TABLE I

THE PERCENTAGE YIELD, B. P., SP. GR., AND REF. INDEX OF LACTIC ESTERS

α-Acetoxypropionate esters	B. p. °C.	Mm.	B. p. 763–5 mm.	Yield, % with Ketene	Yield, % with Acetic anhydride	d^{25}_{25}	$n^{25}D$	Empirical formula	Acetyl, % Calcd.	Acetyl, % Found
Methyl	68–73	14		96.4	92					
Ethyl	73–76	11		98.0	91					
n-Butyl	94–97	8		98.0	92					
Isobutyl	90–92	9	205	94.0	87	0.9952	1.4140	$C_9H_{16}O_4$	22.86	22.86
n-Propyl	77–79	7	196	97.0	87	1.0163	1.4123	$C_8H_{14}O_4$	24.70	24.48
Isopropyl	74–78	9	183	96.5	86	0.9920	1.4069	$C_8H_{14}O_4$	24.70	24.53
n-Amyl	101–103	8	227	97.0	87	0.9822	1.4199	$C_{10}H_{18}O_4$	21.27	21.13
Isoamyl	107–110	12	222	96.0	90	0.9838	1.4190	$C_{10}H_{18}O_4$	21.27	21.14
Benzyl	145–148	7	...	96.0	70					
β-Acetoxyethyl*	141–145	10	265	86.0	..	1.1489	1.4297	$C_9H_{14}O_6$	39.45	39.23

* Glycol monolactate diacetate.

is the result of polymerization of the excess ketene. If the reaction mixture is not allowed to stand for a few hours before distillation, this yellow color may later develop in the final distilled product. The reaction product distilled at 68–73° at 14 mm.; yield, 844 g. or 96.4%.

Methyl, isobutyl, *n*-propyl, isopropyl, *n*-amyl and isoamyl lactate were acetylated with acetic anhydride by the method of Burns.[2] Calcium carbonate was added to neutralize only the sulfuric acid used for catalyst, and the reaction product was fractionated in vacuum with a 24-inch (61-cm.) Widmer fractionating column.

Benzyl lactate was prepared from benzyl chloride and sodium lactate.[10]

Acknowledgment.—The authors are grateful to Dr. J. W. Williams for his helpful suggestions and kind permission to copy the ketene lamp designed by him and now in use in his laboratory at the University of Maryland.

(10) M. Gomberg and C. C. Buchler, THIS JOURNAL, **42**, 2064 (1920).

Summary

The methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl, isoamyl and benzyl lactates and glycol monolactate were acetylated with ketene in the presence of a trace of sulfuric acid as catalyst. The yields were greater than those obtained when acetic anhydride was used, being practically quantitative. Six new compounds were prepared: namely, *n*-propyl, isopropyl, isobutyl, *n*-amyl, and isoamyl α-acetoxypropionates and glycol monolactate diacetate. Some of the physical properties of these compounds are given.

WASHINGTON, D. C. RECEIVED JUNE 8, 1939

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

Synthesis of *t*-Butyl- and *t*-Amylcyclopentane and of their Intermediate Products[1]

BY HERMAN PINES AND V. N. IPATIEFF

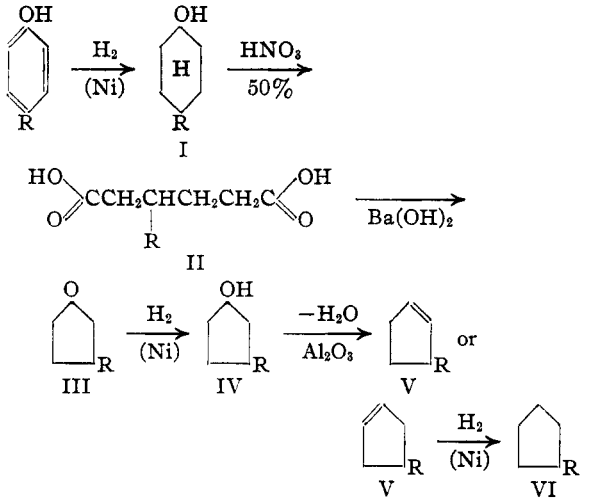
The preparation of *t*-alkylcyclopentanes has not been reported hitherto in the literature. Although the reaction of cyclopentanone with alkylmagnesium halide has been used successfully by others and also in our laboratory[2] for the preparation of several of the alkylcyclopentanes, the use of *t*-butylmagnesium halide did not yield the expected *t*-butylcyclopentanol, which would be an intermediate in the preparation of *t*-butylcyclopentane. Similarly, *t*-butylmagnesium bromide on reacting with cyclopentyl bromide gave only small yields of *t*-butylcyclopentane.

