67%) of 4-methyl-9-hydroxyhexahydrochroman (**5e**), mp 89–90°. The nmr spectrum ($CHCl_3$) included a hydroxyl singlet at τ 6.97; the ir spectrum (0.5 *M* CCl_4) showed bands at 3610 (sharp, free OH) and 3410 cm^{-1} (broad, H-bonded OH).

Anal. Found: C, 70.54; H, 10.80.

Chromic Acid Oxidation of 5c.—Treatment of **5c** (3.69 g, 0.0217 mol) with the above general chromic acid procedure using 0.0319 mol of chromium trioxide gave 4-methyl-6-ketononanolide (**7c**) in 52% yield, bp 105–111° (1.5 mm), with spectra (ir and nmr) identical with those of genuine **7c**.

Dehydration of 5c with Potassium Pyrosulfate.—A mixture of **5c** (8.25 g, 0.0485 mol) and potassium pyrosulfate (0.83 g) was distilled *in vacuo* to give 7.22 g of crude, wet material which was dried in ether solution. After solvent evaporation the residue was distilled to give 6-methyltetrahydrochroman (**5c**): 5.07 g (69%); bp 98–108° (20 mm); identical spectral characteristics (ir and nmr) with those of genuine **6c**.

Registry No.—**2b**, 4147-00-6; **3b**, 16120-95-9; **5b**, 16120-96-0; **5c**, 16120-97-1; **5e**, 16199-04-5; **6b**, 13030-87-0; **6c**, 13030-81-4; **6d**, 13030-80-3; **6e**, 16121-01-0; **6f**, 16121-02-1; **6g**, 13030-86-9; **7b**, 16121-04-3; **7e**, 16121-05-4; **7f**, 16121-06-5; **7g**, 16121-07-6; **8**, 4753-59-7; **9**, 4753-60-0; **11**, 4802-49-7; **12**, 4753-58-6; **14**, 16121-10-1; **16**, 16121-13-4; **17**, 16121-14-5; semicarbazone of **17**, 16121-33-8; **19**, 16121-27-0; 2,4-dinitrophenylhydrazone of **20**, 16121-28-1; **23**-(7-ene), 16121-15-6; **23** (1-ene), 16121-26-9; **25**, 16121-16-7; **27**, 16121-17-8; **28**, 16121-18-9; **29**, 16121-19-0; 2,4-dinitrophenylhydrazone of **29**, 16121-34-9; **30**, 16121-20-3; 2,4-dinitrophenylhydrazone of **30**, 16121-35-0; **31b** (6-ene), 16121-29-2; **31b** (1-ene), 16121-30-5; **31** (6-ene), 16121-31-6; **31c** (1-ene), 16121-32-7; **31d** (6-ene), 16121-21-4; **31d** (1-ene), 16121-22-5; **31e** (6-ene), 16121-23-6; **31e** (1-ene), 16121-36-1; **31f** (6-ene), 16121-24-7; **31f** (1-ene), 16121-37-2; **31g** (6-ene), 16121-25-8; **31g** (1-ene), 16121-38-3.

Acknowledgment.—We wish to thank the National Science Foundation and the National Institutes of Health for funds used in purchasing Varian A-60 and A-60A nmr spectrometers at Lehigh and Yeshiva Universities, respectively. We are indebted to Professor Gilbert Stork, Columbia University, for information on the enamine acrylate method.

meso-Dihydroanthracene Chemistry. II. The Preparation of 1,5- and 1,8-Dimethylanthraquinones[1]

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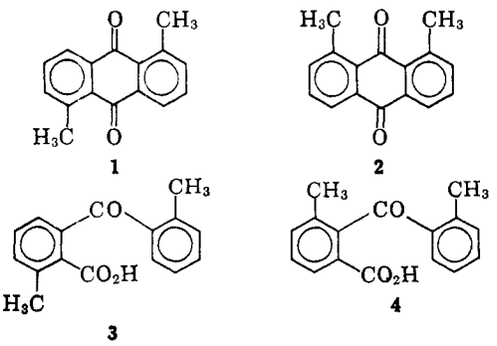
Syntheses of 1,5- (**1**) and 1,8-dimethylanthraquinone (**2**) *via* sulfuric acid catalyzed ring closures of 6-methyl-2-(2-methylbenzoyl)benzoic acid (**3**) and 3-methyl-2-(2-methylbenzoyl)benzoic acid (**4**), *via* ring closures of the corresponding benzylbenzoic acids **18** and **19** and *via* Diels–Alder reactions between 1,3-pentadiene and *p*-benzoquinone, have been studied. Of these, the diene synthesis, followed by oxidation, is probably the most convenient. Ring closures of the benzylbenzoic acids to 1,5-dimethylanthrone (**20**) and 4,5-dimethylanthrone (**21**) proceeded without rearrangement and in good yield, while those of the benzoylbenzoic acids **3** and **4** proceeded with attendant Hayashi rearrangement to give identical mixtures of **1** and **2** from both acids. The effect of sulfuric acid concentration upon the ratio of **1** to **2** was negligible, while the ratio of 6-methyl acid **3** to 3-methyl acid **4** obtained upon dilution of the acid solutions was markedly dependent upon sulfuric acid concentration. The Hayashi rearrangement of 3-methylbenzoylbenzoic acids to 6-methyl acids was shown (for the first time) to be a reversible process. These facts are rationalized with the Newman–Sandin mechanisms for the Hayashi rearrangement and for anthraquinone formation.

