

The Reaction of 1-Tetralones with Potassium Hydroxide–Sodium Hydroxide^{1a}J. M. SPRINGER,^{1b-d} C. W. HINMAN,^{1e,f} AND E. J. EISENBRAUN^{1g}

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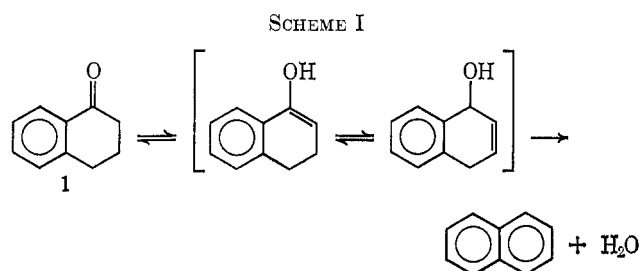
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The course of the alkali fusion of several methyl-substituted 1-tetralones has been found to be stereochemically controlled. The products include naphthalenes, naphthols, tetralols, and dimer acids. The analogous reaction with 2-tetralone gives a dimer acid in 45% yield. Some reactions of the latter are described.

It has been reported² that the fusion of 3,4-dihydro-1(2H)-naphthalenone, hereafter referred to as 1-tetralone (1), with a 1:1 mixture of KOH–NaOH at 220° yields naphthalene (58%); no mention was made of additional products. The proposed mechanism involved dehydration of an isomer of the enol of 1 (Scheme I).

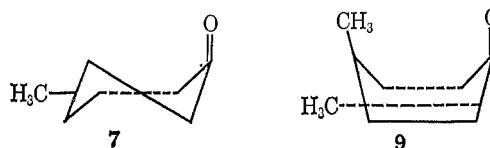


Data resulting from extension of this reaction to several methyl-substituted 1-tetralones are summarized in Table I. The steam-volatile fraction contained the unreacted tetralone (from 2, 3, and 8–13), the corresponding naphthalene (from 1 and 3–7), and the corresponding tetralol (from 1 and 3–7), and the corresponding naphthol (from 2 and 3), dimer acid (from 1, 4, 5, and 7), and unknown components (from 6 and 8–13). These data show that the less reactive 1-tetralones (0–5% yield of the naphthalene) possess one or more of three features: a *peri*-methyl group, 4- and 5-methyl groups, and a 2-methyl group.

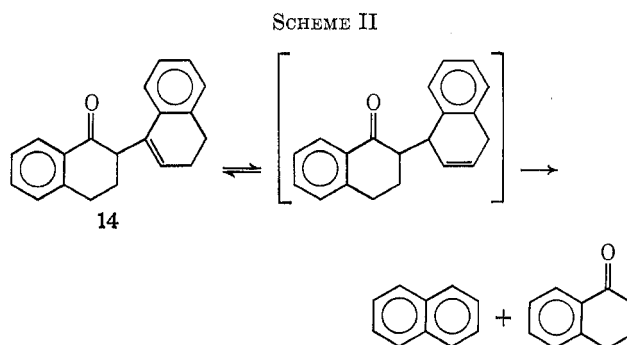
The influence of the *peri*-methyl group can be seen by comparison of the naphthalene yields from 6–8. The unreactivity of 8 is not unexpected, since the steric bulk of the methyl group at position 8 is sufficient to twist the carbonyl out of the plane of the aromatic ring.³ 3,3,6,8-Tetramethyl-1-tetralone is unreactive and was recovered unchanged from the reaction mixture.

It has been shown^{3b} that the 4,5-dimethyl interaction in 1-tetralones causes departure from the normal chair conformation and assumption of the boat conformation with the 4-methyl group in the axial position. The

inhibiting effect of the boat conformation is evidenced by contrasting the 63% yield of 1,3-dimethylnaphthalene from 7 with the negligible yield of 1,3,8-trimethylnaphthalene from 9.



