

TABLE III
p-NITRO-*t*-OCTYL BENZENES AND *p*-AMINO-*t*-OCTYL BENZENES

Benzene derivatives	<i>p</i> -Nitro			Nitrogen, % in C ₁₄ H ₂₁ O ₂ N Calcd., 5.95	<i>p</i> -Amino			Nitrogen, % in C ₁₄ H ₂₁ N Calcd., 6.82
	°C.	B. p.,	Mm.		°C.	B. p.,	Mm.	
2-Methyl-2- <i>p</i> -()-phenylheptane	148-150		2	6.01	108-111		2	6.77
2,3-Dimethyl-2- <i>p</i> -()-phenylhexane	133-135		2	5.99	115-119		4	6.58
2,4-Dimethyl-2- <i>p</i> -()-phenylhexane	135-137		2	5.98	99-101		2	6.87
2,5-Dimethyl-2- <i>p</i> -()-phenylhexane	129-131		2	6.09	99-102		2	6.92
2-Methyl-3-ethyl-2- <i>p</i> -()-phenylpentane	127-130		4	6.09	103-106		2	6.86
2,4,4-Trimethyl-2- <i>p</i> -()-phenylpentane	108-110		4	6.05	112-115		5	6.73

The α -naphthylurethans were prepared by the method of French and Wirtel.¹⁹ Their purification was accomplished from hot ligroin.

Proof of Structure of *t*-Octylphenols.—The method employed was identical with that used by Huston and Hsieh² and by Huston and Hedrick.³ The longer heating both for nitration and reduction, as outlined by the latter workers, was found to be necessary for the octyl derivatives.

The 2,4,4-trimethyl-2-*p*-hydroxyphenylpentane obtained in condensation was found to check with this compound as prepared and reported in the literature.¹⁴

(19) H. E. French and A. F. Wirtel, *THIS JOURNAL*, **48**, 1736 (1926).

Summary

1. The isomeric amyldimethylcarbinols condense with phenol in the presence of aluminum chloride to give *p-t*-octylphenols.
2. The benzoyl esters and α -naphthylurethans of seven of these phenols have been prepared.
3. The structures of six of them have been established by synthesis.
4. A new tertiary dimethyl amyl alcohol, 2,3,4-trimethylpentanol-2, has been prepared and some of its physical constants determined.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Thiol Compounds with Aliphatic Olefins

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It has been shown previously^{1,2} that the addition of thiophenol to an olefinic double bond proceeds contrary to the course suggested by Markownikoff's rule. The present paper deals with the addition of other thiol compounds to aliphatic olefins.

Several patents³ have been granted on the preparation of mercaptans and thioethers by treating hydrogen sulfide and mercaptans with olefins. Except in a few isolated instances, however, no proof has been given of the structure of the products formed. Barr and Keyes⁴ showed that *n*- and isopropyl mercaptans were produced in the ratio of approximately 2:1 by passing hydrogen sulfide and propene over a nickel sulfide catalyst at 250–300°. Kharasch, Read, and Mayo^{4b} found that the addition of thioglycolic acid to iso-

butylene and styrene proceeded abnormally from the standpoint of the Markownikoff rule.

In the present work the addition of hydrogen sulfide, aliphatic mercaptans, and thioacetic acid to aliphatic olefins was carried out under varying conditions of temperature, pressure and contact time. No catalyst was added, but, in those reactions run in a bomb, the materials (stainless steel) of the vessel, especially the sulfides, might have played the part of a catalyst. The data obtained from these experiments are tabulated in Table I.

From these data⁵ and those previously given² it is evident that aliphatic mercaptans and thioacetic acid add to the ethylenic group contrary to Markownikoff's rule, paralleling thiophenol in this respect, whereas hydrogen sulfide adds in accordance with the rule.^{5a} In all instances the

(1) Posner, *Ber.*, **38**, 646 (1905).

(2) Ipatieff, Pines and Friedman, *THIS JOURNAL*, **60**, 2731 (1938).

(3) (a) Lee, U. S. Patent 2,020,421; *C. A.*, **30**, 489 (1936); (b) Williams and Allen, U. S. Patent 2,052,268; *C. A.*, **30**, 7122 (1936); (c) Allen, U. S. Patent 2,051,807; *C. A.*, **30**, 6760 (1936); (d) I. G. Farbenind. A.-G., French Patent 797,606; *C. A.*, **30**, 8244 (1936).

