^{20}_4 0.968.

Reaction of 1-methylcyclopentene with concentrated hydrochloric acid gave an 86% yield of the tertiary chloride.

Alkaline Hydrolysis of *t*-Methylcyclopentyl Chloride.—Forty-eight grams (0.4 mole) of *t*-methylcyclopentyl chloride was added to 200 cc. of water containing 12 g. (0.21 mole) of calcium oxide. The mixture was stirred three hours at 35°. Purification gave 5 g. (15% yield) of 1-methylcyclopentene, b. p. 75° (740 mm.), and 30 g. (75% yield) of *t*-methylcyclopentanol, b. p. 132–133° (740 mm.), m. p. 35–36°.[5a]

Acid Hydrolysis of *t*-Methylcyclopentyl Chloride.—When 48 g. (0.40 mole) of *t*-methylcyclopentyl chloride was stirred with 200 cc. of water, hydrolysis occurred rapidly. Decantation of the top layer (27.5 g., 32.5 cc.) and distillation gave 25 g. (75% yield) of *t*-methylcyclopentene and 2 g. (5% yield) of *t*-methylcyclopentanol.

Preparation of *t*-Methylcyclopentyl Isothiocyanate.—To a solution of 25.4 g. (0.33 mole) of ammonium thiocyanate in 100 cc. of water, heated to 70°, 40 g. (0.34 mole) of *t*-methylcyclopentyl chloride was added during three hours. After heating an additional two hours, the solution was extracted with ether. Distillation of the extract gave 33 g. (71% yield) of *t*-methylcyclopentyl isothiocyanate boiling at 99–101° (30 mm.), $n^{20}D$ 1.5200, d^{20}_4 1.005.

Anal. Calcd. for $C_7H_{11}NS$: N, 9.9; S, 22.7. Found: N, 10.1; S, 23.0.

Conversion of *t*-Methylcyclopentyl Isothiocyanate into *t*-Methylcyclopentylamine.—Nitric acid oxidation of a small sample of *t*-methylcyclopentyl isothiocyanate gave the corresponding amine, characterized as the *p*-nitrobenzamide melting at 112–113°. This derivative was identical with that obtained from authentic *t*-methylcyclopentylamine.

Reaction of *t*-Methylcyclopentyl Isothiocyanate with *t*-Methylcyclopentylamine.—Equal amounts of amine and isothiocyanate were mixed and warmed. Recrystallization of the reaction product from alcohol gave N,N'-di-(*t*-methylcyclopentyl) thiourea, m. p. 120°.

Anal. Calcd. for $C_{13}H_{24}N_2S$: N, 11.7; S, 13.3. Found: N, 11.3; S, 13.7.

Reaction of *t*-Methylcyclopentyl Isothiocyanate with Aniline.—When equal amounts of the isothiocyanate and aniline were warmed gently, N-phenyl-N'-*t*-methylcyclopentyl thiourea, m. p. 116°, was obtained.

Anal. Calcd. for $C_{13}H_{18}N_2S$: N, 11.9; S, 13.6. Found: N, 11.5; S, 13.8. Different results were obtained at higher temperatures.

A mixture of 10 g. of *t*-methylcyclopentyl isothiocyanate and 20 cc. of aniline was heated slowly. Evolution of ammonia occurred between 150 and 180°. Heating was continued until 6.2 g. of distillate had collected. Redistillation gave 4.8 g. of material boiling at 75°, $n^{20}D$ 1.4342, indicating that *t*-methylcyclopentene was one of the decomposition products. The distillation residue (13 g.) after purification melted at 150–151° and gave no depression in melting point when mixed with *sym*-diphenyl thiourea.

Preparation of *s*-Methylcyclopentyl Thiocyanate.—A mixture of 81 g. (1.0 mole) of sodium thiocyanate and 450 cc. of Cellosolve was heated to reflux while 119 g. (1.0 mole) of mixed *s*-methylcyclopentyl chlorides was added dropwise. After twelve hours, the mixture was filtered, washed and dried. *s*-Methylcyclopentyl thiocyanates, 77 g. (55% yield), b. p. 105–130 (30 mm.), $n^{20}D$ 1.5005, d^{20}_4 1.018 were obtained on distillation.