The explanation of the course of the difference in the reactions of 2 and 3 (Table I) is not so clear-cut. If the mechanism proposed by Birch is correct, there can be no argument on such steric grounds as used above; *i.e.*, the most stable ground-state conformation for 2 is that in which the alicyclic ring is a chair with the methyl group in the equatorial position^{3b} and the methyl group appears to have little steric effect either in inhibiting the conjugation of the carbonyl group with the benzene ring⁴ or in hindering the approach of reacting species.^{3b,5} If, however, dimerization is prerequisite to naphthalene formation, then the steric hindrance owing to the 2-methyl (and possibly 3-methyl) group would be important. This is made more probable by the fact that the alkali fusion of the 1-tetralone dimer 14 affords 60% naphthalene (Scheme II). The formation of both



2-methyl-1-tetralol (15) and 2-methyl-1-naphthol (16) suggests a hydride transfer reminiscent of the Cannizzaro reaction, as depicted in Scheme III. The reaction of 3, which yields the corresponding naphthalene, naphthol, and tetralol, would be intermediate between the two extremes, *i.e.*, naphthalene (Schemes I and II) *vs.* naphthol and tetralol formation (Scheme III).

Data on the isolated crystalline dimer acids (Tables II and III) support the fully aromatic structures, 17–20.

(1) (a) E. J. Eisenbraun, J. M. Springer, C. W. Hinman, P. W. K. Flanagan, and M. C. Hamming, *Amer. Chem. Soc., Div. Petrol Chem., Preprints Gen. Papers*, **14** (3), A49 (1969); (b) American Petroleum Institute Graduate Research Assistant, 1965–1967; (c) National Science Foundation Graduate Trainee, 1967–1968; (d) American Chemical Society Petroleum Research Fund Fellow (Grant GF 395), 1968–1969; (e) American Petroleum Institute Graduate Research Assistant, 1962–1965; (f) deceased; (g) to whom correspondence should be addressed.

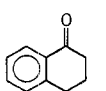
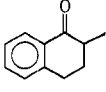
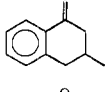
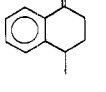
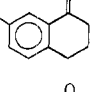
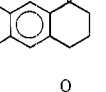
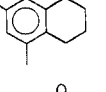
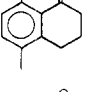
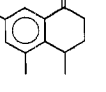
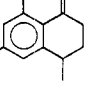
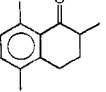
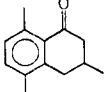
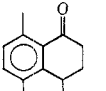
(2) A. J. Birch and D. A. White, *J. Chem. Soc.*, 4086 (1964).

(3) (a) E. A. Braude, "Progress in Stereochemistry," Vol. I, W. Klyne, Ed., Academic Press Inc., New York, N. Y., 1954, pp 144–148; (b) G. D. Johnson, S. Searles, and W. C. Lin, *J. Org. Chem.*, **27**, 4031 (1962).

(4) G. Baddeley, J. W. Rasburn, and R. Rose, *J. Chem. Soc.*, 3168 (1958).

(5) K. Hanaya, *Nippon Kagaku Zasshi*, **87**, 991 (1966); *Chem. Abstr.*, **65**, 18474a (1966).

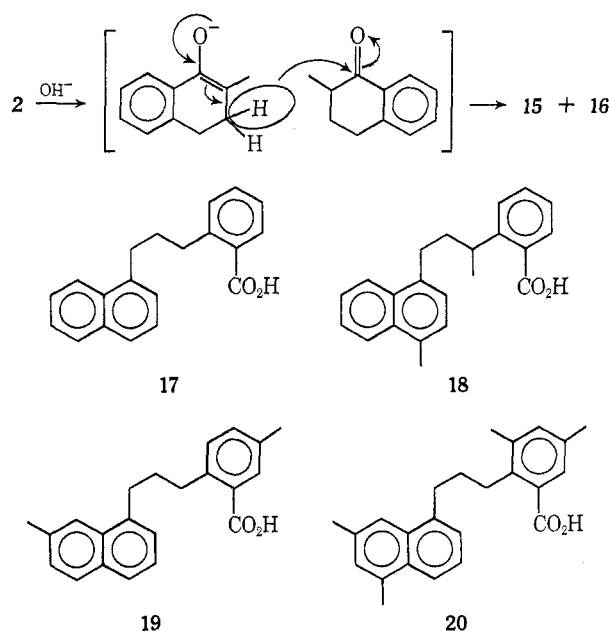
TABLE I
 REACTION OF 1-TETRALONES WITH KOH-NaOH

