halogen increases to second in bromination[9] and probably also in iodination[11] processes.

To check the order of the uncatalyzed reaction of iodine monochloride and to compare the efficiencies of zinc chloride and iodine monochloride in functioning as the reagent E, a few rate runs on the iodination of mesitylene, without catalyst, were made. In analyzing the data from these runs it was assumed that, compared to free iodine monochloride, ICl_2^- (or $HICl_2$) is ineffective as a halogenating agent. Since the runs were self-inhibiting, because of the conversion of free halogen to ICl_2^- as hydrogen chloride was formed, none of the runs was followed to more than 45% of total halogen consumption. The rate law

$$-d(ICl)/dt = k_b(ArH)(ICl)^2 = k_b(ArH)(ICl)_T^2/[1 + K_c(Cl^-)]^2 \quad (6)$$

in which $(ICl)_T = (ICl) + (ICl_2^-)$, was assumed. Values of $(ICl)_T$ during the course of the runs were calculated from the optical densities of the solutions at 370 mμ using the approximation (see Table I) that the trihalide ion has the same extinction coefficient as free iodine monochloride at this wave length. Values of free chloride ion concentrations were estimated from the relationship

$$(Cl^-) = (ICl)_i - (ICl)_T - K_c(Cl^-)(ICl)_T/[1 + K_c(Cl^-)] \quad (7)$$

on the assumption that $K_c = 250$ (see eq. 1, Experimental section).[16] The k_b values were calculated from the measured values of $(ICl)_T$ during the course of the runs by use of eq. 8.

$$[1/(ICl)_T - 1/(ICl)_i]\,[1 + K_c(Cl^-)]^2 = k_b(ArH)_t \quad (8)$$

Average values of k_b for each of the runs are reported in Table V.

TABLE V

THE UNCATALYZED IODINATION OF MESITYLENE (25.2°)

$(ArH)_i$, mole/l.	$(ICl)_i$, 10^3 mole/l.	k_b, mole^{-2} l.^{2} sec.$^{-1}$
0.200	1.84	0.11
.200	3.68	.10
.200	7.36	.09

Since at low zinc chloride concentrations, the k_1 value for mesitylene iodination is approximately 0.06 mole^{-2} l.^{2} sec.$^{-1}$, on a mole for mole basis iodine monochloride is actually a somewhat more effective reagent E than is zinc chloride. The data of previous publications[6,9] indicate, however, that in the bromination of mesitylene in acetic acid zinc chloride is (on a mole for mole basis) about five times more effective as the reagent E than is bromine.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

DAVIS, CALIFORNIA

(16) R. E. Buckles and J. F. Mills, THIS JOURNAL, **76**, 4845 (1954), report much higher values for the association constant of iodine monochloride with quaternary ammonium chlorides in acetic acid.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

A Novel Stereospecific Synthesis of Hydrophenanthrones[1]

BY ERNEST WENKERT AND TRAVIS E. STEVENS[2]

RECEIVED MAY 3, 1956

A new synthetic scheme, leading stereospecifically in only four steps from the Reimer–Tiemann product of 4-methyl-1-naphthol to a hydrophenanthrone, is presented. The stereochemistry of all intermediates is discussed.

The hydrophenanthrene skeleton I is the basic ring structure common to all aromatic tricyclic diterpenes and could serve potentially as a synthetic precursor for the hydroaromatic tricyclic diterpenes as well as possibly for the steroids. Three *formally* different routes have been followed in the past for the synthesis of compounds of general structure I. One procedure has involved the prior coupling of rings A and C by various means and a subsequent formation of ring B by acid-catalyzed cyclization.[3] This scheme has led recently to the non-specific total synthesis of *d,l*-ferruginol[3o] and *d,l*-podocarpic acid.[3s] A second route has consisted of varied syntheses of 1-methyl-2-tetralones for rings B and C and a subsequent incorporation of ring A by the Robinson cyclohexenone synthesis.[4] The utility of this method has been portrayed excellently by the total syntheses of the steroid nucleus[4a] and *d,l*-dehydroabietic acid.[4d] Finally, a third synthetic pathway to the tricyclic ring system I has been accomplished

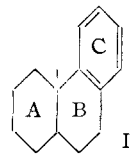
(1) Part of this work was presented at the Symposium on the Chemistry of Natural Products, Technion, Haifa, Israel, June 28–29, 1955, and at the 14th International Congress of Pure and Applied Chemistry, Zurich, Switzerland, July 21–27, 1955.

(2) National Science Foundation predoctoral fellow, 1953–1955.