Our interest in the stereochemistry of 1,4-conjugate elimination[1,2] from 9,10-dihydro-9,10-anthradiol derivatives led us to a utilization of anthraquinones as reaction intermediates. These can be readily reduced to the desired diols.[1,3] The preparation of anthraquinones by acid-catalyzed cyclization of *o*-benzoylbenzoic acids[4] seemed to offer a ready procedure for the synthesis of 1,5-dimethylanthraquinone (**1**) and the 1,8-analog (**2**) in view of the availability[5] of the two isomeric benzoylbenzoic acids **3** and **4** from the reaction of *o*-tolylmagnesium bromide and 3-methylphthalic anhydride.



The sulfuric acid catalyzed cyclization of *either* **3** or **4** led to mixtures containing approximately 80% of the 1,5-dimethylquinone (**1**) and 20% of the 1,8-dimethylquinone (**2**). Both **1** and **2** were stable to the reaction conditions. Quinone **1** has been described previously[6] and was reduced by zinc in ammonia to 1,5-dimethylanthracene, also of known structure.[6] Neither quinone **2** nor 1,8-dimethylanthracene has been reported, but we now have (see below) prepared them by unequivocal syntheses.

The formation of both **1** and **2** from either **3** or **4** is

(1) Paper I: S. J. Cristol, W. Barasch, and C. H. Tieman, *J. Amer. Chem. Soc.*, **77**, 583 (1955).

(2) S. J. Cristol, M. Toji, and M. L. Caspar, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 1M.

(3) M. L. Caspar, Ph.D. Dissertation, University of Colorado, Boulder, Colo., 1960.

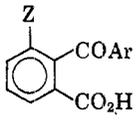
(4) C. Liebermann, *Ber.*, **7**, 805 (1874).

(5) M. S. Newman and C. D. McCleary, *J. Amer. Chem. Soc.*, **63**, 1537 (1941).

(6) R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 1950 (1934).

a result of the rearrangement, discovered by Hayashi,[7] whose mechanism was elaborated in some detail by Sandin and his coworkers[8] and by Newman and Ihrman.[9] The Hayashi interconversion of acids **3** and **4** occurs more rapidly in the strong acid medium than does anthraquinone formation. The ratio of quinones **1** to **2** formed was substantially invariant (17–20% of **2**) over the range 70 to 96% sulfuric acid, even though the temperature of the anthraquinone formation reaction varied correspondingly from 100 to 30°.

The Hayasi rearrangements described earlier[7–10] were all conducted at high acid concentrations, and all apparently proceed from 3-substituted 2-aroylbenzoic acids (**5**) to 6-substituted 2-aroylbenzoic acids (**6**)



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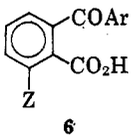

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(when there is only one substituent other than the aroyl group in the benzoic acid ring).[11,12] Although, as noted, the ratio of quinones **1** to **2** is insensitive to the concentration of the acid catalyst, the apparent composition of the equilibrium mixture of **3** and **4** is very sensitive to the acid strength. Table I describes the

TABLE I
EFFECT OF SULFURIC ACID CONCENTRATION UPON COMPOSITION OF MIXTURES OF 3-METHYL-2-(2-METHYLBENZOYL)BENZOIC ACID (**3**) AND 6-METHYL-2-(2-METHYLBENZOYL)BENZOIC ACID (**4**)

Starting acid	[H_2SO_4], %	Mp of recovered acid, °C	Product description
3		117	Starting materials
4		163	
4	96	110–117	All **3**
3	96	111–116	All **3**
3	90	100–120	**3** and **4**
3	80	155–160	Largely **4**
3	70	161–162	All **4**

acid mixture which results when the sulfuric acid solution from either **3** or **4** is allowed to cyclize partially to quinone. The acids were then recovered by pouring the reaction mixture onto ice to stop the reaction, followed by appropriate extraction and isolation. As may be noted, the "normal" Hayashi rearrangement (3-methyl to 6-methyl) of **4** to **3** is observed in 96% sulfuric acid, while a "reverse" rearrangement is observed at the lower acid concentrations. With the possible exception of the case discussed in footnote 11, this appears to be the first example of being able to control the direction of the Hayashi rearrangement.

Our results may be accommodated by an extension of the mechanisms for the Hayashi rearrangement proposed by Sandin[8] and by Newman,[9] and that for anthraquinone formation proposed by Newman.[13] Chart I gives the details of the Sandin–Newman mechanisms, accommodated to our particular system *and* with the addition of simple protonated species (**7** and **17**) which are present in large amounts in moderately concentrated acid[14,15] and which are converted into the lactyl cations **9** and **15** in more concentrated acids.[8,9,13,14,16] Furthermore, one must assume that the formation of intermediate **12** is the slow step in the Hayashi rearrangement, that of intermediate **11** is rate determining in the formation of **2**, and that of **14** is rate determining in the formation of **1**, with all other steps being relatively fast ones.

The modified Sandin–Newman mechanism[17] in Chart I shows that, although the concentrations of **10** and **13** are markedly dependent upon acidity and upon a_{H_2O}, the ratio of [**10**]/[**13**] is independent of these functions. Thus, if the rate constant ratio, k_{10}/k_{13}, is relatively insensitive to medium effects and to temperature, the ratio of anthraquinone products (**2**/**1**) will be invariant (*i.e.*, will be independent of whether the principal species in solution will lead, on treatment with water, to either **4** or to **3**). This, as noted above, is what we have observed.

