

Ketones, Carbinols and Hydrocarbons Containing the *p*-Xylyl Group

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We have prepared ketones, alcohols and hydrocarbons of the type ArCOR, ArCHOHR and ArCH₂R, where Ar is *p*-xylyl and R is methyl

Ketones.—The ketones were prepared on a molar scale, using a standard procedure.¹ After the reaction was complete and the mixture processed in the usual manner, the ketones were fractionated through a 27-plate column. Yields were calculated on the material obtained. A 50-g. sample of each ketone was then refractionated through the same column and the physical properties and analyses were determined on the middle fractions of this second fractionation.

TABLE I
p-XYLYL ALKYL KETONES

Alkyl	Yield, %	B. p.		<i>n</i> ²⁰ _D	<i>d</i> ₄₀	(MR) ²⁰ _D		Analyses, %			
		°C.	mm.			Calcd.	Obs. [†]	Carbon		Hydrogen	
								Calcd.	Found	Calcd.	Found
Methyl ^{a,e}	52.1	101	9	1.5245	0.9870	44.67	45.91	81.8	80.8	8.11	8.32
Ethyl ^{b,f}	70.5	106	7	1.5183	.9730	49.29	50.48	81.5	81.5	8.65	8.84
Propyl ^{c,g}	65.5	119	7	1.5124	.9577	53.90	55.18	81.8	81.7	9.09	9.28
Butyl ^{d,h}	82.8	123	5	1.5080	.9460	58.55	59.87	82.1	82.2	9.48	9.68
Amyl ^d	79.0	137	7	1.5053	.9377	63.14	64.33	82.4	82.5	9.81	9.75
Hexyl ^d	83.3	143	3.5	1.5025	.9308	67.76	69.09	82.6	82.8	10.1	10.3
Heptyl ^d	85.3	144	1	1.5002	.9245	72.38	73.83	82.8	82.9	10.3	10.4

^a 2,4-Dinitrophenylhydrazone, m. p. 99–100°; semicarbazone, m. p. 168–169°. ^b 2,4-Dinitrophenylhydrazone, m. p. 79–80°; semicarbazone, m. p. 170–171°. ^c 2,4-Dinitrophenylhydrazone, m. p. 115–116°; semicarbazone, an oil. ^d 2,4-Dinitrophenylhydrazone, semicarbazone, and oxime are oils. ^e Claus and Wollner, *Ber.*, 18, 1856 (1883); Freund, Fleischer and Gofferje, *Ann.*, 414, 5 (1918). ^f Claus and Fickert, *Ber.*, 19, 3182 (1886). ^g Claus, *J. prakt. Chem.*, [2] 46, 478 (*J. Chem. Soc. Abstracts*, 64 [1], 162 (1893)). ^h Layraud, *Bull. soc. chim.*, [3] 35, 230 (1906). [†] The exaltation shown is characteristic of compounds having a carbonyl conjugated with a benzene ring; cf. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., p. 530, D. Van Nostrand Co., Inc., New York, N. Y., 1948.

TABLE II
p-XYLYLALKYL CARBINOLS

-alkyl-	M. p., °C.	Analyses, %			
		Carbon		Hydrogen	
		Calcd.	Found	Calcd.	Found
Ethyl	36.5–37	80.5	80.3	9.76	10.0
Propyl	59–59.5	81.0	80.8	10.1	10.2
Butyl	51–52	81.3	81.0	10.4	10.6
Amyl	57–58	81.6	81.5	10.7	10.7
Hexyl	63–64	81.9	81.6	10.9	11.1
Heptyl	59–60	82.1	82.2	11.1	11.2

Carbinols.—A 50-g. sample of each ketone was treated with an equimolar quantity of aluminum isopropoxide in anhydrous isopropyl alcohol according to a standard procedure.² The methyl carbinol, previously reported,³ was obtained in 60% yield. The other compounds were obtained in yields of 80–90%. The ethyl through heptyl compounds are listed in Table II.

Hydrocarbons.—The ketones were reduced in 50-g. quantities to the corresponding hydrocarbons according to Method I described by Martin.⁴ The hydrocarbons were twice distilled through a 27-plate column. Yields and other data in Table III are based on the fractions of constant b. p. and index obtained from the second dis-

TABLE III
1,4-DIMETHYL-2-ALKYLBENZENES

2-Alkyl	Yield, %	B. p.		<i>n</i> ²⁰ _D	<i>d</i> ₄₀	(MR) ²⁰ _D		Analyses, %				Sulfonamide m. p. °C.
		°C.	mm.			Calcd.	Obs.	Carbon		Hydrogen		
								Calcd.	Found	Calcd.	Found	
Ethyl ^{a,e}	49	74	15	1.5000	0.8686	44.78	45.48 ^g	89.6	89.5	10.4	10.7	107–108
Propyl ^{a,f}	34	73	6.5	1.4964	.8639	49.40	50.00	89.2	89.2	10.8	11.0	117–118
Butyl ^a	17	85	5.5	1.4931	.8629	54.02	54.57	88.9	88.6	11.1	11.3	107–108
Amyl ^b	23	96	4.5	1.4914	.8621	58.68	59.17	88.6	88.6	11.4	11.4	99–100
Hexyl ^b	16	110	5	1.4903	.8584	63.27	64.02	88.4	88.3	11.6	11.5	94–95
Heptyl ^{c,d}	19	123	4	1.4885	.8571	67.87	68.63	88.2	88.3	11.8	12.0	100–101
Octyl ^c	11	134	4	1.4882	.8579	72.49	73.23	88.0	87.9	12.0	11.9	100–101

^a Reaction time fifteen hours. ^b Reaction time twenty-three hours. ^c Reaction time twenty-seven hours. ^d Second reduction of reaction time ninety-six hours increased yield to 36%. ^e Ref. 3. ^f Footnote e, Table I, 2nd ref. ^g A value of 45.38 at 25° is reported in "Selected Values of Properties of Hydrocarbons," Table 14b, A. P. I. Research Project 44, National Bureau of Standards, Washington, D. C.

through *n*-heptyl. These compounds have been prepared as part of a program of study of the effect of ortho-meta substitution on reactivity.

