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THE SYNTHESIS OF *o*-DIETHYLBENZENE AND THE CATALYTIC OXIDATION OF THE DIETHYLBENZENES

ERNST D. BERGMANN[1] and CHAIM RESNIK[2]

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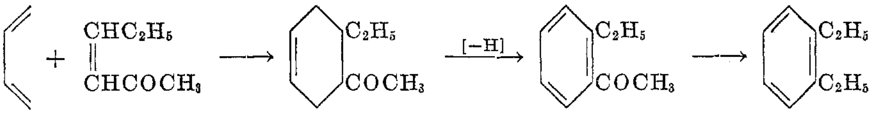
For the study of the catalytic oxidation and the spectrographic (infrared) determination (1) of the three diethylbenzenes, unambiguous methods for their preparation were investigated. The diethylation of benzene which yields *m*- and *p*-diethylbenzene [Voswinkel (2); see Copenhauer and Reid (3)] is not suitable for the preparation of the pure compounds, as the direction of the second ethyl group appears to be influenced by unknown factors. Thus, Norris and Arthur (4) have described the preparation of *m*-diethylbenzene by the condensation of ethyl acetate and benzene, while a German patent (5) claims that this method gives practically only the *p*-compound.

Instead of separating isomeric substitution products of ethylbenzene, as Karabinos, *et al.* (6) and Birch, Dean, Fidler, and Lowry (7) have done [see also Nickels and Heintzelman (18)], the direct synthesis of *p*- and particularly *o*-diethylbenzene was studied, satisfactory methods being available for *m*-diethylbenzene (8, 8a).

p-Diethylbenzene. The synthesis of ethylacetophenone from ethylbenzene, acetyl chloride, and aluminum chloride (9), led to a product which, upon subsequent reduction, gave a mixture of 10 ± 5% *m*-, 30 ± 10% *o*-, and only 45–60% *p*-diethylbenzene [analysis based on the infrared spectrum (1)]. Clemmensen reduction of *p*-diacetylbenzene, which is available by the method of Berend and Harms (10), gave spectrographically pure *p*-diethylbenzene, though not in good yield (26%).

o-Diethylbenzene. For the synthesis of the *o*-compound, the Diels-Alder reaction between propylideneacetone and butadiene was used:



According to Pastreau and Zamenhoff (11), the condensation of propionaldehyde and acetone to hexan-4-ol-2-one, $CH_3CH_2CHOHCH_2COCH_3$, proceeds with 60% yield under the influence of alkali in ether; using only catalytic quantities of alkali and an excess of acetone as solvent, the formation of by-products [diacetone-alcohol, higher-boiling substances; see Kyriakides (12)] can be avoided. The ketol could be dehydrated quantitatively (by distillation in presence of a trace of iodine) to propylideneacetone which was characterized by its 4-nitrophenylhydrazone.

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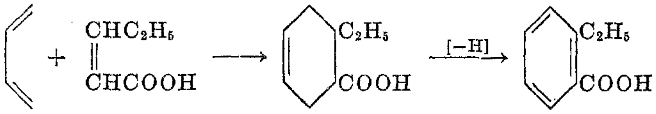
[1] Present address: Scientific Department, Israeli Ministry of Defense, Tel-Aviv, Israel.

[2] Part of a thesis, submitted by Chaim Resnik to the Hebrew University, Jerusalem, in fulfillment of the requirements for the degree of M. Sc.

The condensation of propylideneacetone with butadiene at 160°, gave, at 60% conversion, 30% of 4-ethyl-5-acetylcyclohexene, characterized by its 2,4-dinitrophenylhydrazone. Catalytic dehydrogenation gives, in quantitative yield, *o*-ethylacetophenone, and the Clemmensen reduction of the latter a 50% yield of pure *o*-diethylbenzene.

The analogous condensation of butadiene and β-ethylacrylic acid led in 50% yield to 5-ethylcyclohexene-4-carboxylic acid which was easily dehydrogenated to *o*-ethylbenzoic acid:



For the catalytic oxidation of the isomeric diethylbenzenes in the liquid phase, two catalysts were used, one consisting of chromic oxide and cobalt oxide in the ratio 4:1, the other of chromic oxide and calcium oxide in the ratio 1:4, activated by heating at 450° and 250°, respectively; the former proved considerably superior in its activity. In accordance with the experience of Mowry (13) who oxidized the *meta*-compound in presence of chromic oxide-calcium carbonate, only one ethyl group was attacked, giving the corresponding ethylacetophenones, together with small quantities of the ethylbenzoic acids. The acetyl groups appear to deactivate the catalyst or the second ethyl group. A marked difference in the reactivity of the three isomers was observed; the *m*-compound was oxidized more quickly than the *p*-, and the *p*- more quickly than the *o*-derivative. *o*- and *m*-Ethylacetophenone are best characterized by their semicarbazones; for the *p*-compound, the 2,4-dinitrophenylhydrazone is preferable.