At high acid strengths (*e.g.*, 96–100% H_2SO_4), it may be noted that each of these benzoylbenzoic acids exists in large part (or entirely) as the corresponding lactyl cation.[8,9,13,14,16] Thus, a solution of **3** is rapidly transformed to one of **15**, and a solution of **4** to one of **9**. With time, the **15** $\rightleftarrows$ **9** equilibrium will be reached *via* the intermediates **13**, **12**, and **10** and the position of equilibrium (and thus the product to be isolated upon dilution with water) will depend upon the relative stabilities of **9** and **15**. Work done in this laboratory[17] shows that *ortho* steric effects are undoubtedly responsible for the high [**15**]/[**9**] ratio which leads to the isolation of almost pure **3** upon dilution with water, and which leads in general to the normal Hayashi rearrangements of acids **5** to acids **6**.

On the other hand, in dilute acid solution, the acids exist as protonated species or as the free acids.[14,15] The results (Table I) suggest that **4** and **7** are more stable than **3** and **17**, respectively. Both steric and electronic factors may be involved in these relative stabilities. The fact that the acids or their protonated forms have stabilities opposite to those of the lactyl cations leads to a useful synthetic device, as the Hayashi

(7) (a) M. Hayashi, *J. Chem. Soc.*, 2516 (1927); 1513, 1520, 1524 (1930); (b) M. Hayashi, S. Tsuruoka, I. Morikawa, and H. Namikawa, *Bull. Soc. Chem. Jap.*, **11**, 184 (1936).

(8) R. B. Sandin, R. Melby, R. Crawford, and D. G. McGreer, *J. Amer. Chem. Soc.*, **78**, 3817 (1956).

(9) M. S. Newman and K. G. Ihrman, *ibid.*, **80**, 3652 (1958). This paper gives a summary of the examples available at that time.

(10) J. W. Cook, *J. Chem. Soc.*, 1472 (1932).

(11) R. Goncalves, M. R. Kegelman, and E. V. Brown [*J. Org. Chem.*, **17**, 705 (1952)] report that 6-nitro-2-(2-thenoyl)benzoic acid is converted into the 3-nitro analog in "concentrated" sulfuric acid. Schroeder and Weinmeyer[12] report that the reaction proceeds in the opposite sense in 100% sulfuric acid, and Newman and Ihrman[9] confirm the latter finding. Newman and Ihrman suggest that the extensive decomposition in this system and impure mixtures of starting materials explain the results of Gonclaves and coworkers, and point out that the 3-nitro compound was observed not to isomerize to the 6-nitro compound in sulfuric acid concentrations of 85–95.5%.[12] This experiment was assumed to show that the two isomers were not interconverted in the more dilute solutions, but unfortunately no test was made with the pure 6-nitro compound to attempt to verify the Gonclaves experiments (see below).

(12) H. E. Schroeder and V. Weinmeyer, *J. Amer. Chem. Soc.*, **74**, 4357 (1952).

(13) M. S. Newman, *ibid.*, **64**, 2324 (1942).

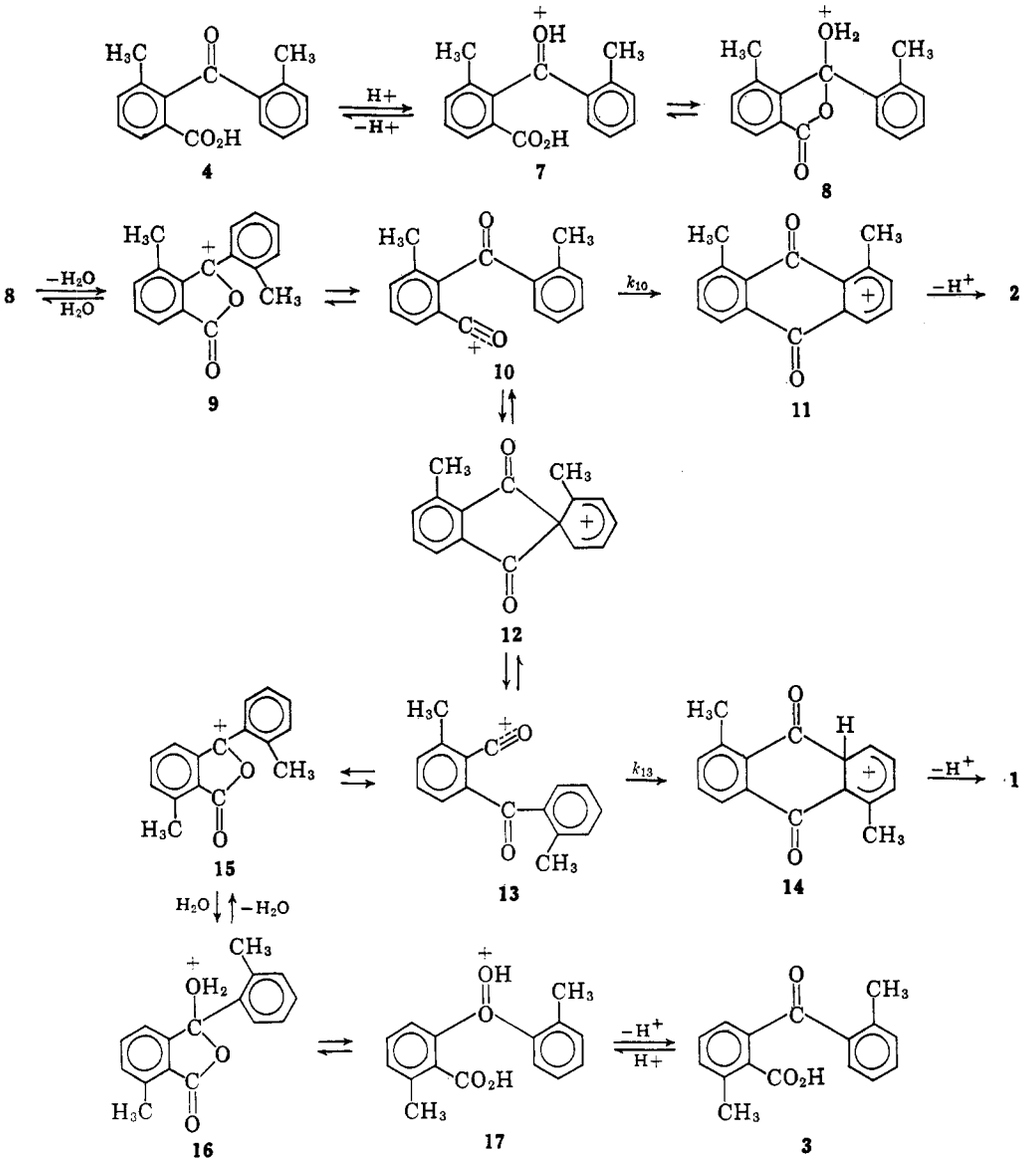
(14) S. J. Cristol, K. Schwarzenbach, and M. L. Caspar, Abstracts, the 19th International Congress of Pure and Applied Chemistry, London, July 1963, part A, p 71.

