[CONTRIBUTION FROM THE FLIGHT PROPULSION RESEARCH LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

o-, *m*- and *p*-*t*-Butyltoluenes

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The fuel evaluation program conducted at this Laboratory involving the synthesis and purification of aromatic hydrocarbons included the preparation of five-gallon quantities of *m*- and *p*-*t*-butyltoluenes. One reference was found in the literature on *o*-*t*-butyltoluene[1] and the physical properties attributed to this compound were not in accordance with expectations. Accordingly, a smaller scale preparation of this hydrocarbon was undertaken in order to obtain physical constants data for the three isomeric compounds, including a brief analysis of the infrared spectra.

The alkylation of monoalkylbenzenes by the alcohol–boron trifluoride method has been described in the preparation of some *p*-dialkylbenzenes.[2] This procedure was followed in the present work in several relatively large-scale runs and an analysis of the resulting product by careful fractionation using a distillation column rated above 100-theoretical plates indicated that nearly equal amounts of the *m*- and *p*-isomers were obtained. This result is not in agreement with the earlier work and the formation of the *m*-isomer may possibly be attributed to some slight deviation in the experimental conditions when applied on a larger scale. However, the refractive index value reported in the previous work for *p*-*t*-butyltoluene indicates a mixture of both isomers of nearly identical composition with that obtained in this investigation. The proximity of the boiling points of the two isomers as shown in Table I indicates that complete separation would require a precise fractionation.

The use of aluminum chloride in the alkylation of toluene with *t*-butyl alcohol[3] similarly resulted in mixtures which upon fractionation indicated the presence of both isomers. The total yield of dialkylbenzenes was nearly identical in both procedures as shown in Table I but the *m*-isomer was obtained in appreciably higher yield when aluminum chloride was used. Both procedures gave substantial yields of higher boiling material which was not investigated further at this time.

No trace of the *o*-isomer was apparent in the reaction products of these two methods of preparation. This compound was obtained by the condensation of *t*-butyl chloride with *o*-methylphenylmagnesium bromide and the physical properties of the three isomeric hydrocarbons are summarized in Table I. A high state of purity of each compound was indicated by the time–temperature freezing or melting curves. The physical properties were obtained by methods previously described[4] with the exception of the density values which were measured by means of apparatus described by Forziati, *et al.*[5]

TABLE I

PHYSICAL PROPERTIES, YIELDS AND ANALYSES OF *o*-, *m*- AND *p*-*t*-BUTYLTOLUENES

Hydrocarbon		Butyltoluene *o*-*t*-	*m*-*t*-	*p*-*t*-
M. p., °C.		−50.32	−41.39	−52.49^{a}
B. p., °C. (760 mm.)		200.45	189.29	192.75
Density, g./ml., 20°C.		0.88976	0.86587	0.86115
$n^{20}\text{D}$		1.50766	1.49456	1.49185
Yield, %		18	28^{b} 34^{c}	23^{b} 14^{c}
Anal., % Calcd.:	Carbon	89.11	89.11	89.11
	Hydrogen	10.89	10.89	10.89
Anal., % Found:	Carbon	89.00	89.22	88.96
	Hydrogen	11.00	10.73	10.60

[a] Value obtained from freezing curve. [b] Reaction using boron trifluoride and calculated on basis of *t*-butyl alcohol after initial separation of product. [c] Reaction using aluminum chloride and calculated on basis of *t*-butyl alcohol after initial separation of product.

The physical properties of *o*-*t*-butyltoluene described in the previously cited reference[1] are the boiling point and the refractive index[6] and the values are seen to differ significantly from the corresponding values obtained in this investigation.