The method described in this paper for the preparation of *t*-alkylcyclopentane consists in cyclicizing alkyladipic acid to alkylcyclopentanone, a method which had been employed for the preparation of methylcyclopentanone. The starting products for the preparation of *t*-butyl- and *t*-amylcyclopentane were, respectively, *p*-*t*-butyl- and *p*-*t*-amylphenol, compounds which are now commercially available. The phenols were converted by catalytic hydrogenation to the corresponding *t*-alkylcyclohexanol; the latter on oxidation with nitric acid solution yielded β-*t*-butyl- and β-*t*-amyladipic acid. The β-*t*-alkyladipic

(1) Presented before the Division of Organic Chemistry at the American Chemical Society Meeting, Baltimore, Md., April 3–6, 1939.

(2) Chavanne and Becker, *Bull. soc. chim. Belg.*, **36**, 591 (1927); Pines and Ipatieff, THIS JOURNAL, **61**, 1076 (1939).

acids were converted into the 3-*t*-alkylcyclopentanones which were characterized by their solid semicarbazones and 2,4-dinitrophenylhydrazones. The yield of the 3-*t*-alkylcyclopentanone obtained based on the 4-*t*-butyl- and 4-*t*-amylcyclohexanol used was of the order of 60–75%. The alkyl cyclopentanone was hydrogenated catalytically to 3-*t*-butyl- and 3-*t*-amylcylopentanol, characterized by the α-naphthylurethans they yield with α-naphthyl isocyanate. The carbinols were dehydrated by the use of aluminum oxide to the olefins and the latter hydrogenated to *t*-butyl- and *t*-amylcyclopentane. The position of the double bond in the *t*-alkylcyclopentane is being investigated. The yields obtained on hydrogenation and dehydrogenation are almost quantitative. The methods of preparation may be illustrated as follows



(R = *t*-Butyl or *t*-Amyl)

Experimental

1. **4-*t*-Alkylcyclohexanol.**—The compounds were prepared by hydrogenation in an Ipatieff type electrically heated rotating autoclave of 10 parts of the *p*-*t*-butyl- and *p*-*t*-amylphenols in the presence of 1 part of nickel catalyst with 100 atmospheres of hydrogen at 125°. The hydrogenated product did not contain any unreacted alkylphenol, since it gave a negative test with ferric chloride.

4-*t*-Butylcyclohexanol, m. p. 82° (crystallized from *n*-heptane).

4-*t*-Amylcyclohexanol, m. p. 24–25°, b. p. 154–155° at 40 mm., d^{20}_4 (vac.) 0.9034. *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.56; H, 13.03. Found: C, 77.50; H, 12.95.

α-Naphthylurethan crystallized twice from heptane, m. p. 113°. *Anal.* Calcd. for $C_{22}H_{29}O_2N$: C, 77.95; H, 8.91. Found: C, 77.79; H, 8.48.

II. β-*t*-Alkyladipic Acids.—These were prepared by the procedure described by Niederl and Smith.[3] Several portions consisting of 1 mole of *t*-alkylcyclohexanol and 560 cc. of 50% nitric acid were heated in the presence of 0.5 g. of ammonium vanadate.

β-*t*-Butyladipic acid (yield 87%) crystallized twice from hot water, m. p. 117° (uncorr.). *Anal.* Calcd. for $C_{10}H_{18}O_4$: C, 59.36; H, 9.44. Found: C, 59.12; H, 9.25.

β-*t*-Amyladipic acid (yield 95%) crystallized twice from hot water, m. p. 77–78°. *Anal.* Calcd. for $C_{11}H_{20}O_4$: C, 61.06; H, 9.31. Found: C, 61.09; H, 9.35.

III. 3-*t*-Alkylcyclopentanone.—One hundred and eighty grams of β-alkyladipic acid was heated in a short-necked distilling flask with 18 g. of barium hydroxide at 280°. Water and alkylcyclopentanone generated during heating were collected in a receiver; at the end of one and one-half to two hours of heating the content of the flask was composed of a solid mass and no more liquid distilled over. The alkylcyclopentanone was separated from the water layer, washed with sodium bicarbonate solution and then dried over anhydrous sodium sulfate.

3-*t*-Butylcyclopentanone (yield 64–70%), boiling point 200–201° at 759 mm., $d^{20}_{vac.}$ 0.9031; n^{20}_D 1.4505. *Anal.* Calcd. for $C_9H_{16}O$: C, 77.07; H, 11.50. Found: C, 76.83; H, 11.43.