EXPERIMENTAL

The physical constants of the diethylbenzenes are summarized in Table I. All m.p.'s and b.p.'s are uncorrected.

p-Diethylbenzene. The Clemmensen reduction of 100 g. of *p*-diacetylbenzene (10), m.p. 112–113° (from alcohol), gave 2.5 g. of *p*-ethylacetophenone, b.p. 129–130°/23 mm., and 21.5 g. (26%) of *p*-diethylbenzene. The purity of the latter was ascertained by its infrared spectrum (1). The hydrocarbon is best characterized as its tetrabromo-derivative, m.p. 110–111° (from alcohol) (14). Also *m*-diethylbenzene gives a characteristic tetrabromo-derivative, m.p. 76–77° (from alcohol) (2).

o-DIETHYLBENZENE

(*a*) *Hexan-4-ol-2-one.* In a three-necked flask, equipped with stirrer, thermometer, and dropping-funnel, 1200 g. of freshly distilled acetone and 12 cc. of 10% sodium hydroxide solution were placed and, at a temperature of 8–10°, 150 g. of propionaldehyde was added during six hours. The stirring was continued for another hour and 2 g. of tartaric acid was added. Then, the excess acetone was distilled off (986 g.) and the residue distilled under 23 mm. pressure. After a head fraction (12 g.), two main cuts were isolated: (a) 71–73°/23 mm., 4.5 g.; (b) 88–89°/23 mm., 182 g. The slight residue distilled at 112–120°/23 mm. and was not further investigated. Fraction (a) was identified as diacetonealcohol by dehydration (distillation in presence of a trace of iodine) to mesityl oxide, b.p. 32–33°/22 mm.; *4-nitrophenylhydrazone*, m.p. 205–206°, from isopropyl alcohol. Fraction (b) is the desired ketol, yield 60.6%; d_4^{18} 0.95073; n_D^{20} 1.4309; MR (calc'd), 31.45; MR (found), 31.61.

TABLE I

PHYSICAL CONSTANTS OF THE DIETHYLBENZENES

	Ortho		*Meta*		*Para*	
	Present Authors	Literature	Present Authors	Literature	Present Authors	Literature
B.P., °/mm.	73–74/20 183/760	184.4 (26) 183.42 (27) 177/740 (28) 183.30/760 (7)	72–73/20 182–183/760	180.7 (26) 181.10/760 (27) 181.25/760 (7) 182/760 (29)	73–74/20 183–184/760	182.8 (26) 183.75/760 (27) 183.60/760 (7) 183/760 (28)
REFRACTIVE INDEX[a]	n_D^{20} 1.5046	n^{22} 1.50257 (26) n_D^{20} 1.5039 (28) n_D^{20} 1.5034 (7)	n_D^{20} 1.4961	n 1.4946 (26) n_D^{20} 1.4955 (3) n_D^{20} 1.4956 (7)	n_D^{20} 1.4958	n 1.4969 (26) n_D^{25} 1.4949 (30) n_D^{20} 1.4947 (7)
DENSITY	d_4^{20} 0.8837	d^{18} 0.8682 (26) d_4^{20} 0.8797 (28) d_4^{20} 0.8805 (7)	d_4^{20} 0.8621	d 0.8607 (26) d_4^{20} 0.860 (29) d_4^{20} 0.8641 (7)	d_4^{20} 0.8632	d 0.8633 (26) d_4^{20} 0.865 (29) d_4^{20} 0.8619 (7)

[a] According to Forziati, Norris, and Rossini (27), the n_D^{25} for the *o*- and *m*-compound differ by 0.0078.

Anal. Calc'd for $C_6H_{12}O_2$: C, 62.1; H, 10.3.
Found: C, 62.2; H, 10.4.

(*b*) *Propylideneacetone.* The mixture of hexan-4-ol-2-one (180 g.) and a few crystals of iodine was distilled under ordinary pressure. The distillate was freed from water and distilled again. B.p. 138–140°/760 mm.; 48–50°/25 mm.; 36–38°/16 mm. Yield, 136 g. (88.3%). n_D^{20} 1.4418; d_4^{20} 0.86654. MR (calc'd), 29.45 (without exaltation); MR (found), 30.00.