The hydrocarbons were oxidized to the corresponding *t*-butylbenzoic acids by the alkaline–permanganate method.[7] *o*-*t*-Butylbenzoic acid is reported for the first time and the analyses, neutral

TABLE II

DATA ON *t*-BUTYLBENZOIC ACIDS OBTAINED FROM ALKALINE-POTASSIUM PERMANGANATE OXIDATION OF *t*-BUTYLTOLUENES

Oxidation product		Butylbenzoic Acid *o*-*t*-	*m*-*t*-	*p*-*t*-
M. p., °C. lit.		....	127^{a}	164^{b}
M. p., °C. obs.^{c}		80.3–80.8^{d}	127.0–127.6^{e}	165.0–165.6^{e}
Anal., % Calcd.:	Carbon	74.12	74.12	74.12
	Hydrogen	7.91	7.91	7.91
Anal., % Found:	Carbon	73.74	73.82	73.97
	Hydrogen	7.66	7.72	7.54
Neut. equiv.	Calcd.	178.2	178.2	178.2
	Found	174.4	179.2	178.3

[a] Kelbe and Pfeiffer, *Ber.*, 19, 1726 (1886). [b] Kelbe and Pfeiffer, *ibid.*, 19, 1725 (1886); Bialobrzeski, *Ber.*, **30**, 1775 (1897). [c] Observed melting points are corrected. [d] Recrystallized out of neohexane. [e] Recrystallized out of ethyl alcohol. Identical acids also obtained by use of dilute nitric acid.

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(1) Kozak, *Chem. Zentr.*, **78**, I, 1787 (1907).

(2) Welsh and Hennion, THIS JOURNAL, **63**, 2603 (1941).

(3) Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry" Reinhold Publishing Corp., New York, N. Y., p. 621.

(4) Gibbons, *et al.*, THIS JOURNAL, **68**, 1130 (1946).

(5) Forziati, Mair and Rossini, *J. Research Natl. Bur. Standards*, **35**, 513 (1945).

(6) This compound is described as prepared by the condensation of *o*-bromo-*t*-butylbenzene with methyl bromide in the presence of sodium; b. p. 170° at 743 mm. and $n^{17}\text{D}$ 1.49423.

(7) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., p. 164.

equivalents and melting points of the acids are shown in Table II.

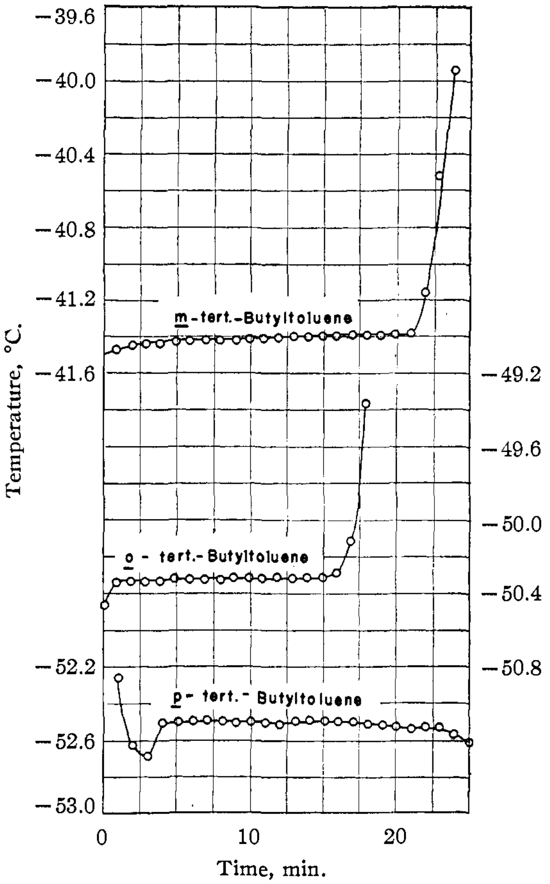

Fig. 1.—Time-temperature freezing or melting curves of *o*-, *m*- and *p*-*t*-butyltoluenes.

The infrared absorption spectra of the three hydrocarbons were obtained by the use of a spectrometer previously described[8] with the photoelectric amplifier of McAlister, *et al.*[9] The data are given in Table III with the intensity of absorption arbitrarily indicated as shown. The wave length certainty is estimated to be ±0.05 μ. Since the only purpose for the analysis of the absorption spectra of these compounds was to supplement the conclusions with respect to *o*-, *m*- and *p*-isomerism[10] a limited portion of the spectra is presented. The wave length regions 8.20–9.25 μ and 11.90–13.90 μ are of particular significance in the analysis of structure for the di-substituted aromatics[11] and Table IV is a summary from a portion of the data in the cited reference. The indicated wave length regions in the table are characterized by relatively high absorption for *o*-, *m*- and *p*-substituted compounds. The infrared data for the designated *t*-butyltoluenes show fairly good agreement as indicated by a comparison between Tables III and IV.