(4) (a) Barr and Keyes, *Ind. Eng. Chem.*, **26**, 1111 (1934); (b) Kharasch, Read and Mayo, *Chem. and Industry*, **57**, 752 (1938).

(5) No attempt was made to free the reagents from peroxides or to run the reactions in the absence of air. Professor M. S. Kharasch has informed us that he is investigating the peroxide effect in connection with the reaction of thiols with olefins. Cf. Reference 4b.

(5a) Cf. the paper (which appeared just after this manuscript was submitted for publication) by Jones and Reid, *THIS JOURNAL*, **60**, 2452 (1938), on the addition of sulfur, hydrogen sulfide and mercaptans to unsaturated hydrocarbons.

TABLE I

YSH Moles	Olefin Moles	Time, hours	Temp., °C.	Yield, %	Products	B. p., °C.	Press., mm.	n_D^{20}	d_4^{20}	Deriv. compd.	M. p., °C. uncorr.	
HSH	Propene	3	150	<1	Mixture							
1.05	1.1	4	200	4	Mixture							
HSH	Isobutene	5	150	2	$(l-i)C_4H_9SC_4H_9-i)^a$	152-156						
1.3	1.5	4	100	36		$t-C_4H_9SH$	63-65°	750	1.4231 ^d	(RS) ₂ Hg	157.5-159°	
HSH	Trimethyl-ethylene	0.57	8	150			45 ^b	$t-C_6H_{11}SH$	98-100° ^f	762	1.4379	(RS) ₂ Hg
HSH	Isopropyl-ethylene	0.66	.428	5	150	No mercaptan						
C ₂ H ₅ SH	Propene	4	100 ^p	64	C ₂ H ₅ SC ₃ H _{7-n}	115-117.5 ^h	750	1.4471	0.8391	Sulfone	25 ⁱ	
0.25	.38											
C ₂ H ₅ SH	Isobutene	3	100 ^p	94	C ₂ H ₅ SC ₄ H _{9-i}	132-133 ^k	749	1.4461		RSR'-2HgCl ₂	107-108	
0.22	.73					133.5-134.7 ^l	753	1.4452	.8321			
C ₂ H ₅ SH	Isopropyl-ethylene	.21	33 days	Room	5	C ₂ H ₅ SC ₆ H _{11-i}	155-157 ^{l,m}	748	1.4493		RSR'-2HgCl ₂	86-87
0.16	.163					158-159 ⁱ	753	1.4495	.8349			
C ₂ H ₅ SH	Trimethyl-ethylene	.163	27 days	Room	90	C ₂ H ₅ SC ₆ H _{11-s-i} ⁿ	150-152.5	751	1.4527	(RSR') ₂ -PdCl ₂	92.5-94	
0.11	.28											
<i>n</i> -C ₄ H ₉ SH	Isobutene	2	100 ^q	66	<i>n</i> -C ₄ H ₉ SC ₄ H _{9-i}	173-176 ^o	745	1.4500	.8341	RSR'-2HgCl ₂	105-106	
0.11						178-179°	753	1.4999				
CH ₃ COSH	Propene	3	100	Negli.								
0.2	.4	3	150		Mixt. of products							
CH ₃ COSH	Isobutene					69-71	44	1.4577	.9392	(<i>i</i> -C ₄ H ₉ S) ₂ Hg	93-94 ^s	
0.24	.43	3	100	60	CH ₃ COSC ₄ H _{9-i}	151-152 ^r	744					
CH ₃ COSH	Isopropyl-ethylene	.17	3	100	86	CH ₃ COSC ₆ H _{11-i} ^u	175-177	748	1.4590	.9256	(<i>i</i> -C ₆ H ₁₁ S) ₂ Hg	100-101 ^s
0.126												
CH ₃ COSH	Trimethyl-ethylene	.19	11 days	Room	20	CH ₃ COSC ₆ H _{11-s-i} ^v	75-76	30	1.4621	(<i>s-i</i> -C ₆ H ₁₁ SC ₂ H ₅) ₂ -PdCl ₂	92.5-94	
0.2	.42	4	70	87								
.33												