TABLE II

OXIDATION OF *o*-DIETHYLBENZENE[a]

CATALYST	TIME (hours)	RECOVERED, g.	*o*-ETHYLACETOPHENONE[b]		*o*-ETHYLBENZOIC ACID		RESINOUS RESIDUE, g.
			g.	%	g.	%	
A	24	15	5.1	19.0	—	—	4.5
A	24	16	4.9	18.2	—	—	4.8
A	36	14.5	5.2	19.3	0.5	2.0	6.0
B	24	16	3.9	14.5	—	—	5.0
B	36	15	4.0	15.0	0.5	2.0	5.5

[a] Conditions used: *o*-diethylbenzene, 25 g.; catalyst, 1.25 g.; 1150 cc. of air per minute. [b] For *o*-ethylacetophenone, the following constants were observed: b.p. 114–115°/25 mm.; n_D^{20} 1.5256; d_4^{20} 0.99252; *Semicarbazone,* from alcohol, m.p. 180–181°.

TABLE III

OXIDATION OF *m*-DIETHYLBENZENE[a]

CATALYST	TIME (hours)	RECOVERED, g.	*m*-ETHYLACETOPHENONE[b]		*m*-ETHYLBENZOIC ACID[c]		RESINOUS RESIDUE, g.
			g.	%	g.	%	
A	24	15	21.0	38.0	1.1	2.0	8.0
A	24	14	20.6	37.5	1.2	2.0	8.5
A	24	15	21.5	39.0	0.5	1.0	9.0
A	36	10	22.5	41.0	1.8	3.5	12.0
A	48	8	23.5	42.5	2.8	5.0	13.5
B	24	17	17.5	32.0	0.5	1.0	7.0
B	36	16	17.5	32.5	1.2	2.0	9.0

[a] Conditions used: *m*-diethylbenzene, 50 g.; catalyst, 2.5 g.; 1020 cc. of air per minute. [b] For *m*-ethylacetophenone, the following constants were determined: b.p. 120–121°/20 mm.; n_D^{25} 1.5233; d_4^{20} 0.9912. MR (calc'd without exaltation) 44.78; MR (found) 45.75 (13, 16, 21). *Semicarbazone,* m.p. 175–176°, from isopropyl alcohol (16). [c] *m*-Ethylbenzoic acid, from alcohol fine needles, m.p. 46–47° (22).

Anal. Calc'd for $C_6H_{10}O$: C, 73.5; H, 10.2.
Found: C, 73.1; H, 10.5.

The *4-nitrophenylhydrazone,* m.p. 127–128°, from alcohol.

(*c*) *4-Ethyl-5-acetylcyclohexene.* In an autoclave, a mixture of 50 g. of butadiene, 31 g. of propylideneacetone, and 1.5 g. of hydroquinone was heated at 160–165° during 12 hours. The reaction product was fractionated and gave after a head fraction of unreacted propylideneacetone, 15 g. (30% of theory) of the desired cyclic ketone, b.p. 103–104°/23 mm. The substance has a camphor-like odor; n_D^{25} 1.4671; d_4^{30} 0.92822. MR (calc'd), 45.72; MR (found), 45.35.

Anal. Calc'd for $C_{10}H_{16}O$: C, 78.9; H, 10.5.
Found: C, 79.1; H, 10.5.

The *2,4-dinitrophenylhydrazone*, yellow crystals from alcohol, m.p. 121–122°.

Anal. Calc'd for $C_{16}H_{20}N_4O_4$: C, 57.6; H, 6.0; N, 16.9.
Found: C, 57.8; H, 5.8; N, 16.9.

(*d*) *o-Ethylacetophenone* (7, 15, 16). The preceding substance was dehydrogenated with almost a quantitative yield, when 50 g. was refluxed for 4½ hours in the presence of palladium deposited on carbon (10%). B.p. 114–115°/25 mm.; yield, 46 g.; d_4^{20} 0.9901; n_D^{20} 1.5235. MR (calc'd), 44.79 (without exaltation); MR (found), 45.75.

The *semicarbazone*, m.p. 181–182°, from isopropyl alcohol (15, 16, 17).

(*e*) *o-Diethylbenzene*. The Clemmensen reduction of *o*-ethylacetophenone was carried out in the modification suggested by Brady and Day (18). From 50 g. of the ketone, 22 g. (48%) of the hydrocarbon was obtained, and 12 g. of *o*-ethylacetophenone (24%) was recovered.