TABLE III

PARTIAL INFRARED SPECTRA OF THE ISOMERIC *t*-BUTYLTOLUENES

Previously designated as *o*-*t*-butyltoluene		Previously designated as *m*-*t*-butyltoluene		Previously designated as *p*-*t*-butyltoluene	
λ, (μ)	Intensity of absorption[a]	λ, (μ)	Intensity of absorption	λ, (μ)	Intensity of absorption
7.75	W	8.30	M	8.05	W
7.95	M	8.50	W	8.35	M
8.35	W	9.20	M	9.00	S
8.80	W	9.65	W	9.75	S
9.20	M	10.80	W	10.60	W
9.45	M	11.20	S	11.75	W
9.65	W	11.35	W	12.20	S
10.65	M	12.70	S	12.55	W
10.75	W			14.00	M
11.65	W				
11.75	W				
13.20	S				
13.85	S				

[a] W, M and S indicating weak, medium and strong intensities of absorption.

TABLE IV

CHARACTERISTIC INFRARED ABSORPTION BANDS FOR DI-SUBSTITUTED AROMATIC COMPOUNDS[11]

Position of substituents	Wave length, (μ)		
o-	9.15 ± 0.10	13.60 ± 0.3	
m-	8.70 ± 0.10	12.80 ± 0.3	
p-	8.30 ± 0.10	9.05 ± 0.10	12.20 ± 0.3

Experimental

Alkylation of Toluene Using Boron Trifluoride.—The reaction vessel consisted of a 10-gal., copper-lined reactor equipped with a stirrer, reflux condensor and a copper inlet tube in the form of a perforated coil submerged below the liquid level. An ice-chilled brine solution was circulated through the outer jacket of the reaction vessel by means of a pump. A typical run consisted of 25 moles of *t*-butyl alcohol and 100 moles of toluene cooled to approximately 5° after which 25 moles of boron trifluoride was bubbled through the coil in approximately two hours. The reaction mixture was stirred at 5–15° for four hours and then allowed to come to room temperature. The reaction product was then transferred to a stainless steel reactor and heated for six hours at 70–80°. After cooling, the hydrocarbon layer was separated off, washed twice with water, then with dilute sodium carbonate solution and again with water. The combined material from several such runs was dried by passage through alumina. The unreacted toluene was then stripped off and the remainder was fractionated on a Fenske-type column as previously mentioned.

Alkylation of Toluene Using Aluminum Chloride.—The Friedel–Crafts reaction was carried out in a 30-gal., glass-lined reactor. The quantities of reactants and reaction conditions closely followed the general procedure.[3] A mixture of 500 moles of toluene and 150 moles of aluminum chloride was cooled by cold water circulating through the jacket. To this was gradually added 150 moles of *t*-butyl alcohol dissolved in 250 moles of toluene, the total addition time being six hours. The reaction mixture was stirred for twelve hours and the complex was then hydrolyzed by passing it through a pipe to a second reactor which

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[8] Brattain, Rasmussen and Cravath, *J. Applied Phys.*, **14**, 418 (1943).

[9] McAlister, Matheson and Sweeney, *Review Scientific Instruments*, **12**, 314 (1941).

[10] Barnes, Liddel and Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 659 (1943).

[11] Barnes, Gore, Stafford and Williams, *Anal. Chem.*, **20**, 402 (1948).

was partially filled with water and ice and located one floor-level below. After a short period of stirring, the hydrocarbon layer was removed and worked up as in the previous procedure. Final purification was effected by a second fractionation of the individual isomers accumulated from both syntheses.

o-t-Butyltoluene.—The Grignard reagent was made using 85 moles of magnesium covered with 12 liters of dry ether to which was added over a period of five hours 80 moles of *o*-bromotoluene (f.p. −26.91° and $n^{20}\text{D}$ 1.5563) dissolved in 5 liters of dry ether. This was condensed with 72 moles of *t*-butyl chloride dissolved in 5 liters of dry ether and the reaction mixture was stirred overnight. After hydrolysis with dilute hydrochloric acid, the hydrocarbon layer was separated and the ether was evaporated.