^a Structure not determined. ^b Calculated on olefin consumed. ^c Rheinboldt, Mott and Motzhus, *J. prakt. Chem.*, [3] 134, 257 (1932); *C. A.*, 26, 5544 (1932), reported 63.7-74.2° (760 mm.) for the boiling point and gave 159-160° for the melting point of the mercury mercaptide. ^d Reuter and Gauss, U. S. patent 2,101,096, reported 1.4228. ^e Rheinboldt, Dewald and Diepenbruck, ⁶ reported 78° b. p. for the mercaptan and 157° m. p. for its mercaptide. ^f Backer⁷ reported 97° b. p. ^g See experimental part. ^h Stromholm, *Ber.*, 33, 830 (1900), reported 114-117°. ⁱ Fenton and Ingrid, *J. Chem. Soc.*, 2338 (1929), reported 25°. ^j From potassium ethyl mercaptide and corresponding alkyl bromide. ^k Wuyts, *Bull. soc. chim.*, [3] 35, 168 (1906), reported 132-134°, n_D^{16} 1.4467. ^l Saizew, *Ann.*, 139, 361 (1866), reported 158-159°. ^m Beckmann, *J. prakt. Chem.*, 17, 450 (1878), reported 159.7-160.1° (754.7 mm.). ⁿ Von Braun, *Ber.*, 59B, 1202 (1926), reported 177-178°. ^o From potassium butyl mercaptide and isobutyl bromide. ^p Initial nitrogen pressure 40 kg./cm.². ^q Initial nitrogen pressure 30 kg./cm.². ^r Wallach and Bleibtreu, *Ber.*, 12, 1062 (1879), reported 148-150°. ^s Wertheim, *THIS JOURNAL*, 51, 3661 (1929), reported 94-95° for *i*-butyl and 100° for *i*-amyl. ^t *Anal.* Calcd. for C₇H₁₆S: C, 63.63; H, 12.12. Found: C, 63.74; H, 12.18. ^u *Anal.* Calcd. for C₇H₁₄OS: C, 57.53; H, 9.58. Found: C, 57.46; H, 9.67. ^v *Anal.* Calcd. for C₇H₁₄OS: C, 57.53; H, 9.58. Found: C, 57.58; H, 9.63.

yield of adduct increases with increased branching of the olefin. Judged by the extent to which the addition of the thiol compound to isobutene and propene takes place, both thiophenol and ethyl mercaptan are more reactive than thioacetic acid and hydrogen sulfide; in fact, the higher temperatures necessary to effect the addition of each of the latter two compounds to propene resulted in side reactions which rendered difficult the identification of the products.

The structure of the products obtained by the addition of the thiol compounds to the olefins was established by a study of the physical properties of the products and by preparation of crystalline derivatives. The physical properties of several of the reference compounds which were synthesized are included in Table I.

The mercaptans obtained by the addition of hydrogen sulfide to olefins were identified readily as their mercury salts, most of which have been reported previously. It was found that the melting point of the mercury salt of *t*-amyl mercaptan has been reported incorrectly as 157° by Rheinboldt and co-workers,⁶ who prepared the mercaptan by the action of zinc sulfide on *t*-amyl iodide. Their mercaptan boiled at 78°, whereas Backer⁷ reported 97° as the boiling point for the same compound synthesized by the action of *t*-amyl Grignard reagent on sulfur; he did not prepare the mercury salt. The *t*-amyl mercaptan synthesized by Backer's method yielded a mercury salt, the melting point of which (60.5–61.5°) was identical with that found for the mercury salt of the mercaptan (b. p. 98–100°) obtained by the addition of hydrogen sulfide to trimethylethylene.

As would be expected, an excess of hydrogen sulfide favored the production of mercaptans, whereas an excess of olefin led to the formation of thioethers.

The structure of the thioethers formed by the addition of aliphatic mercaptans to aliphatic olefins was established (a) by comparison of physical properties with thioethers synthesized by standard methods, (b) by preparation of mercuric chloride and palladous chloride coordination compounds, and (c) by oxidation to the sulfones. Since it was shown that the amyl group in the compounds obtained by the addition of ethyl mercaptan and thioacetic acid to trimethylethylene is

(6) Rheinboldt, Dewald and Diepenbruck, *J. prakt. Chem.*, [2] **130**, 133 (1931).