(15) D. S. Noyce and P. A. Kittle, *J. Org. Chem.*, **30**, 1896 (1965).

(16) D. S. Noyce and P. A. Kittle, *ibid.*, **30**, 1899 (1965).

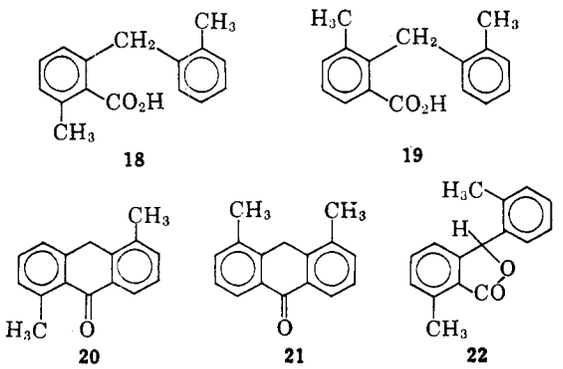
(17) One of us (S. J. C.) and K. Schwarzenbach have conducted a study[14] of the effects of substituents upon the rates of Hayashi rearrangements and the rates of anthraquinone formation. These results, which are consistent with the suggestions made here, will be reported in a separate paper.

CHART I



rearrangement is now[11] amenable to being driven in either direction.

In contrast to the benzoylbenzoic acid ring closures described above and in agreement with previous examples,[12,18] the derived benzylbenzoic acids **18** and **19** were cyclized readily to the anthrones **20** and **21** in good yield and without rearrangement.



These anthrones were readily oxidized to the quinones **1** and **2**. These reactions were useful for the proof of structures **1** and **2**, but the poor yields that we obtained in the reduction of **3** to **18** owing to the concomitant formation of lactone **22** limit the present synthetic usefulness of this procedure.

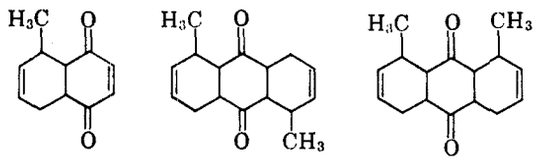
In addition we developed a very convenient synthesis of compounds **1** and **2** *via* a Diels–Alder process. Diels and Alder[19] found that isoprene could be added to *p*-benzoquinone to give two isomeric addition products, which on oxidation gave 2,6- and 2,7-dimethylanthraquinone. Similarly,[20] 1,5-diphenylanthraquinone was obtained from 1-phenylbutadiene. Arbuzov and Spekterman[21] reported that 1,3-pentadiene gave only the monoaddition product **23** with *p*-benzoquinone. Adduct **23** is of course the in-

(18) The fact that certain benzoylbenzoic acids undergo rearrangement while the corresponding benzylbenzoic acids do not rearrange to benzoylbenzyl alcohols seems readily rationalized by considering the strong deactivating effect of an aroyl group upon the *ortho* position which is attacked in quinone cyclization as compared with the activating effect of the alkyl group in the benzylbenzoic acid cyclization.

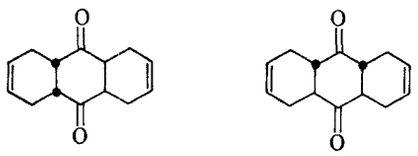
(19) O. Diels and K. Alder, *Ber.*, **62**, 2348 (1929).

(20) E. Bergmann, L. Haskelberg, and F. Bergmann, *J. Org. Chem.*, **7**, 303 (1942).

(21) B. A. Arbuzov and S. M. Spekterman, *Trans. Kirov. Inst. Chem. Technol. Kazan*, **8**, 21 (1940); *Chem. Abstr.*, **35**, 2498 (1941).



23 24a, mp 155° b, mp 225° 25



26 27

termediate in the synthesis of the desired diaddition products **24** and **25**.

We found, in fact, that the diaddition goes readily, under a variety of conditions, yielding approximately equal amounts of a solid 1,5-dimethyloctahydroanthraquinone **24a** which was oxidized readily to **1** and an oil (**25**) which was readily oxidized to **2**.