(3) (a) G. A. R. Kon, *J. Chem. Soc.*, 1081 (1933); (b) E. C. Sterling and M. T. Bogert, *J. Org. Chem.*, **4**, 20 (1939), and preceding papers; (c) R. Ghosh, *Science and Culture*, **3**, 120 (1937) [*C. A.*, **32**, 145 (1938)]; (d) R. Grewe, *Ber.*, **72**, 426, 785 (1939); (e) R. D. Haworth and R. Barker, *J. Chem. Soc.*, 1299 (1939); (f) S. N. Slater, *ibid.*, 68 (1941); (g) C. D. Nenitzescu, E. Cioranescu and M. Maican, *Ber.*, **74**, 687 (1941); (h) M. S. Newman and M. D. Farbman, THIS JOURNAL, **66**, 1550 (1944); (i) B. K. Bhattacharyya, *J. Indian Chem. Soc.*, **22**, 165 (1945); (j) R. D. Haworth and B. Moore, *J. Chem. Soc.*, 633 (1946); (k) W. B. Renfrow, A. Renfrow, E. Shoun and C. Sears, THIS JOURNAL, **73**, 317 (1951); (l) G. Stork and A. Burgstahler, *ibid.*, **73**, 3544 (1951); (m) E. M. Fry, *J. Org. Chem.*, **17**, 1484 (1952); (n) N. C. Deno and H. Chafetz, *ibid.*, **19**, 2015 (1954); (o) F. E. King, T. J. King and J. G. Topliss, *Chemistry and Industry*, 108 (1954); (p) N. N. Saha, P. N. Bagchi and P. C. Dutta, THIS JOURNAL, **77**, 3408 (1955), and preceding paper; (q) W. Parham, E. L. Wheeler and R. M. Dodson, *ibid.*, **77**, 1166 (1955), and preceding paper; (r) R. A. Barnes and M. T. Beachem, *ibid.*, **77**, 5388 (1955), and preceding papers; (s) F. E. King, T. J. King and J. G. Topliss, *Chemistry and Industry*, 113 (1956).

(4) (a) J. W. Cornforth, O. Kauder, J. E. Pike and Sir R. Robinson, *J. Chem. Soc.*, 3348 (1955), and preceding papers; (b) C. A. Grob and W. Jundt, *Helv. Chim. Acta*, **31**, 1691 (1948); (c) W. F. Newhall, S. A. Harris, F. W. Holly, E. L. Johnston, J. W. Richter, E. Walton, A. N. Wilson and K. Folkers, THIS JOURNAL, **77**, 5646 (1955); (d) G. Stork and J. W. Schulenberg, *ibid.*, **78**, 250 (1956).

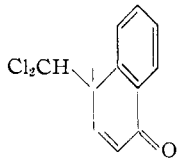
most recently by the condensation of unsaturated ketones with 1-methyl-2-naphthol.[5]



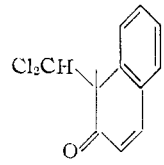
I

It was of interest to uncover yet another avenue toward I whose main attributes would be the brevity of the synthesis, the stereospecificity of securing a A/B *trans* fusion and the availability of a suitable functional group in the final product for elaboration to a natural product. For this purpose the Reimer–Tiemann product of 4-methyl-1-naphthol was chosen as the starting material and its chemistry came under scrutiny. The Reimer–Tiemann reaction has been used to advantage previously for the construction of bi- and tri-carbocyclic ring systems but always with the view of the dichloromethyl function in the resulting cyclohexadienones being converted to an angular methyl group in the end.[6] It was the goal of the present investigation, however, to use the dichloromethyl substituent as a potential ring methylene group.[7]

Previous preparation of the unsaturated ketone II consisted of sulfonation of 1-methylnaphthalene,[8] alkali fusion of the sodium sulfonate[8,9] and alkaline chloroform treatment of the resulting naphthol.[10] When this procedure was used on a large scale, without purification of intermediates, a 3–4% yield of ketone III[6b] accompanied the desired product. This observation was indicative of the fact that sulfonation of the naphthalene proceeded not only *para* to the methyl group but, as might have been expected, also to some extent *ortho* to the latter 4-Methyl-1-naphthol, the immediate precursor of II, was also obtainable by a Clemmensen reduction[11] of the known 4-hydroxy-1-naphthaldehyde.[12]

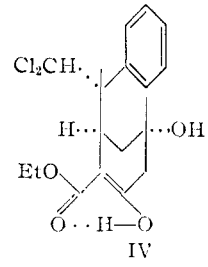


II

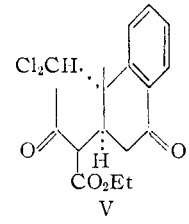


III

Sodium ethoxide-catalyzed Michael condensation of acetoacetic ester with ketone II led to a 94% yield of a $C_{18}H_{20}O_4Cl_2$ compound. While the latter's elemental analysis indicated the product to be a simple Michael adduct, the lack of any aliphatic or aromatic carbonyl absorption in the 1650–1750 cm.$^{-1}$ region in the infrared and the presence of an OH band at 3600 cm.$^{-1}$ and of 1640 and 1605 cm.$^{-1}$ bands, characteristic of a conjugated, chelated enol of a β-ketoester,[13] suggested strongly that the adduct had undergone intramolecular aldolization. This secondary process has been shown previously to follow the Michael reaction of β-ketoesters and cyclohexenones.[14] Thus structure IV could be assigned to the condensation product, although the steric implications contained therein required further discussion (*vide infra*).