Semicarbazone crystallized from 50% ethanol; m. p. 194–194.5° (uncorr.) decomposes. *Anal.* Calcd. for $C_{10}H_{19}N_3O$: N, 21.32. Found: N, 21.26.

2,4-Dinitrophenylhydrazone.—Crystallized from 95% ethanol, m. p. 139° (uncorr.). *Anal.* Calcd. for $C_{15}H_{20}O_4N_4$: N, 17.50. Found: N, 17.53.

3-*t*-Amylcyclopentanone, yield 75–80%, b. p. 120° at 27 mm., $d^{20}_{vac.}$ 0.9159; $n^{20}D$ 1.4601. *Anal.* Calcd. for $C_{10}H_{18}O$: C, 77.85; H, 11.77. Found: C, 78.06; H, 11.72.

Semicarbazone.—Crystallized from 50% ethanol, m. p. 189° (uncorr.). *Anal.* Calcd. for $C_{11}H_{21}N_3O$: N, 19.88. Found: N, 19.66.

2,4-Dinitrophenylhydrazone.—Crystallized from 95% ethanol, m. p. 174.5° (uncorr.). *Anal.* Calcd. for $C_{16}H_{22}O_4N_4$: N, 16.75. Found: N, 16.72.

IV. 3-*t*-Alkylcyclopentanol.—The alcohol was prepared by hydrogenating 10 parts of *t*-alkylcyclopentanone in the presence of 1 part of nickel catalyst at 80° and 100 atmospheres initial hydrogen pressure. When the pressure during hydrogenation decreased to 60 atmospheres, the bomb was recharged to 100 atmospheres. The hydrogenation was considered completed when there was no decrease in hydrogen pressure for a period of two hours.

3-*t*-Butylcyclopentanol.—B. p. 196–198° at 744 mm., $d^{20}_{vac.}$ 0.9006; $n^{20}D$ 1.4574. *Anal.* Calcd. for $C_9H_{18}O$: C, 75.98; H, 12.77. Found: C, 76.11; H, 12.74.

α-Naphthylurethan.—Crystallized from heptane, m. p. 95°. *Anal.* Calcd. for $C_{20}H_{25}O_2N$: C, 77.12; H, 8.09; N, 4.50. Found: C, 76.94; H, 7.60; N, 5.00.

3-*t*-Amylcyclopentanol.—B. p. 217° at 738 mm., $d^{20}_{vac.}$ 0.9114, $n^{20}D$ 1.4656. *Anal.* Calcd. for $C_{10}H_{20}O$: C, 76.84; H, 12.91. Found: C, 77.07; H, 12.76.

α-Naphthylurethan crystallized from heptane, m. p. 82°. *Anal.* Calcd. for $C_{21}H_{27}O_2N$: C, 77.48; H, 8.37; N, 4.30. Found: C, 77.18; H, 8.15; N, 4.57.

V. *t*-Alkylcyclopentenes.—The olefins were prepared by dehydrating *t*-alkylcyclopentanols by passing the carbinols over 40 g. of activated alumina with a rate of 40

(3) Niederl and Smith, THIS JOURNAL, **59**, 717 (1937).

cc. per hour and at a temperature of 345°. The dehydration was quantitative. The olefins were separated from the water, dried over sodium sulfate and distilled over metallic sodium. The position of the double bond in the dehydrated *t*-alkylcyclopentanol is being studied.

***t*-Butylcyclopentene.**—Boiling point by Cottrell[4] method, 139.6° at 760 mm., dT/dP (770 to 730 mm.) = 0.048°/mm., $d^{20}_{vac.}$ 0.8021; $d^{40}_{vac.}$ 0.7861; $n^{20}D$ 1.4421; $n^{20}H_\beta$ 1.4486; $n^{20}H_\alpha$ 1.4397; Δ^{20} (dispersion) 88.8; δ^{20} (specific dispersion) 110.7. *Anal.* Calcd. for C_9H_{18}: C, 87.08; H, 12.92. Found: C, 87.35; H, 12.90.

***t*-Amylcyclopentene.**—B. p. 163–165° at 743 mm., $d^{20}_{vac.}$ 0.8256; $n^{20}D$ 1.4554; $n^{20}H_\beta$ 1.4618; $n^{20}H_\alpha$ 1.4527; Δ^{20} 90.8; δ^{20} 110.0. *Anal.* Calcd. for $C_{10}H_{18}$: C, 86.86; H, 13.14. Found: C, 86.72; H, 13.27.