Compd. no. Tetralone structure	Yield, %	
	Naphthalene ^a	Dimeric or phenolic products ^b
1 	75	23 ^c
2 	0 ^d	47 ^e
3 	22 ^f	47 ^e
4 	51	43 ^e
5 	65	22 ^e
6 	62	30 ^e
7 	63	26 ^e
8 	5	39 ^h
9 	5	89 ^e
10 	5	41 ^h
11 	0	6 ^e
12 	0	26 ^e
13 	0	32 ^h

^a Yield determined by glpc. ^b Yield determined gravimetrically and based on 5 g of tetralone. ^c Dimer acid. ^d Steam-volatile fraction contains 2-methyl-1-tetralol. ^e Corresponding naphthol. ^f Steam-volatile fraction contains 3-methyl-1-tetralol. ^g Unknown crystalline solid. ^h No useful product isolated from residue.

The probable intermediates are the α,β -unsaturated ketones, such as 14. In addition to naphthalene (Scheme II), the alkali fusion of 14 gives 17 in 26% yield.

SCHEME III



The alkali fusion of 3,4-dihydro-2(1H)-naphthalenone (2-tetralone, 21) was found to give the crystalline dimer acid 22b in 45% yield. The proposed rationalization in Scheme IV is analogous to that suggested by Cairns, *et al.*,⁶ to explain the formation of dimer acid in the reaction of cyclohexanone with fused alkali. Hydrogenation and dehydrogenation yielded 23 and 24, respectively. Structure 22a was eliminated as a possibility through the isolation of 25 and the absence of 21 in the indicated sequence^{7a,b} of Scheme V.

Separate but identical alkali fusions of 1 and 2 were found by mass spectrometric analysis to produce hydrogen.^{7c} Peak height comparisons of the mass spectra of the off-gases from these reactions showed the ratio 5.3:2.4 (1 to 2) for hydrogen. The yield of hydrogen probably did not exceed 0.03 mol/mol of tetralone.

Experimental Section⁸

The ketones used in this study were purchased (1, 4, 6, and 7) or were prepared by one of the following three methods.

Friedel-Crafts condensation of *m*-xylene or *p*-xylene with γ -valerolactone in the presence of $AlCl_3$ was used to give a 4-arylpentanoic acid.⁹ These acids then were cyclized to 9, 10, and 13 by reaction with hot PPA.¹⁰ Where necessary, the ketones were purified by preparative glpc (9 and 10).

Friedel-Crafts condensation of succinic anhydride¹¹ or methylsuccinic anhydride¹² with benzene or *p*-xylene in the presence of

(6) T. L. Cairns, R. M. Joyce, and R. S. Schreiber, *J. Amer. Chem. Soc.*, **70**, 1689 (1948).

(7) (a) R. E. Ireland and J. Newbold, *J. Org. Chem.*, **28**, 23 (1963); (b) J. S. Baran, *ibid.*, **25**, 257 (1960); (c) F. X. Werber, J. E. Jansen, and T. L. Gresham, *J. Amer. Chem. Soc.*, **74**, 532 (1952).

(8) Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were determined on Varian HR-60 and A-60 spectrometers. Mass spectrometric data were compiled using a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. Ir and uv spectra were obtained on Beckman IR-5A and Cary 14 spectrophotometers, respectively. Melting points are corrected. Glpc analyses and preparative separations were made with Hewlett-Packard Model 5750 and F & M Model 700 equipment.

(9) W. L. Mosby, *ibid.*, **74**, 2564 (1952).

(10) H. R. Snyder and F. X. Werber, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley & Sons, Inc., New York, N. Y., 1955, pp 798-800.

(11) E. de Barry Barnett and F. G. Sanders, *J. Chem. Soc.*, 434 (1933).

(12) F. Mayer and G. Stamm, *Chem. Ber.*, **56**, 1424 (1923).