We have not investigated the stereochemistry of these products in any detail. We noted, however, that the bis-1,3-pentadiene–*p*-benzoquinone adduct (**24a**), mp 155°, was isomerized by base or by chromatographic grade alumina to an isomeric 1,5-dimethyloctahydroanthraquinone (**24b**), mp 225°. Alder and Stein[22] have noted a similar transformation when the octahydroanthraquinone obtained from the diaddition of 1,3-butadiene to *p*-benzoquinone was treated with base. Hill and coworkers[23] have shown that the bis-butadiene–benzoquinone adduct has the *cis,anti,cis* configuration (**26**) and that the product of base-catalyzed isomerization has the *trans,syn,trans* configuration (**27**). The *cis,anti,cis* configuration has also been proven for the bisnorbornadiene–*p*-benzoquinone adduct.[24] It thus seems likely that Diels–Alder addition products **24a** and **25** also have the *cis,anti,cis* ring junctions. Pmr spectra on the two isomers of **24** which we have isolated suggest that each of them may be symmetrical, but do not allow us to reach absolute conclusions regarding the stereochemistry at the methyl-substituted carbon atoms.

Experimental Section

Sulfuric Acid Catalyzed Cyclization of 6-Methyl-2-(2-methylbenzoyl)benzoic Acid (3).—Compound **3** (35 g, 138 mmol), mp 116–117°,[5] was dissolved in 170 ml of concentrated sulfuric acid at room temperature to give a bright red solution. The solution was heated at 95° for 4 hr and was then poured onto 2 kg of chipped ice. The resulting mixture was warmed overnight and filtered. After removal of unreacted **3** by exhaustive washing with ammonium hydroxide there was obtained 14.3 g (44%) of a mixture of 1,5- (**1**) and 1,8-dimethylanthraquinone (**2**), mp 170–185°. A quantitative infrared analysis indicated 80% of **1** and 20% of **2**. Recrystallization from ethanol and ethanol–dioxane gave 5.0 g (15.4%) of 1,5-dimethylanthraquinone (**1**), mp 188–190°.[6] Further crystallization from acetic acid gave an analytical sample of (**1**) as yellow needles, mp 191.5–192°.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.10; H, 4.92.

The crystallization residues from the isolation of **1** were combined and repeatedly chromatographed on alumina with carbon tetrachloride as the eluent to give 1,8-dimethylanthraquinone (**2**), mp 158–159.5°, nearly free of **1**. Final purification was effected by repeated crystallization from acetic acid to give quinone **2** as shiny yellow platelets, mp 161.5–162°.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.37; H, 5.22.

Acidification of the basic aqueous filtrate yielded 11.5 g (33%) of unreacted keto acid **3**, mp 111–116°, mmp 112–116°.

Sulfuric Acid Catalyzed Cyclization of 3-Methyl-2-(2-methylbenzoyl)benzoic Acid (4).—A mixture of 200 mg (0.79 mmol) of **4**, mp 162–163° (lit.[5] 158–161.4°), and 2 ml of concentrated sulfuric acid was swirled for several minutes until solution was complete. The red-orange solution was heated at 95° for 3 hr. The resulting deep red solution was poured into 100 ml of ice water and extracted with 100 ml of benzene. The benzene solution was extracted with 50 ml of sodium bicarbonate, washed with water and dried over anhydrous magnesium sulfate. The bright yellow solution was evaporated to dryness on a rotary evaporator to give 135 mg (73%) of a mixture of quinones **1** and **2** (mp 170–182°). A quantitative infrared analysis indicated 79% of **1** and 21% of **2**. The sodium bicarbonate solution was extracted with 25 ml of benzene, acidified with dilute hydrochloric acid, and then extracted with 50 ml of benzene. This benzene solution was washed with water and saturated sodium chloride solution, dried over anhydrous magnesium sulfate and filtered. The solid remaining after evaporation on a rotary evaporator was recrystallized from acetone–Skellysolve B (petroleum ether, bp 60–70°). A 16% yield (32 mg) of keto acid **3**, mp 110–117° and mmp 111–116°, was obtained. The infrared spectrum (KBr) of the crude product showed complete absence of characteristic absorption for the isomeric keto acid **4**.

Stability of 1,5- and 1,8-Dimethylanthraquinone to Concentrated Sulfuric Acid.—A solution of 100 mg of each of the pure isomeric quinones **1** and **2** in 10 ml of concentrated sulfuric acid was heated at 80–90° for 3 hr, then allowed to stand at room temperature overnight. The deep red solutions were poured onto 25 g of ice, and, after warming to room temperature, the solid quinones were filtered on fine sintered glass funnels and washed with water. The solids were dried over phosphoric anhydride at 0.1 mm overnight. In each case the recovery of quinone was 100%, the melting points were not altered and the infrared spectra (KBr) were completely identical with the spectra of the starting materials. 1,8-Dimethylanthraquinone (**2**) was also heated at 95° for 6 days with concentrated sulfuric acid. Considerable charring occurred, but isomerization to 1,5-dimethylanthraquinone (**1**) could not be detected.