VI. *t*-Alkylcyclopentane.—This hydrocarbon was prepared by hydrogenating at 60° *t*-alkylcyclopentene in the presence of 10% by weight of nickel catalyst and 100 atmospheres of hydrogen. The hydrogenation proceeded to completion, for the final product was stable toward a nitrating mixture composed of 2 volumes of concentrated sulfuric acid and 1 volume of concentrated nitric acid.

***t*-Butylcyclopentane,** m. p. −96 ± 0.2°, boiling point by Cottrell method 145.2° at 760 mm., dT/dP (770–730 mm.) = 0.052°/mm., $d^{20}_{vac.}$ 0.7911; $d^{40}_{vac.}$ 0.7753; $n^{20}D$ 1.4341; $n^{20}H_\beta$ 1.4396; $n^{20}H_\alpha$ 1.4320; Δ^{20} 76.4; δ^{20} 96.6. *Anal.* Calcd. for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.75; H, 14.49.

***t*-Amylcyclopentane.**—Boiling point by Cottrell method 173.9° at 760 mm., dT/dP (770–730 mm.) = 0.054°/mm., $d^{20}_{vac.}$ 0.8071; $d^{40}_{vac.}$ 0.7923; $n^{20}D$ 1.4457; $n^{20}H_\beta$ 1.4511; $n^{20}H_\alpha$ 1.4433; Δ^{20} 78.0; δ^{20} 96.6. *Anal.* Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.63; H, 14.25.

(4) Cottrell, THIS JOURNAL, **41**, 721 (1929); Bruun and Hicks-Bruun, *Bur. Standards J. Research*, **6**, 871 (1931).

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Summary

Synthesis of *t*-butyl- and *t*-amylcyclopentane from *p*-*t*-butyl- and *p*-*t*-amylphenols is described.

The following compounds and their derivatives were synthesized for the first time: 4-*t*-amylcyclohexanol, β-*t*-butyl- and β-*t*-amyladipic acid, 3-*t*-butyl- and 3-*t*-amylcyclopentanone, 3-*t*-butyl- and 3-*t*-amylcyclopentanol, *t*-butyl- and *t*-amylcyclopentene, *t*-butyl- and *t*-amylcyclopentane.

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[CONTRIBUTION NO. 174 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

Utilization of Alkoxy Ketones in the Synthesis of Quinolines by the Pfitzinger Reaction

BY LOY B. CROSS[1,2] WITH HENRY R. HENZE

Although the utilization of simple aldehydes and ketones in the synthesis of quinoline acids has received considerable attention, but little effort has been made to use bifunctional carbonyl compounds in this manner. Indeed, Henze[3] has reported the initial investigation in which keto ethers were employed in the Pfitzinger reaction, namely, the preparation of four 3-aryloxy-4-quinaldinecarboxylic acids from the appropriate aryloxyacetones.

Our study of the utilization of keto ethers in the Pfitzinger reaction has been extended to include alkoxy ketones and the condensation of ethoxyacetone and ethoxymethyl ethyl ketone with isatin to produce the corresponding 2-alkyl-3-ethoxycinchoninic acids. However, no evidence has been obtained of the formation of any of the isomeric 2-ethoxyalkylcinchoninic acids.[4] The substituted cinchoninic acids are readily decarboxylated by heating at the temperature of their melting points to form 2-alkyl-3-ethoxyquinolines. Also, these 3-alkoxycinchoninic acids are cleaved at the ether linkage by heating with concentrated hydrochloric acid under pressure. The cinchoninic acids and the 2-alkyl 3-ethoxyquinolines are both extremely resistant to reduction by means of hydriodic acid and red phosphorus and no hydrogenation of the pyridine nucleus was observed. However, 2-ethyl-3-hydroxyquinoline was converted, by means of the reducing action of tin and hydrochloric acid, into 2-ethyl-1,2,3,4-tetrahydroquinoline. An attempt was made to form the phthalone of 3-ethoxyquinaldinic acid by heating with phthalic anhydride. Although the temperature employed was approxi-

(1) From the Ph.D. dissertation of Loy B. Cross, June, 1938.
(2) Present address: Emory University, Atlanta, Ga.
(3) Calaway with Henze, THIS JOURNAL, **61**, 1355 (1939).

(4) Methyl ethyl ketone reacts with isatin in alkaline solution to form both 2,3-dimethylcinchoninic acid [Pfitzinger, *J. prakt. Chem.*, **56**, 283 (1897)] and 2-ethylcinchoninic acid [von Braun, Gmelin and Schultheiss, *Ber.*, **56**, 1344 (1923)].