TABLE II
 COMPARISON OF GLPC AND NMR DATA FROM DIMER ACIDS

Precursor ketone	Dimer acid	Retention time, ^a min	Proton absorptions ^b			
			CH ₃	>CH ₂ , >CH	ArH	Miscellaneous
21	22b	10.5		2.0-3.2 (m, 8)	6.77-7.3 (m, 8)	3.55 (s, 2) ^{e,d} 6.07 (s, 1) ^e
21	23	9.5		1.6-3.1 (m, 13)	7.0-7.25 (m, 8)	
21	24	11.5		2.26-3.17 (m, 4)	7.07-7.87 (m, 11)	4.16 (s, 2) ^f
1	17	12		1.8-2.4 (m, 2)	7.05-8.18 (m, 11)	3.0-3.4 (m, 4) ^e
4	18	15	1.38 (d, 3) 2.60 (s, 3)	1.7-2.3 (m, 2)	7.12-8.12 (m, 10)	2.82-3.20 (m, 2) ^e 3.8-4.23 (q, 1) ^e
5	19	15	2.37 (s, 3) 2.48 (s, 3)	1.8-2.26 (m, 2)	7.12-7.93 (m, 9)	2.92-3.33 (m, 4) ^e
7	20	26.5	2.22 (s, 3) 2.28 (s, 3) 2.42 (s, 3) 2.61 (s, 3)	1.77-2.18 (m, 2)	7.04-7.92 (m, 7)	2.90-3.38 (m, 4) ^e

^a As methyl ester using a 6 ft × 0.25 in. column of 5% silicone rubber on acid-washed, DMCS-treated Chromosorb W at 275°. ^b CDCl₃ solvent with δ in parts per million from TMS. ^c ArCH₂. ^d —C=CCH₂. ^e —C=CH. ^f Ar₂CH₂. ^g ArCH.

AlCl₃ using excess hydrocarbon or nitroethane solvent was used to prepare ketones 2, 3, 8, 11, and 12. In the case of methylsuccinic anhydride, a mixture of β-aryloxypropionic acids having a methyl group at either an α or β position was obtained. These γ-oxo acids were separated by a combination of crystallization and distillation. The γ-oxo acids were reduced (Clemmensen reduction or catalytic hydrogenolysis) to the corresponding γ-arylbutyric acids, which were cyclized with hot PPA¹⁰ to the expected ketone.

7-Methyl-1-tetralone (5) was prepared by air oxidation of uv-irradiated 1,2,3,4-tetrahydro-6-methylnaphthalene to a mixture of hydroperoxides.¹³ These hydroperoxides were decomposed with alkali to a mixture of tetralols and tetralones that in turn was oxidized with chromic acid¹⁴ to a 45:55 mixture of 6-methyl-1-tetralone and 5. The latter was isolated from this mixture by preparative glpc and crystallized from petroleum ether.

Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,3-dimethylnaphthalene, and 1,4-dimethylnaphthalene were commercially available. The other naphthalenes necessary for the preparation of standard solutions for glpc analyses were obtained by one of the following three routes.

Clemmensen reduction of the corresponding tetralone and subsequent dehydrogenation (Pd-C) of the tetralin gave 1,4,5- and 1,4,6-trimethylnaphthalene.

Catalytic hydrogenation of the appropriate tetralone followed by dehydrogenation (Pd-C) of the tetralin gave 1,3,5- and 1,3,8-trimethylnaphthalene.

Dehydrogenation (Pd-C) of 5,7-dimethyl-1-tetralone gave 1,3-dimethylnaphthalene.

General Reaction of 1-Tetralones with KOH-NaOH. Apparatus.—The reaction vessel is a 25-ml, one-necked, flat-bottomed, stainless steel flask surmounted by a water-cooled, straight-bore glass condenser. One end of the condenser is a ball joint fitted with a Teflon O ring which provides a seal with the flask. The other end is threaded and fitted with a screw cap containing a 0.25-in.-o.d., thin-walled, stainless steel tube which extends ca. one-third the distance into the flask. The tube, which provides a helium inlet, is sealed to the screw with silicone rubber. An extra side arm of the condenser located above the water jacket acts as the helium outlet. The inlet and the outlet are fitted with Tygon tubing. The end of the latter tube is immersed in water so that gas flow may be observed. Heating is accomplished with a Wood's metal bath held at 220° (measured with a thermocouple probe and pyrometer).