Anal. Calcd. for $C_7H_{11}NS$: N, 9.9; S, 22.7. Found: N, 9.9; S, 22.7.

Oxidation to *s*-Methylcyclopentane Sulfonic Acids.—About 5 cc. of material was oxidized with concentrated nitric acid according to Muspratt.[19] The sulfonic acids were converted into the potassium salts and the neutral solution was evaporated to dryness and extracted with 95% ethyl alcohol. The potassium salts crystallized from the alcohol on cooling.

(12) All melting points are uncorrected.
(13) Vogel, *J. Chem. Soc.*, 907 (1931).
(14) "Organic Syntheses," Coll., Vol. I, p. 18.
(15) Godchot, *Bull. soc. chim.*, [4] **13**, 592 (1913).
(16) "Organic Syntheses," Coll. Vol. II, p. 119.
(17) Linstead, *J. Chem. Soc.*, 940 (1934).
(18) Van Rysselberge, *Bull. Soc. Chim. Belg.*, **35**, 311 (1926).
(19) Muspratt, *Ann.*, **65**, 251 (1848).

Preparation of S-*t*-Methylcyclopentylthiuronium Chloride.—To 80 cc. of 95% ethanol were added 38 g. (0.50 mole) of thiourea and 60 g. (0.51 mole) of *t*-methylcyclopentyl chloride. The mixture was refluxed for two and one-half hours. Ninety grams (92% yield) of S-*t*-methylcyclopentylthiuronium chloride, m. p. 136 to 137°, was isolated from the mixture.

Anal. Calcd. for $C_7H_{15}N_2SCl$: Cl, 18.2; N, 14.4. Found: Cl, 18.6; N, 14.6.

Identification of S-*t*-Methylcyclopentylthiuronium Chloride.—Hydrolysis of 21 g. (0.11 mole) of the chloride with 175 cc. of 6% aqueous sodium hydroxide yielded 7.5 g. of a chloroform-soluble liquid distilling at 133–135° (750 mm.). This was identified as *t*-methylcyclopentyl thiol by converting to the 2,4-dinitrochlorophenyl thioether, m. p. 74°. This gave no depression in melting point with the 2,4-dinitrophenyl thioether derivative of *t*-methylcyclopentyl thiol[8] obtained from *t*-methylcyclopentene and hydrogen sulfide. While evaporating the chloroform solution, dicyandiamide, m. p. 206°, separated.

Anal. Calcd. for $C_2H_4N_4$: N, 66.7. Found: N, 67.0.

Preparation of *p*-(*t*-Methylcyclopentyl)-phenol.—To 204 g. (2.2 moles) of phenol heated to 130° was added 52 g. (0.44 mole) of *t*-methylcyclopentyl chloride over a two-hour period. The mixture was subsequently heated at 150° for two hours. After removal of 155 g. (1.7 moles) of phenol at reduced pressure, there was obtained 80 g. of material boiling at approximately 110° (1.5–2 mm.). This contained about 3% of phenol which was removed by washing with hot water. Recrystallization from petroleum ether (b. p. 30–60°) gave a nearly quantitative yield of *p*-(*t*-methylcyclopentyl)-phenol,[11] m. p. 94–95°.

Condensation of *t*-Methylcyclopentyl Chloride with Cresols.—To 108 g. (1.0 mole) of *o*-cresol heated to 120° was added dropwise 56 g. (0.39 mole) of *t*-methylcyclopentyl chloride dissolved in 60 g. (0.55 mole) of technical *o*-cresol. Fractionation gave 60 g. of a viscous liquid distilling at 113–115° (2.4 mm.), $n^{20}D$ 1.5445, d^{20}_4 1.0277.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 82.0; H, 9.6.

Similarly, from 219 g. of *m*-cresol and 50 g. of *t*-methylcyclopentyl chloride, there was obtained 66.5 g. of material distilling at 117–120° (1.6 mm.), $n^{20}D$ 1.5433, d^{20}_4 1.0230.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 81.7; H, 9.5.

From 272 g. of *p*-cresol and 60 g. of *t*-methylcyclopentyl chloride was obtained 77.5 g. of material distilling at 110° (1.2 mm.). The product, when recrystallized from petroleum ether (b. p. 30–60°) melted at 45°.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 81.6; H, 9.3.