Preparation of 6-Methyl-2-(2-methylbenzyl)benzoic Acid (18).—6-Methyl-2-(2-methylbenzoyl)benzoic acid (**3**) (1 g, 3.94 mmol), mp 116–117°, was dissolved in 100 ml of 10% sodium hydroxide, 5 g of zinc dust[25] was added, and the vigorously stirred mixture was heated at reflux for 24 hr. The mixture was filtered through a sintered-glass funnel and the acidified filtrate was extracted with benzene. The benzene solution was extracted with a 5% solution of sodium bicarbonate. The bicarbonate solution was then acidified and extracted with benzene. The benzene solution was washed with water, dried over anhydrous magnesium sulfate, and concentrated. On cooling, 300 mg (31%) of 6-methyl-2-(2-methylbenzyl)benzoic acid (**18**), mp 114–116°, was obtained. The infrared spectrum (KBr) of the benzyl acid (**18**) showed a single carbonyl absorption at 5.90 μ, while the infrared spectrum (KBr) of the benzoyl acid **3** showed carbonyl absorptions at 5.86 and 6.01 μ. Four recrystallizations from acetone–Skellysolve B gave large colorless crystals, mp 118–119°.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.76; H, 6.65.

The original benzene extract of the reaction mixture, after washing with sodium bicarbonate solution, was washed with water, dried over anhydrous magnesium sulfate, and concentrated. On cooling, 580 mg (62%) of the lactone of 6-methyl-2-(α-hydroxy-2-methylbenzyl)benzoic acid (**22**), mp 95–97°, was obtained. The infrared spectrum (KBr) showed an intense carbonyl band at 5.68 μ. The lactone **22** was insoluble in 5% sodium hydroxide at room temperature and dissolved only slowly in hot 10% sodium hydroxide; acidification regenerated the lactone **22**. Recrystallization from acetone–Skellysolve B and methanol gave an analytical sample, mp 97–99°.

(22) K. Alder and G. Stein, *Ann.*, **501**, 247 (1933).

(23) R. K. Hill, J. G. Martin, and W. H. Stouch, *J. Amer. Chem. Soc.*, **83**, 4006 (1961).

(24) L. deVries, R. Heck, R. Piccolini, and S. Winstein, *Chem. Ind.* (London), 1416 (1959).

(25) R. Scholl, C. Seer, and A. Zinke, *Monatsh.*, **41**, 583 (1920).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.87; H, 6.16.

The yield of benzyl acid **18** from the zinc–sodium hydroxide reduction of benzoyl acid **3** was quite variable. In some cases only the lactone **22** was obtained. The use of zinc powder activated with copper sulfate or of Raney nickel–aluminum alloy[26] in either sodium or potassium hydroxide for reaction times of up to 4 days at reflux gave the lactone **22** as the main product.

Sulfuric Acid Catalyzed Cyclization of 6-Methyl-2-(2-methylbenzyl)benzoic Acid.—A 1-g (4.16 mmol) sample of 6-methyl-2-(2-methylbenzyl)benzoic acid (**18**), mp 116–118°, was finely ground in a glass mortar with 5 ml of water. The mortar was then placed in an ice bath and 45 ml of ice-cold 90% sulfuric acid was added. The mixture was stirred for 30 min while warming to room temperature, giving a clear lemon-yellow solution. The color did not change on standing at room temperature for another 30 min. The solution was poured onto 100 g of ice and filtered. The pale yellow solid, after washing with water and drying, was recrystallized from Skellysolve B–acetone to obtain 0.70 g (76%) of nearly colorless 1,5-dimethylanthrone (**20**), mp 142–143°.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.49; H, 6.29.

The infrared spectrum (KBr) of anthrone **20** did not show absorption at 13.60 μ characteristic of the isomeric 4,5-dimethylanthrone (**21**). Oxidation of 222 mg (1 mmol) of **20** with 3.0 g (30 mmol) of chromic anhydride in 10 ml of acetic acid at 80–90° for 1 hr yielded 226 mg (96%) of 1,5-dimethylanthraquinone (**1**), mp 189–191°.

Preparation of 3-Methyl-2-(2-methylbenzyl)benzoic Acid (19).—To a solution of 1 g (3.94 mmol) of 3-methyl-2-(2-methylbenzoyl)benzoic acid (**4**), mp 162–163°, in 100 ml of 10% sodium hydroxide solution was added 5 g of zinc dust. The vigorously stirred mixture was heated at reflux for 24 hr (magnetic stirring) and then was filtered. The filtrate was poured into 100 ml of dilute sulfuric acid, cooled and filtered to yield, after drying, 900 mg (96%) of 3-methyl-2-(2-methylbenzyl)benzoic acid (**19**), mp 161–165°. Three recrystallizations from acetone–Skellysolve B gave an analytical sample, mp 161–162°.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.88; H, 6.79.

Sulfuric Acid Catalyzed Cyclization of 3-Methyl-2-(2-methylbenzyl)benzoic Acid (19).—A 62-mg (0.26 mmol) sample of 3-methyl-2-(2-methylbenzyl)benzoic acid (**19**), mp 160–162°, was finely ground with 0.5 ml of concentrated sulfuric acid at room temperature to give a clear yellow solution. The solution was allowed to stand at room temperature for 30 min and then poured onto 20 g of ice. The mixture was stirred for 30 min and then filtered through a fine sintered-glass funnel. The colorless solid was washed with 25 ml of boiling water and then dried over phosphoric anhydride to give 54 mg (94%) of 4,5-dimethylanthrone (**21**), mp 180–195°. Recrystallization from acetic acid gave an analytical sample as very pale yellow needles, mp 196.5–198°.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.42; H, 6.14.

The infrared spectrum (KBr) of anthrone **21** did not show absorption at 13.15 and 13.97 μ characteristic of the isomeric 1,5-dimethylanthrone (**20**). Oxidation of 222 mg (1 mmol) of **21** with 5.0 g (50 mmol) of chromic anhydride at 80–100° for 2 hr yielded 190 mg (80%) of 1,8-dimethylanthraquinone (**2**), mp 161.5–162°.