Procedure.—A 5-g sample (in most cases) of the tetralone, 0.8 g of KOH pellets, and 0.8 g of NaOH pellets are added to the flask and the assembled system is purged for several minutes with a fast stream of helium. The flow is lessened to maintain a slight positive pressure and the flask is lowered into the preheated (220°) metal bath. After 3 hr of heating, the reaction

 TABLE III
 INSTRUMENTAL DATA FOR DIMER ACIDS

Precursor ketone	Dimer acid	Mp, °C	Uv, ^{a,b} mμ (log ε)	Ir, ^c cm ⁻¹	Mass spectra (parent ion)
1	17	113.5-115	225 (4.90) 283 (3.97)	1672	290 304 ^d
4	18 ^e	145-147	228 (4.71) 288 (3.97)	1692	f
5	19	145-146	228, 284	1686	f
7	20	186-187.5	232, 290	1686	f

^a These spectra were determined in 95% ethanol. ^b ε values for 19 and 20 are omitted, since the purity of these acids was questionable. The ratio of their ε values is ca. 10:1, the hypsochromic value predominating. ^c In CHCl₃. ^d The parent ion of the methyl ester. ^e Anal. Calcd for C₂₂H₂₀O₂: C, 82.98; H, 6.96. Found: C, 82.83; H, 7.04. ^f The parent ion was not observed.

mixture is allowed to cool under a helium atmosphere. The reaction mixture, after steam distillation for a few hours, is acidified with concentrated hydrochloric acid and extracted with ether. The ethereal extract is washed with water and saturated sodium chloride solution, dried (MgSO₄), filtered, and concentrated to give a tarlike residue. This residue is triturated with hot petroleum ether (bp 60-68°), and the liquid is decanted and refrigerated; any resulting crystals are naphthols or dimer acids. If the former is the case, purification is accomplished by recrystallization from petroleum ether or by sublimation; if the latter is the case, only recrystallization from chloroform-petroleum ether is employed, since decomposition occurs on attempted sublimation.

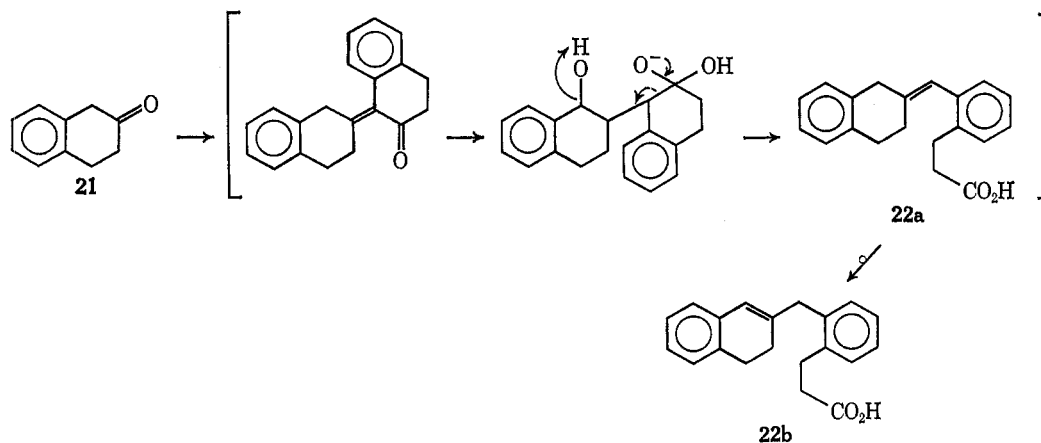
The steam distillate (above) is extracted with ether and the extract is washed with saturated sodium chloride solution, dried (MgSO₄), and filtered. The filtrate is concentrated to ca. 15 ml by distillation at atmospheric pressure. The concentrate is added to a 25- or 50-ml volumetric flask and diluted with ether. A 25- or 50-ml standard solution (in ether) of the naphthalenic product is prepared using a weight close to that of the expected yield. Identical aliquots (10-20 μl) of the unknown and the standard are injected under identical conditions on a suitable glpc column¹⁵ and the percentage yield of the unknown is calcu-

(15) Analysis of reaction mixtures can be carried out on any of three columns: 11 ft × 0.25 in. 10% SE-31 on DMCS-treated, acid-washed Chromosorb G; 10 ft × 0.25 in. 25% Carbowax 20M on acid-washed Chromosorb W; 6 ft × 0.25 in. 5% silicone rubber on acid-washed, DMCS-treated Chromosorb W. Appropriate temperatures are 160-242°, depending on alkyl substitution. For the separation of 4,5,8-trimethyl-1-tetralone and 1,4,5-trimethylnaphthalene, a 10 ft × 0.25 in. column of 5% phenyldiethanolamine succinate on acid-washed Chromosorb P should be used.