Reaction of *t*-Methylcyclopentyl Chloride with Aromatics.—A mixture of 105 g. (1.3 moles) of benzene and 12 g. (0.07 mole) of anhydrous ferric chloride was cooled to 10° and 30 g. (0.25 mole) of *t*-methylcyclopentyl chloride was added during one-half hour. Purification after two and one-half hours gave 15 g. (37% yield) of *t*-methylcyclopentylbenzene, distilling at 94–95° (10 mm.), $n^{20}D$ 1.5241, d^{20}_4 0.9446.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.9; H, 10.1. Found: C, 89.8; H, 10.2. There was also obtained 16 g. (26% yield) of di-(*t*-methylcyclopentyl)-benzene which melted at 94° after crystallizing from ethanol.

Anal. Calcd. for $C_{18}H_{26}$: C, 89.2; H, 10.8. Found: C, 88.8; H, 11.0.

Alkylation of toluene was carried out in the same manner, except that the temperature was 10 to 15° higher. From 129 g. of toluene, 10 g. of anhydrous ferric chloride, and 30 g. of *t*-methylcyclopentyl chloride there was obtained 31 g. (71% yield) of *t*-methylcyclopentyltoluene, distilling at 99–101° (5 mm.), $n^{20}D$ 1.5219, d^{20}_4 0.9383.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.6; H, 10.4. Found: C, 89.5; H, 10.6.

From 130 g. of *m*-xylene, 12 g. of anhydrous ferric chloride, and 30 g. of *t*-methylcyclopentyl chloride was obtained 25 g. (52% yield) of *t*-methylcyclopentyl-*m*-xylene distilling at 114–117° (6 mm.), $n^{20}D$ 1.5220.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.3; H, 10.7. Found: C, 89.4; H, 11.0.

Preparation of *t*-Methylcyclopentyl Phenyl Sulfide.—On heating 89 g. (0.8 mole) of thiophenol with 37 g. (0.30 mole) of *t*-methylcyclopentyl chloride for three hours at 130° there was obtained 38 g. (66% yield) of material distilling mostly at 115° (4 mm.). This was characterized as *t*-methylcyclopentyl phenyl sulfide by oxidizing to the corresponding sulfone, m. p. 85–86°, with hydrogen peroxide in glacial acetic acid.[20]

Anal. Calcd. for $C_{12}H_{16}O_2S$: S, 14.3. Found: S, 13.8.

Preparation of *s*-Methylcyclopentyl Acetates.—Thirty grams (0.25 mole) of *s*-methylcyclopentyl chlorides and 21 g. (0.26 mole) of anhydrous sodium acetate were heated together under pressure at 175° for five hours. Fractionation of the mixture gave 11 g. (55% yield) of methylcyclopentenes, b. p. 65–75° (756 mm.), $n^{20}D$ 1.4270, and 9.2 g. (37% yield) of *s*-methylcyclopentyl acetates, b. p. 157–173° (748 mm.), $n^{20}D$ 1.4298, d^{20}_4 0.952.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.6; H, 9.9. Found: C, 67.7; H, 9.9.

Alkaline hydrolysis of *s*-methylcyclopentyl acetates gave a 90% yield of *s*-methylcyclopentanols boiling at 144–147° (738 mm.), $n^{20}D$ 1.4479.

Acknowledgment.—This investigation was carried out under the sponsorship of the Standard Oil Company (Indiana), and the results are published with their permission.

Summary

1. The chlorination of methylcyclopentane by sulfuryl chloride and by chlorine has been investigated.

2. Methods of synthesizing the three isomeric methylcyclopentyl chlorides have been worked out.

3. Hydrolysis of *t*-methylcyclopentyl chloride has been found to give *t*-methylcyclopentanol or *t*-methylcyclopentene depending on conditions.

4. Reaction of *s*-methylcyclopentyl chlorides with inorganic thiocyanates has been shown to give *s*-methylcyclopentyl thiocyanates, while *t*-methylcyclopentyl chloride gives *t*-methylcyclopentyl isothiocyanate.

5. Several other reactions of the methylcyclopentyl chlorides have been described.

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(20) Ipatieff, THIS JOURNAL, **60**, 2733 (1938).