(7) Backer, *Rec. trav. chim.*, **54**, 215 (1935).

not *t*-amyl, it may reasonably be assumed that it possesses the *sec-iso*-configuration.

The thioacetates formed by addition of thioacetic acid to the aliphatic olefins were characterized readily by saponification to the mercaptans which were identified as the mercury salts.

Experimental

The mercaptans and thioacetic acid used in these reactions were obtained from Eastman Kodak Company; the hydrogen sulfide from the Matheson Company.

Hydrogen Sulfide with Olefins.—The required amount of hydrogen sulfide was obtained from a cylinder by condensing it in a trap cooled with dry ice-acetone. This, along with the liquefied olefin, was placed in a glass liner equipped with a capillary and heated in an Ipatieff type rotating bomb. After the bomb was cooled, unreacted gases were discharged, and the product distilled through a vacuum-jacketed, total reflux column containing a nichrome spiral.

Aliphatic Mercaptan and Thioacetic Acid with Olefins.—When the reaction was run at room temperature, as in the case of the pentenes, the reactants were placed in a glass-stoppered bottle and allowed to stand for several weeks. If a higher temperature was used, the procedure was the same as for the reaction of hydrogen sulfide with olefins. The product was washed with alkali, dried over anhydrous sodium carbonate, and distilled.

Preparation of Alkyl Thioethers.—In a 200-cc. flask equipped with a reflux condenser was placed a solution of 0.2 mole of potassium hydroxide in 100 cc. of 95% ethanol. Two-tenths of a mole of the mercaptan was added (during one minute), then 0.2 mole of the alkyl bromide (dropwise) and the solution refluxed thirty minutes. The product was diluted with 200 cc. of water and taken up in ether. The ether solution was washed with water and alkali, dried over anhydrous sodium carbonate, and distilled.

Identification of Products

Mercaptans.—The mercury salts were prepared by adding a few drops of the mercaptan to 20 cc. of a saturated alcoholic solution of mercuric cyanide. Water was added dropwise with stirring until the mercaptide precipitated. The precipitate was separated by filtration and recrystallized from 95% or more dilute alcohol.

Thioethers.—The directions given by Faragher, Morrell, and Comay⁸ were followed in preparing the mercuric chloride coordination compounds of the aliphatic thioethers; these were satisfactory derivatives except in the case of *s*-isoamyl ethyl sulfide. This sulfide was characterized by means of its palladous chloride coordination compound prepared according to the directions given previously.⁹ *n*-Propyl ethyl sulfone was formed by oxidation of the sulfide with acetic acid and 30% hydrogen peroxide,⁹ and recrystallized from hexane.

Thioesters of Acetic Acid.—One cc. of the ester was saponified by refluxing for fifteen minutes with 5 cc. of ethanol and 5 cc. of 20% potassium hydroxide solution.

(8) Faragher, Morrell and Comay, *THIS JOURNAL*, **51**, 2774 (1929).

(9) Ipatieff and Friedman, *ibid.*, **60**, 2733 (1938).

TABLE II
DERIVATIVES OF ALIPHATIC THIOETHERS AND MERCAPTANS

Compound	M. p., °C.	Form ^a	Solvent	Formula	Analyses, %			
					Calcd.		Found	
					Hg	Pd	Hg	Pd
(<i>i</i> -C ₄ H ₁₁ S) ₂ Hg	59-60	Silky needles	Dil. alc.	C ₁₀ H ₂₂ HgS ₂	49.2		49.36	
(<i>i</i> -C ₄ H ₉ SC ₂ H ₅) ₂ ·2HgCl ₂	107-108	Prisms	Bz	C ₈ H ₁₄ SHg ₂ Cl ₄	60.84		61.40	
(<i>i</i> -C ₄ H ₁₁ SC ₂ H ₅) ₂ ·2HgCl ₂	86-87	Glistening flakes	Dil. acetone	C ₇ H ₁₆ SHg ₂ Cl ₄	59.40		60.03	
(<i>s</i> - <i>i</i> -C ₄ H ₁₁ SC ₂ H ₅) ₂ ·PdCl ₂	92.5-94	Yel. rect. prisms	Dil. acetone	C ₁₄ H ₂₈ S ₂ PdCl ₂		24.14		23.94
(<i>n</i> -C ₄ H ₉ SC ₄ H ₉ - <i>i</i>) ₂ ·PdCl ₂	73.5	Yellow-orange flakes	Dil. alc.	C ₁₆ H ₃₂ S ₂ PdCl ₂		22.71		22.85

^a All mercury derivatives were colorless.