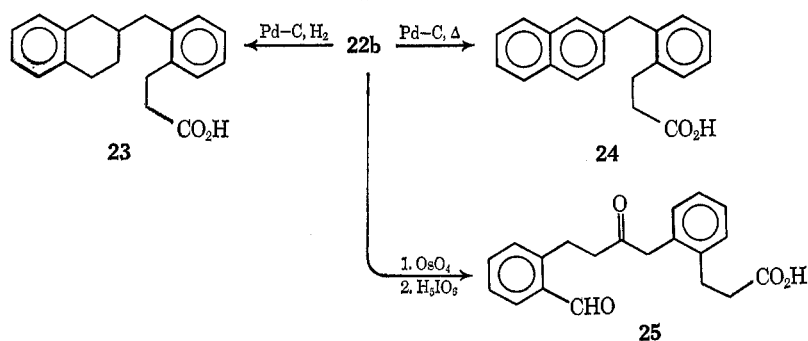
(13) R. B. Thompson, *Org. Syn.*, **20**, 94 (1940).

(14) E. J. Eisenbraun, *ibid.*, **45**, 28 (1965).

SCHEME IV



SCHEME V



lated from the ratio of the peak areas. The chart speed, injected volume, column temperature, and attenuation are so chosen that a peak of sufficient height and width at half-height for reliable measurement is obtained.

Employment of the above procedure gave yields of 72, 74, and 75% for three separate reactions of 1 with KOH-NaOH.

Identification of Tetralols in the KOH-NaOH Reactions of 2 and 3.—The ir spectra of the steam-volatile materials obtained from 2 and 3 showed absorptions which were due to the presence of hydroxyl (3390 cm⁻¹) and carbonyl (1680 cm⁻¹) functions. Analysis (glpc) revealed peaks which did not correspond to the appropriate tetralones, tetralins, naphthalenes, or naphthols. Oxidation with chromic acid¹⁴ gave products showing neither the unknown peaks in the gas chromatograms nor hydroxyl absorption in the ir spectra. The retention times of the unknown peaks were the same as those of authentic samples of the tetralols prepared by reduction of 2 and 3 with diisobutylaluminum hydride.

Dimerization¹⁵ of 1-Tetralone (1) to 14.—To a 250-ml, three-necked flask equipped with a gas-inlet tube and reflux condenser was added 168 g (1.15 mol) of distilled 1. Anhydrous hydrogen chloride was bubbled into 1 at a moderate rate for 15 min. The reaction mixture then was heated at 80–90° for 96 hr, being recharged each 24 hr with hydrogen chloride gas. The dark orange-brown, viscous reaction product was diluted to ca. 500 ml with ether, which precipitated 40 g of a tan solid. The latter was isolated by filtration and a portion was triturated with acetone, filtered, and recrystallized from acetone to give 14 as white crystals: mp 132–135° (lit.¹⁶ mp 132.5–134.2°); mass spectrum (70 eV) *m/e* (rel intensity) 274 (77), 146 (75), 129 (100), 43 (97), and 29 (91); nmr (CDCl₃) δ 8.24 (m, 1, ArH), 7.63–7.24 (m, 7, ArH), 5.88 (t, 1, C=CH), 3.89 (t, 1, C=CCH and adjacent to >C=O), 3.21–2.02 (m, 8, >CH₂); uv max (95% C₂H₅OH) 2.08 μ (log ε 4.65) and 253 (4.36) [lit.¹⁶ 208 μ (log ε 4.45) and 253 (log ε 4.3)]; ir (CHCl₃) 3.23, 3.26, 3.42, 3.46, and 3.53 μ¹⁷

(16) M. Orchin, L. Reggel, and R. A. Friedel, *J. Amer. Chem. Soc.*, **71**, 2743 (1949); this repetition of the reported preparation of tetralyldene-tetralone afforded 14 instead, as shown by nmr analyses. The agreement of the uv and ir spectrum and melting point of 14 and the melting point of the 2,4-dinitrophenylhydrazone of 14 with the literature values show that the previously reported ketone is probably 14 rather than tetralyldene-1-tetralone.