The Effect of Time, Temperature, and Sulfuric Acid Concentration on the Cyclization of Keto Acids 3 and 4.—The reaction of keto acids **3** and **4** described in this section were carried out in a manner similar to the corresponding cyclizations described above. An estimation of the relative amounts of quinones **1** and **2** formed in these cyclizations was obtained by a comparison of the infrared spectrum of the mixture with the infrared spectra of prepared mixtures of **1** and **2**. 1,5-Dimethylanthraquinone (**1**) showed characteristic absorption at 13.08, 13.88, and 14.10 μ, whereas 1,8-dimethylanthraquinone (**2**) showed characteristic absorption at 11.03, 12.05, and 13.68 μ. Potassium bromide pellets were prepared by adding appropriate aliquots of benzene stock solutions of **1** and **2** to 200 mg of potassium bromide, giving a final total quinone (**1** + **2**) concentration of 1%. The resulting mixture was ground in an agate mortar and pestle while the benzene was removed with a gentle stream of dry air. The resulting mixture was then dried under vacuum and pressed into a pellet. The relative intensities of the 13.38-μ band for **1** and of the 13.68-μ band for **2** were such that at a 78:22 ratio of **1**/**2** the infrared spectrum of the mixture showed bands of equal intensity at these two wavelengths. Thus, for concentrations of **2** near 22% a comparison of the relative intensities of the 13.38 and 13.68 μ bands was a sensitive analytical technique. The approximate composition of mixtures of keto acids **3** and **4** was determined by fractional crystallization, melting point behavior, and infrared spectrum comparisons.

A. Cyclization of 3 in 96% Sulfuric Acid at 30–40°.—The reaction of 200 mg of **3** in 2.0 ml of 96% sulfuric acid was carried out in a glass-stoppered flask for 7 days at 30–40°. From the neutral fraction there was obtained 9 mg (5%) of a mixture of quinones **1** and **2**. Quantitative infrared analysis indicated 20% of 1,8-dimethylanthraquinone (**2**) in the mixture. The unreacted acid (150 mg, 75%) melted at 105–110°. Recrystallization from Skellysolve B–acetone gave 110 mg of **3**, mp and mmp 116–117°. The crude acid had an infrared spectrum identical with that of the starting material.

B. Cyclization of 3 in 90% Sulfuric Acid at 95°.—The reaction of 60 g of **3** in 650 ml of 90% sulfuric acid was carried out at 95° for 4 hr. From the neutral fraction there was obtained 41.5 g (74%) of a mixture of quinones **1** and **2**. Quantitative infrared analysis indicated 19% of 1,8-dimethylanthraquinone (**2**) in the mixture. From the acidic fraction there was obtained 7.9 g (13%) of a mixture of keto acids **3** and **4**, mp 100–120°. The relative intensity of absorption bands at 14.15 μ characteristic of **3**, and at 14.40 μ characteristic of **4** in the infrared spectrum of the mixture suggested about a 1:1 ratio of the two isomeric keto acids.

C. Cyclization of 3 and 4 in 80% Sulfuric Acid at 95°.—The reaction of 200 mg of **3** in 1.75 ml of 80% sulfuric acid was carried out in a glass stoppered flask for 6 hr on a steam bath. From the neutral fraction there was obtained 140 mg (75%) of a mixture of quinones **1** and **2**. Quantitative infrared analysis indicated 19% of 1,8-dimethylanthraquinone in the mixture. From the acidic fraction there was obtained 12 mg (6%) of keto acid **4**, mp and mmp 155–160°.

In a parallel experiment 200 mg of **4** yielded 125 mg (67%) of a mixture of quinones **1** and **2**. The infrared spectrum of this mixture was superimposable on the spectrum of the mixture obtained from keto acid **3**. Quantitative infrared analysis showed 19% of 1,8-dimethylanthraquinone (**2**).

D. Cyclization of 3 in 70% Sulfuric Acid at 95°.—The reaction of 200 mg of **3** in 3.5 ml of 70% sulfuric acid was carried out in a glass stoppered flask for 10 hr on a steam bath. From the neutral fraction there was obtained 22 mg (12%) of a mixture of quinones **1** and **2**. Quantitative infrared analysis indicated 13% of 1,8-dimethylanthraquinone (**2**) in the mixture. The presence of a rather intense absorption at 5.65 μ, indicating the presence of a third compound, makes this analysis suspect. From the acidic fraction there was obtained 153 mg (77%) of keto acid **4**, mp and mmp 161–162°. Absorption at 11.85, 14.15, and 15.65 μ characteristic of the isomeric keto acid **3** could not be detected in the infrared spectrum of the recovered unrecrystallized keto acid.

The Addition of 1,3-Pentadiene to *p*-Benzoquinone.—A Pyrex combustion tube containing 22.5 g (220 mmol) of *p*-benzoquinone and 55 g (740 mmol) of 1,3-pentadiene was kept at room temperature, with occasional rocking, for 1 day, then placed in a water bath at 65–70° for 45 hr. The benzoquinone had dissolved and the solution was only a very pale yellow at the end of this time. On cooling to room temperature the contents of the tube solidified to a colorless crystalline mass.

The solid was stirred with 400 ml of ethanol and filtered. After drying there was 18.5 g (36%) of **24a**, mp 140–148°. The infrared spectrum (KBr) of this compound showed an intense carbonyl band at 5.85 and a shoulder at 6.05 μ. Several crystallizations from ethanol gave an analytical sample, mp 151–155°. The infrared spectrum of the crude product, except for weak small bands at 13.70, 14.05, and 14.55 μ, was identical with that of the analytical sample.