The crude product was then dried over sodium sulfate and fractionated on a 15-theoretical plate column. Halogen impurities were removed by treatment with sodium in liquid ammonia. It was finally fractionated on a six-foot Podbielniak column and the yield of pure hydrocarbon based on the *t*-butyl chloride is shown in Table I.

Oxidation of *t*-Butyltoluenes.—No difficulty was encountered in the oxidation of the *m*- and *p*-isomers. The *t*-butylbenzoic acids obtained by the alkaline-permanganate method were found to be identical with those obtained by dilute nitric acid oxidation after maximum purity was attained by successive recrystallizations out of ethyl alcohol. Several attempted oxidations of the *o*-isomer using alkaline permanganate resulted in an oil which could not be crystallized. When the oil was purified by distillation at reduced pressure, a solid product was obtained which was recrystallized out of neohexane and found upon analysis to be *o-t*-butylbenzoic acid. The data on these acids are shown in Table II.

The oxidation of *o-t*-butyltoluene was also carried out in a sealed tube using dilute nitric acid and heating at 170° for twelve hours. Phthalic acid was precipitated out by the addition of chloroform to the oil resulting in this procedure and this was sublimed to phthalic anhydride, which gave no depression in melting point when mixed with an authentic sample (m.p. 130.8°).

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Summary

1. The use of boron trifluoride as an alkylation catalyst has been shown to result in mixtures of *p*- and *m-t*-butyltoluenes in the reaction between toluene and *t*-butyl alcohol. The yield of each isomer is nearly the same but when aluminum chloride is used as the catalyst the *m*-isomer is appreciably greater with a corresponding decrease in yield of the *p*-compound.

2. The preparation and characterization of *o-t*-butyltoluene has been described. The physical properties have been shown to differ from those reported in the only earlier work on the synthesis of this hydrocarbon.

3. The physical properties of the three isomeric *t*-butyltoluenes in high purity have been described and time-temperature freezing or melting curves for these compounds are shown.

4. The oxidation of *o*-, *m*- and *p-t*-butyltoluenes to the corresponding *t*-butylbenzoic acids has been described and *o-t*-butylbenzoic acid has been reported for the first time.

5. Partial infrared absorption data for the *t*-butyltoluenes have been determined for purposes of gross structural analysis and the data have been shown to be in good agreement with previous work wherein characteristic absorption spectra for disubstituted aromatic compounds have been evaluated.

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Erythrina Alkaloids. XVI. Studies on the Constitution of Erysodine, Erysovine and Erysopine[1]

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Structure studies on erysodine, erysovine and erysopine have elucidated the functional groups and the number of rings of each alkaloid, and have shown that each has the same ring system.

These three *Erythrina* alkaloids[2,3,4] have interesting curare-like pharmacologic action.[5] Erysodine and erysovine have the same molecular formula, $C_{18}H_{21}NO_3$; each has two methoxyl groups and one phenolic hydroxyl group. Therefore, the functional groups containing all the oxygen atoms of erysodine and erysovine are known.[2] Erysopine[2] has the formula $C_{17}H_{19}NO_3$, one methoxyl group, and two phenolic hydroxyl groups which are ortho as indicated by a color reaction with ferric chloride. None of these three alkaloids showed the presence of an N-methyl group or a C-methyl group. The presence of methoxyl groups, and particularly the phenolic hydroxyl groups, implies the presence of at least one benzenoid nucleus in all three alkaloids.

A facile reaction between erysodine and methyl iodide to give the crystalline quaternary salt, erysodine methiodide, proved the tertiary nature of the nitrogen atom in erysodine.

Erysodine reacted with two molar equivalents of hydrogen with Adams platinum catalyst at atmospheric pressure. The ease of hydrogenation was

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(1) Presented in part at the Meeting of the American Chemical Society in Atlantic City, N. J., September 10, 1941; Abstracts of Papers, Division of Organic Chemistry, p. 30.

(2) Folkers and Koniuszy, THIS JOURNAL, **62**, 1677 (1940).

(3) Gentile and Labriola, *J. Org. Chem.*, **7**, 136 (1942).

(4) Deulofeu, Labriola, Hug, Fondovila and Kauffman, *J. Org. Chem.*, **12**, 486 (1947).

(5) Unna and Greslin, *J. Pharmacol.*, **80**, 53 (1944).