(17) We thank Dr. M. Evens, Continental Oil Co., for this spectrum.

[lit.¹⁶ 3.31, 3.40, and 3.47 μ]. A portion of these crystals was converted into the orange 2,4-dinitrophenylhydrazone, recrystallized from 95% ethanol and melting at 245–248° dec (lit.¹⁶ mp 247–248° dec).

The ethereal mother liquor was washed with 10% NaOH solution and water, dried (MgSO₄), filtered, and concentrated. Fractional distillation *in vacuo* of the resulting dark brown oil afforded 96 g of unreacted 1 and 17 g of a viscous, yellow oil which crystallized from acetone as white crystals. The total amount of crude dimer isolated was 57 g; the total amount of dimer after one recrystallization from acetone was 39 g (59% yield based on consumed 1 or 25% actual yield). The gas chromatograms (10% UC-W98 on 80/100s Chromosorb W, DMCS treated) at 290° of all fractions showed the same peak as for 14.

Reaction of 14 with KOH-NaOH.—A 3.66-g (0.013 mol) sample of 14 was heated for 3 hr with 1 g of KOH pellets and 1 g of NaOH pellets using the same apparatus and procedure as described for the general reaction of 1-tetralones with KOH-NaOH. After the reaction product was steam distilled, the alkaline pot residue was extracted with ether, acidified with concentrated hydrochloric acid, and extracted with ether. The latter ethereal extract was washed with water, dried (MgSO₄), filtered, and concentrated to give 1 g (26% yield) of crude 17. Three recrystallizations from chloroform-petroleum ether gave 0.31 g of pale gray, fibrous solid, mp 114.5–115.5°.

Anal. Calcd for C₂₀H₁₈O₂: C, 82.73; H, 6.25. Found: C, 82.59; H, 6.34.

The steam distillate was worked up and analyzed as described for the general reaction of 1-tetralones. The yield of naphthalene was 2.05 g (60%).

Formation of 22b from 2-Tetralone (21).—A 4.98-g (0.034 mol) sample of 21, 0.82 g of KOH pellets, and 0.85 g of NaOH pellets were heated at 220° for 2 hr as described for 1-tetralones. The cooled reaction mixture was steam distilled and the residue was extracted with ether (the frequently occurring emulsions were broken up with saturated sodium chloride solution). The alkaline solution was acidified with concentrated hydrochloric acid and extracted with ether. The extract was washed with water and saturated sodium chloride solution, dried (MgSO₄), filtered, and concentrated to give 2.00 g of yellow-brown solid (40% crude yield, other runs gave yields of 45 and 48%). Recrystallization from isopropyl alcohol afforded 22b as a cream-colored powder

which was sublimed *in vacuo* to deposit white crystals: mp 118–120°; mass spectrum (70 eV) *m/e* (rel intensity) 189 (92), 133 (100), 40 (84), 18 (82), and 15 (100); for nmr, see Table II.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.98. Found: C, 81.84; H, 6.66.

The methyl ester of **22b** was prepared with diazomethane and evaporatively distilled *in vacuo* as a white solid: mp 46–50°; mass spectrum (70 eV) *m/e* (rel intensity) 129 (100), 128 (67), 117 (27), 115 (28), and 91 (31).

Dehydrogenation (Pd-C) of 22b.—A 0.31-g (0.0011 mol) sample of **22b**, 0.1 g of 10% Pd-C, and 8 ml of distilled 1-methylnaphthalene were added to a 15-ml, one-necked flask equipped in the same manner as for the KOH-NaOH reactions. The reaction mixture was refluxed vigorously (245°) for 6.5 hr under a helium atmosphere, cooled, dissolved in ether, filtered through Dicalite, and extracted with 10% NaOH solution. The cloudy, alkaline solution was filtered first through Whatman No. 31 filter paper, and then through Dicalite to remove an unknown white solid. The clear solution was acidified with concentrated hydrochloric acid and extracted with ether. The extract was dried ($MgSO_4$), filtered, concentrated, and dried *in vacuo* to give 0.17 g (55% crude yield) of cream-colored solid. Sublimation *in vacuo* afforded **24** as a white powder: mp 126–127.5°; mass spectrum (70 eV) *m/e* (rel intensity) 290 (69), 217 (100), 105 (96), 43 (58), and 41 (59); for nmr, see Table II.