IV



V

When piperidine was used as a catalyst for the Michael reaction, an isomer of IV could be obtained. Its α-tetralone-like ultraviolet absorption maximum at 252 mμ (log ϵ 4.00) and its infrared maxima at 1715 and 1680 cm.$^{-1}$, corresponding to saturated and aromatic carbonyl absorption, respectively, revealed it to be the unaldolized Michael adduct V. It could be shown that this reaction was an equilibrium process, wherein an optimum yield of 18% of the diketoester V, 1% of its aldol IV and 78% of recovery of starting ketone II was achieved, when the reaction was permitted to proceed at room temperature in benzene solution for 52 days. Any variation of reaction time, temperature or solvent tended to dislodge the equilibrium in favor of starting material and hence decrease the yield of desired product V. The stereochemical assignment for the latter followed the same arguments as those for compound IV. The two isomers were readily interrelated when it was shown that sodium ethoxide treatment of the diketoester V produced a 35% yield of its aldol IV as well as 62% of the unsaturated ketone II, apparently by a reversal of the Michael reaction.[15]

Acid-catalyzed hydrolysis of either of the above esters led to a 3:1 mixture of isomeric $C_{15}H_{16}O_2Cl_2$

(5) E. Wenkert and T. E. Stevens, THIS JOURNAL, **78**, 2318 (1956).

(6) (a) R. B. Woodward, *ibid.*, **62**, 1208 (1940); (b) R. M. Dodson and W. Webb, *ibid.*, **73**, 2767 (1951); (c) M. S. Gibson, *Experientia*, **7**, 176 (1951).

(7) An unsuccessful attempt of carrying out a similar scheme on the Reimer–Tiemann product of *p*-cresol is recorded in R. Corley, Ph.D. dissertation, Harvard University, 1950.

(8) K. Elbs and B. Christ, *J. prakt. Chem.*, **106**, 17 (1923).

(9) R. Steiger, *Helv. Chim. Acta*, **13**, 173 (1930).

(10) R. C. Fuson and T. Miller, *J. Org. Chem.*, **17**, 316 (1952).

(11) R. Robinson and R. Shah, *J. Chem. Soc.*, 1491 (1934).

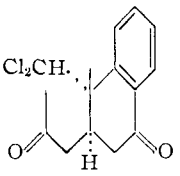
(12) R. Adams and I. Levine, THIS JOURNAL, **45**, 2373 (1923).

(13) N. Leonard, H. Gutowsky, W. Middleton and E. Peterson, *ibid.*, **74**, 4070 (1952).

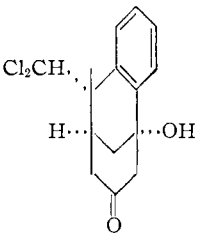
(14) (a) P. Rabe and K. Appuhn, *Ber.*, **76**, 982 (1943), and previous papers; (b) V. Prelog and M. Osgan, *Helv. Chim. Acta*, **36**, 1640 (1953).

(15) It is noteworthy that the ketoester IV exists completely as an enol in the solid state as well as in solution, while the β-ketoester V, as other similar acyclic systems, consists mainly of a keto form and a six-membered cyclic ketoester such as ethyl cyclohexanone-2-carboxylate is 74% enolic as liquid. While IV is only one of a few examples of compounds containing a β-ketoester function as part of a *rigid* polycyclic ring system [*cf.* also R. B. Woodward, M. P. Cava, W. D. Ollis, A. Hunger, H. U. Daeniker and K. Schenker, THIS JOURNAL, **76**, 4749 (1954)], and hence no rigorous generalization regarding their enolization is yet possible, it would not be surprising if future cases were found also to be 100% enolic. Because of their general mode of formation, enolizable cyclohexanone-2-carboxylates would have the ester group in an equatorial conformation. Under such circumstances the geometry of the two carbonyl groups would produce the most unfavorable dipole interaction, which would be best overcome by the interposition of a hydrogen between two oxygen atoms, thus forming a hydrogen-chelated enol. [For a complete discussion of similar systems *vide* G. S. Hammond, "Steric Effects on Equilibrated Systems," in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., 1956, New York, N. Y., and references therein.]