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.89; H, 8.53.

To the ethanol filtrate, from which further amounts of **24a** could not be isolated, was added 1 l. of ethanol, 100 ml of water, and 30 g of sodium hydroxide. A stream of air was bubbled through the solution at room temperature for 12 hr, then at reflux temperature for 24 hr. Dilution with water and filtration

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gave 18.2 g (36%) of 1,8-dimethylanthraquinone (2), mp 152–156°, which could best be purified by recrystallization from acetic acid containing a small amount of chromic anhydride. The Diels–Alder reaction of 1,3-pentadiene and *p*-benzoquinone was also carried out with benzene or nitrobenzene as the solvent at room temperature for 30 days, at 95° for 12 days and at 150° for 3 days. In each case the results were similar to those described above.

Isomerization of 1,5-Dimethyloctahydroanthraquinone 24a to 24b.—To a solution of 2.44 g (1.0 mmol) of 1,5-dimethyloctahydroquinone (**24a**), mp 146–150°, in 250 ml of ethanol was added 50 ml of 1 *M* sodium hydroxide. The solution was stirred at room temperature under nitrogen for 8 hr, then diluted with water and filtered to yield 2.15 g (88%) of an isomeric 1,5-dimethyloctahydroanthraquinone (**24b**), mp 220–223°. The infrared spectrum (KBr) of this compound showed an intense carbonyl band at 5.85 and a shoulder at 6.05 μ. Recrystallization from ethyl acetate gave an analytical sample as thick, pliable, colorless needles, mp 224–225°.

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.46; H, 7.86.

This isomerization could be also effected by chromatographing **24a** on Merck acid-washed alumina using Skellysolve B and carbon tetrachloride as the eluents.

Air Oxidation of 1,5-Dimethyloctahydroanthraquinone (24a).—A solution of 3.65 g (15 mmol) of the Diels–Alder adduct (**24a**), mp 146–149°, in 250 ml of warm ethanol was added dropwise over 30 min to a refluxing solution of 400 ml of 5% ethanolic sodium hydroxide while a rapid stream of air was passed into the solution through a sintered-glass filter stick. After 2 hr 500 ml of water was added to the cooled solution and the resulting solid filtered and washed with dilute sulfuric acid and water. This solid was dissolved in 175 ml of warm toluene to give a dark red solution. Charcoal (1 g) and absorption alumina (10 g) were added, and the hot solution was filtered through a Celite pad to give a clear bright yellow solution. Evaporation to dryness on a rotary evaporator gave 2.7 g (77%) of yellow 1,5-dimethylanthraquinone, mp 188–191°.

Air Oxidation of 1,5-Dimethyloctahydroanthraquinone (24b).—This oxidation was carried out in a manner similar to that of the proceding reaction. The isomerized Diels–Alder adduct (**24b**) was only slightly soluble in hot ethanol (less than 1%), thus 4.0 g (16.4 mmol) of the isomerized adduct was dissolved in a boiling mixture of 100 ml of toluene and 250 ml of ethanol. This hot solution was then added to 400 ml of a 10% ethanolic sodium hydroxide solution. The toluene solution (which was obtained as above) had to be treated with two portions of charcoal and alumina in order to give a yellow solution. Evaporation of this solution gave 2.0 g (52%) of 1,5-dimethylanthraquinone, mp 188–191°.

Preparation of 1,8-Dimethylanthracene.—A mixture of 265 mg (1.12 mmol) of 1,8-dimethylanthraquinone (2), mp 160–162°, 1 g of zinc dust, and 75 ml of concentrated ammonia solution was stirred overnight at room temperature. After 12 hr another 25 ml of concentrated ammonia and 1 g of zinc dust were added and the mixture was heated at 50° for 2 hr. The red solution was filtered through a sintered-glass funnel. The zinc residues were washed with 25 ml of acetone and 50 ml of benzene. The aqueous solution was extracted with 125 ml of benzene. The combined organic solutions were washed with water, dried over magnesium sulfate, and evaporated to dryness on a rotary evaporator. The resulting yellowish solid was dissolved in 20 ml of Skellysolve B and chromatographed on an column of 50 g of Merck acid-washed alumina. Elution with Skellysolve B gave 150 mg (65%) of brilliantly blue fluorescent 1,8-dimethylanthracene, mp 130–131°. Recrystallization from ethanol followed by sublimation gave an analytical sample, mp 131–131.5°.

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.00; H, 6.93.

Preparation of 1,5-Dimethylanthracene.—A vigorously stirred mixture of 1 g (4.24 mmol) of 1,5-dimethylanthraquinone (1), mp 190–191°, 10 g of zinc dust, and 250 ml of concentrated ammonia was heated at 50° for 16 hr. The red solution was filtered and the residues were washed with 200 ml of hot benzene. The benzene solution was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness to give a pale yellow solid which was chromatographed on 100 g of Merck acid-washed alumina. Elution with Skellysolve B gave 630 mg (72%) of blue fluorescent 1,5-dimethylanthracene, mp 139–139.5 (lit.[6] mp 139–140°).

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.14; H, 6.87.

Registry No.—**1**, 15815-39-1; **2**, 15815-40-4; **18**, 15815-41-5; **19**, 15815-42-6; **20**, 15815-43-7; **21**, 15815-44-8; **22**, 15815-45-9; **24**, 15815-46-0; 1,8-dimethylanthracene, 15815-47-1; 1,5-dimethylanthracene, 15815-48-2.

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