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.49; H, 6.31.

Hydrogenation (Pd-C) of 22b.—To a 100-ml, one-necked flask were added 0.25 g (0.001 mol) of **22b**, 0.012 g of 10% Pd-C, and 50 ml of ethanol. The stirred solution was hydrogenated at room temperature for 17 hr. The reaction mixture was filtered through Dicalite, concentrated, and dried *in vacuo* to give 0.22 g (crude yield 86%) of white solid. Sublimation *in vacuo* afforded **23** as white crystals: mp 131–133°; mass spectrum (70 eV) *m/e* (rel intensity) 131 (100), 130 (28), 115 (28), 91 (27), 41 and (28); for nmr, see Table II.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.31; H, 7.58.

The methyl ester was prepared with diazomethane and evaporatively distilled *in vacuo*: mass spectrum (70 eV) *m/e* (rel intensity) 131 (100), 130 (32), 129 (32), 91 (34), and 28 (68).

Degradation of 22b.—To a three-necked, 100-ml flask were added in order 1.25 g (4.94 mmol) of OsO_4 , 30 ml of anhydrous pyridine (dried with KOH), and 1.33 g (4.55 mmol) of **22b**. The yellow solution of OsO_4 in pyridine turned black immediately on addition of **22b**. The solution was stirred magnetically for 25 hr. The osmic ester was decomposed by addition of a solution consisting of 45 ml of H_2O , 22.5 ml of anhydrous pyridine, and 3 g of $NaHSO_5$. The reaction mixture was stirred for 12 hr and the liquid was decanted from the precipitate. The resulting red solution was extracted with five 40-ml portions of $CHCl_3$ and the

extract was dried ($MgSO_4$), decanted, and concentrated to give the crude, oily diol. The crude product was dissolved in 50 ml of ether and transferred to a 250-ml erlenmeyer flask. To this solution was added 75 ml of anhydrous ether containing 1.13 g (4.96 mmol) of H_6IO_6 . The reaction mixture was stirred for 4 hr. The ethereal solution was decanted from the white precipitate (HIO_3), washed with water, dried (Na_2SO_4), decanted, and evaporated to dryness under reduced pressure to give 1.09 g (74% yield) of a yellow solid. Recrystallization from a $CHCl_3$ -petroleum ether mixture gave 0.42 g of **25** as a white solid: mp 89.5–91.5°; mass spectrum (70 eV) *m/e* (rel intensity) 306 (5), 288 (16), 246 (5), 160 (4), 143 (100), and 115 (29); nmr ($CDCl_3$) δ 10.18 (s, 1, CHO), 9.3 (broad absorption, 1, COOH), 7.7 (s, 1, ArH *ortho* to CHO), 7.5–7.0 (m, 7, ArH), 3.75 (s, 2, ArCH₂ adjacent to $>C=O$), 3.28 (t, 2, ArCH₂ *ortho* to CHO), and 2.96–2.46 (m, 6, $>CH_2$ and ArCH₂).

Anal. Calcd for $C_{20}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.86; H, 6.65.

In a separate experiment, the products of the periodic acid cleavage were steam distilled and **21** could not be detected nor were there any uv-active, steam-volatile products.

Mass Spectrometric Analysis of Reaction Gases.—Normal alkali fusions of **1** and **2** were carried out in a closed system and the off-gases were trapped in two evacuated steel bombs. Mass spectrometric analysis at 70 eV showed *m/e* of **2** in excess of the fragmentation peak in the helium carrier gas. The ratio of hydrogen in equal samples was 5.3:2.4 (**1** to **2**).¹⁸

Registry No.—**14**, 23804-16-2; 2,4-dinitrophenylhydrazone of **14**, 23796-79-4; **17**, 23804-17-3; **18**, 23804-18-4; **19**, 23804-19-5; **20**, 23804-20-8; **22b**, 23796-80-7; methyl ester of **22b**, 23796-81-8; **23**, 23804-21-9; methyl ester of **23**, 23804-22-0; **24**, 23804-23-1; **25**, 23804-24-2; potassium hydroxide, 1310-58-3; sodium hydroxide, 1310-73-2.

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