Starting Materials.—The acid chlorides, butyryl and higher, were prepared from the corresponding acids by reaction with excess thionyl chloride. Propionyl chloride was prepared from propionic acid by reaction with phosphoric pentachloride. The acetyl chloride was Eastman Kodak Co. Yellow Label. All the acid chlorides were freshly distilled before use. The *p*-xylene was Eastman White Label, used without additional purification.

tillation. A sulfonamide derivative of each hydrocarbon was prepared according to a standard procedure.⁵

(1) Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

(2) Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 203.

(3) Klages and Keil, *Ber.*, 36, 1639 (1903).

(4) Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 164.

(5) Shriner and Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 194.

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Peroxide Formation in Propionaldehyde

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During the purification of propionaldehyde for use in the study of hemiacetal formation,² it was found not possible to store a pure sample in the presence of air without absorption of oxygen and a simultaneous change in physical properties.

of peroxides by a spot test.³ Fractions boiling below 48.0° gave dark red colorations with the indicator, while the fractions boiling at 48.0° or higher produced only a very light orange color. When the aldehyde was distilled and collected in a nitrogen atmosphere, no coloration was obtained with the peroxide indicator.

During each distillation, a light yellow oily substance, presumably a polymer, was formed. Buckler^{4,5} reported sporadic spontaneous polymerization of his propionaldehyde samples. Polymerization may have been initiated by ozone or ultraviolet light from the occasional use of mercury lamps in his laboratory.

The refractive index for propionaldehyde has been reported to be n_D^{20} 1.3636.⁶ When freshly distilled, propionaldehyde was found to have n_D^{25} 1.3601; this value increased rapidly over a period of minutes and then more slowly until a constant value of n_D^{25} 1.3630 was reached after twenty-four hours. The change in refractive index was found to be at least partially dependent on the previous treatment of the Pyrex flasks in which the alde-

TABLE I

CHANGE IN REFRACTIVE INDEX OF PROPIONALDEHYDE WITH PREVIOUS TREATMENT OF THE GLASS CONTAINERS

Atmosphere	Treatment of glass containers	Period of time with constant $n = 1.3601$	Change ^a to $n = 1.3611$	Period of time with constant $n = 1.3611$	Change ^a to $n = 1.3630$
Air	No treatment	Immediate change from this value	45 min.	24 hr.	2-3 days
Air	Boiled out with water for 20 min.	35 min.	40 min.	27 hr.	10 days ^b
N ₂	Boiled out with water for 20 min.	90 min.	After 3 hr., $n = 1.3603$ (no further measurements)		
Air	Boiled out with 6N-H ₂ SO ₄ for 20 min.	Immediate change from this value	30 min.	45 min.	11 days ^b
Air	Boiled out with 6N-NaOH for 20 min.	5 min.	30 min.	40 min.	3 days ^b
Air	Super-heated steam (105-125°) for 20 min.	35 min.	55 min.	8 days ^c
COLORATION OF PEROXIDE INDICATOR					
Air	No treatment	Light orange; constant shade	Gradual intensification of color	Red orange; constant shade	

^a "Change" indicates the period of time during which the index changed from 1.3601 to 1.3611, or from 1.3611 to 1.3630. ^b The refractive index remained constant for nineteen days; no measurements were made after that period. ^c No further observations.

The propionaldehyde was Eastman White Label product with a boiling range of 47.8-50.5°. The fraction which distilled at 48.0 ± 0.05° (760 mm.) represented about 80% of the total material. During redistillation of such a fraction boiling 48.0 ± 0.05°, distillation began at 44.1°. When the temperature reached 46.0°, the boiling liquid frothed violently and the temperature rose abruptly to 48.0°; about 15% of the material had distilled between 44.1-46.0°.

Violent frothing of the propionaldehyde during distillation suggested the presence of peroxide. The several fractions were tested for the presence

of peroxides by a spot test.³ Fractions boiling below 48.0° gave dark red colorations with the indicator, while the fractions boiling at 48.0° or higher produced only a very light orange color. When the aldehyde was distilled and collected in a nitrogen atmosphere, no coloration was obtained with the peroxide indicator.

Change of refractive index and change in color of the peroxide indicator were simultaneously compared; a correlation between increase in refractive index and increase in peroxide content is evident from Table I. The change in refractive

(3) The presence of peroxides was detected by addition of a drop of a 10% ammonium thiocyanate solution (to which a crystal of ferrous ammonium sulfate, free of ferric, had been added) to a drop of the aldehyde. When peroxides are present, a red coloration is obtained whose intensity is roughly proportional to the peroxide content.

(4) Buckler, *J. Chem. Soc.*, 1036 (1937).

(5) Buckler, private communication.

(6) Brühl, *Ann.*, **200**, 139 (1880).

(1) Present address: Air Reduction Sales Company, Research Laboratories, Murray Hill, New Jersey.

(2) McKenna, Lingafelter and Tartar, *THIS JOURNAL*, **71**, 729 (1949).