Acetic acid was added until the solution was slightly acid to phenolphthalein, then 10 cc. of aqueous solution of mercuric cyanide was added (hood!). The mercaptide was separated by filtration and recrystallized from dilute ethanol.

The ester prepared by the addition of thioacetic acid to trimethylethylene yielded on saponification a mercaptan whose mercury salt was an oil. The mercaptan was converted to a sulfide by the following procedure. Nine grams (0.06 mole) of the ester was saponified by refluxing fifteen minutes with a solution of 6.72 g. (0.12 mole) of potassium hydroxide in 50 cc. absolute alcohol. To the warm solution was added 20 g. of ethyl iodide and the reaction completed by boiling the mixture fifteen minutes. The product was isolated by dilution of the reaction mixture with water, extraction with ether, and distillation under reduced pressure. The palladous chloride complex of the sulfide melted at 92.5-94°, mixed melting point with

the complex of the sulfide formed by the addition of ethyl mercaptan to trimethylethylene was 93-94°.

Summary

Aliphatic mercaptans, thioacetic acid and hydrogen sulfide add to aliphatic olefins to give good yields of thioethers, thioesters and mercaptans, respectively. The aliphatic mercaptans and thioacetic acid resemble thiophenol and differ from hydrogen sulfide in that they add to the olefins more readily and in better yields, and in that they add practically completely in accordance with Markownikoff's rule.

In all cases the yield of addition product increases with increasing branching of the olefins.

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Researches on Pyrimidines. CLX. The Catalytic Hydrogenation of 5-Benzyl- and 6-Benzyluracils¹

BY JOSEPH C. AMBELANG² AND TREAT B. JOHNSON

The structural relationship of hydrouracils to β -amino acids, paralleling that of hydantoin to α -amino acids, has been pointed out in a previous paper³ from this Laboratory. In that paper was discussed the possible synthesis of difficultly accessible β -amino acids from the corresponding hydrouracils. Brown and Johnson prepared their hydrouracil by hydrogenation of uracil at 75° over the Adams catalyst. Although the same catalyst was effective for the hydrogenation of ethyl uracil-6-acetate⁴ and of 1-methyluracil,⁴ it failed in the case of N-1-methyl-6-phenyluracil-N-3-acetic acid⁵ and its methyl ester.⁵

(1) Constructed from a dissertation presented by Joseph C. Ambelang in June, 1938, to the Graduate Faculty of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Sterling Professorship of Chemistry Research Assistant 1938-1939.

(3) Brown and Johnson, *THIS JOURNAL*, **45**, 2702 (1923).

(4) Hilbert, *ibid.*, **54**, 2078 (1932).

(5) Evans and Johnson, *ibid.*, **52**, 500 (1930).

In the present study hydrogenation of 5-benzyl- and 6-benzyluracils was attempted at elevated temperatures and pressures over Raney nickel and copper-chromium oxide catalysts, which in the desoxouracils⁶ investigated by Folkers and Johnson made possible selective hydrogenation of the benzene and pyrimidine nuclei, respectively.

Over Raney nickel at 175° 6-benzyluracil (I) was hydrogenated with moderate ease to 6-benzylhydrouracil (III); at 225° over the same catalyst 2-keto-6-benzylhexahydropyrimidine (IV) resulted. No products of further reduction, other than a gum, were in evidence. Oxidation of 2-keto-6-benzylhexahydropyrimidine (IV) with the formation of benzoic acid demonstrated the failure of the benzene ring to undergo hydrogenation. Hydrolysis with barium hydroxide in aqueous methanol yielded 4-phenyl-1,3-butanediamine

(6) Folkers and Johnson, *ibid.*, **56**, 1180 (1934).