The 3,4,5,6-tetrabromo-derivative (9) had m.p. 65–66°, after recrystallization from alcohol.

TABLE IV

OXIDATION OF *p*-DIETHYLBENZENE[a]

CATALYST	TIME (hours)	RECOVERED, g.	*p*-ETHYLACETOPHENONE[b]		*p*-ETHYLBENZOIC ACID[c]		RESINOUS RESIDUE g.
			g.	%	g.	%	
A	24	11	8.0	30.0	0.5	2 0	6.0
A	24	10	7.8	29.0	0.9	2.9	6.5
A	36	8	8.4	30.5	1.1	4.0	7.5
B	24	10	6.8	25.0	0.3	1.0	6.5
B	36	9	7.1	26.3	0.6	2.0	8.0

[a] Conditions used: *p*-diethylbenzene, 25 g.; catalyst, 1.25 g.; 1100 cc. of air per minute. [b] *p*-Ethylacetophenone: b.p. 122–123°/20 mm.; n_D^{20} 1.5287; d_4^{20} 0.99272. MR (calc'd without exaltation), 44.78; MR (found) 45.75 (7, 16, 23). *2,4-Dinitrophenylhydrazone*, red crystals from alcohol, m.p. 202–203° (16). *Anal.* Calc'd for $C_{16}H_{16}N_4O_4$: C, 58.5; H, 4.9; N, 17.1. Found: C, 58.3; H, 4.7; N, 17.0.[c] *p*-Ethylbenzoic acid, from alcohol colorless needles, m.p. 114–115° [literature (24, 25): 110–111°; 112–113°].

DIENE SYNTHESIS OF *O*-ETHYLBENZOIC ACID

(*a*). A mixture of 2-pentenoic acid [(19); b.p. 105°/19 mm.] (28 g.), butadiene (44 g.), and hydroquinone (1 g.) was heated at 150° during 12 hours (autoclave). The product was dissolved in benzene, and the 5-ethylcyclohexene-4-carboxylic acid formed was extracted with aqueous sodium carbonate solution. From petroleum ether, the acid gave prisms of m.p. 82–83°. Yield, 50%.

Anal. Calc'd for $C_9H_{14}O_2$: C, 70.1; H, 9.1.
Found: C, 70.0; H, 9.1.

(*b*). The dehydrogenation was carried out in the presence of the palladium-carbon catalyst (1% by weight of the acid) in boiling *p*-cymene; it was complete in six hours. The *o*-ethylbenzoic acid was extracted from the filtered solution with aqueous sodium hydroxide and precipitated by acidification. From hot water, m.p. and mixed m.p. with an authentic specimen, 71° [literature (20), 68°]. Yield, 61.3%.

CATALYTIC OXIDATION OF THE DIETHYLBENZENES

(*a*) *Method.* Into the reaction vessel, air was introduced from the bottom through a sintered-glass plate, which ensured an intimate contact between the oxygen and the hydrocarbon and also had a stirring effect. Between the neck of the reaction vessel and the reflux condenser, a trap was inserted for the water formed.

The catalyst was used in a quantity amounting to 5% of the weight of the hydrocarbon. The reaction was carried out at 120–130°. After the desired period of time, the reaction product was freed from the catalyst, extracted with 10% aqueous sodium hydroxide solution, dried with sodium sulfate, and fractionated.

(*b*) *Catalysts*. Chromic oxide was prepared by cautiously adding methanol to a solution of chromic acid in dilute hydrochloric acid and refluxing the mixture for several hours. The excess methanol was distilled off and ammonia added. The oxide was dried at 450°. *Catalyst A*. An intimate mixture of 80 g. of chromic oxide and 20 g. of cobaltic oxide was heated at 450°. *Catalyst B*. An intimate mixture of 160 g. of calcium oxide and 40 g. of chromic oxide was heated at 250°.

SUMMARY

1. Pure *p*-diethylbenzene is obtained by the Clemmensen reduction of *p*-diacetylbenzene.

2. A new synthesis of *o*-diethylbenzene has been worked out, based on the condensation of propylideneacetone and butadiene to 4-ethyl-5-acetylcyclohexene.

3. Analogously, condensation of β-ethylacrylic acid and butadiene, and subsequent dehydrogenation, leads to 2-ethylbenzoic acid.

4. The catalytic oxidation of the three diethylbenzenes in the liquid phase has been studied; the reaction fails to give diacetylbenzenes but, as identified products, the corresponding ethylacetophenones, accompanied by small quantities of the ethylbenzoic acids, were found.

TEL-AVIV, ISRAEL

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