compounds. Spectral analysis showed them to be the diketone VI and its aldol VII. Thus the more abundant product had 1715 and 1680 cm.$^{-1}$ infrared peaks, for an aliphatic and aromatic carbonyl group, respectively, and high-intensity ultraviolet absorption at 252 mμ (log ϵ 4.03), corresponding to a α-tetralone chromophore (*cf.* VI). The second substance VII revealed the presence of a hydroxyl group at 3570 cm.$^{-1}$ and a six-membered cyclic saturated keto group at 1705 cm.$^{-1}$ in the infrared, while only a low-intensity tetralin maximum at 265 mμ (log ϵ 2.3) appeared in the ultraviolet spectrum.[16]



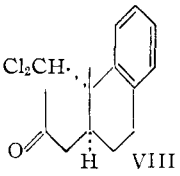
VI



VII

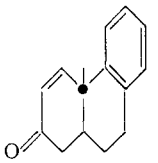
The formation of the same product mixtures by the irreversible decarbethoxylation of both the enol-ester IV and the diketoester V indicated that the acetoacetic ester moiety in both substances had the identical steric relationship with respect to its neighboring substituents. In view of this fact it was possible to arrive at an unambiguous stereochemical formulation for IV and V and their reaction products. Since compound V was undoubtedly the equilibrium product of the Michael reaction, its two vicinal bulkiest substituents, *i.e.*, the dichloromethyl group and the acetoacetic ester function, would have been expected to be oriented equatorially, and hence *trans* with respect to each other. It is of interest that the resulting stereoformula V most probably represents also the initial product of a kinetically controlled step, since the attack of acetoacetic ester anion on enone II during the Michael condensation would be expected to have occurred on the latter's least sterically hindered side, *i.e.*, *cis* to the methyl group and hence *trans* to the dichloromethyl group. The chemical interdependence of all other products with V points to a similar stereochemistry for all systems under discussion.

Taking advantage of the ready acid-catalyzed equilibrium attainable in solution between the diketone VI and its aldol VII, both compounds could be hydrogenated quantitatively in acid medium to the saturated ketone VIII. It would appear that retroaldolization precedes hydrogenation and hydrogenolysis of ketol VII.

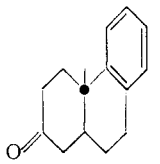


VIII

It was hoped that the open-chain ketone VIII could be induced to undergo an internal base-catalyzed cyclization to produce the desired tricyclic ring system. Despite the neopentyl nature of the chlorine atoms, the intramolecularity of the reaction was assumed to be able to facilitate the initial halide displacement.[17] Preliminary experiments with such strong bases as potassium *t*-butoxide and sodium hydride as condensing agents gave no positive results. However, sodium triphenylmethyl, when used in excess, produced a chlorine-less compound whose 228 mμ (log ϵ 4.1) and 1670 cm.$^{-1}$ carbonyl absorption maxima in the ultraviolet and infrared, respectively, identified it as the hydrophenanthrone IX. Both cyclization and β-elimination of chloride had taken place. Catalytic hydrogenation of the unsaturated ketone produced the known *trans* tricyclic ketone X,[5] thus corroborating the assigned stereochemistry of all its precursors.



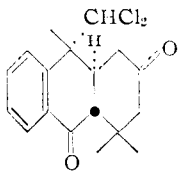
IX



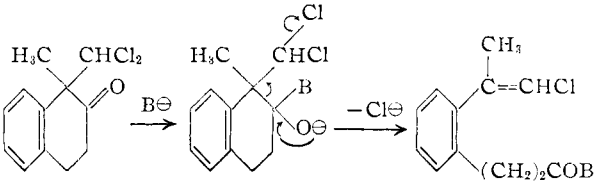
X

Of the various products that the above stereospecific hydrophenanthrone synthesis has given access to, compound IX appears most suited to lead the way to the total synthesis of diterpenic natural products.

(16) Michael addition of acetone to the unsaturated ketone II yielded only trace amounts of the acetone adducts VI and VII but led preponderantly (62%) to a mixture of two $C_{27}H_{26}O_2Cl_4$ compounds whose chemical and physical properties identified them as unaldolized triketones derived from a 2:1 interaction of II with acetone. Excess acetone in the Michael condensation resulted in the isolation of a $C_{18}H_{20}O_2Cl_2$ diketone. Its chemical and spectral characteristics suggested it to be a mesityl oxide addition product (the mesityl oxide having been preformed by a base-catalyzed aldol condensation) to which the following structure could be assigned



(17) The chemistry of umbellulone [R. H. Eastman and A. Oken, THIS JOURNAL, **75**, 1029 (1953); R. H. Eastman, *ibid.*, **76**, 4115 (1954)] yields several examples of intramolecular displacements of neopentyl halide systems, most of the latter have included other functional groups, which, due to their participation in the reaction, have been mainly responsible for the cleavage of the carbon–halogen bonds. The loss of chloride during the alkaline treatment of III (ref. 6b) as well as its dihydro derivative, observed in this Laboratory, can be cited as an excellent illustration of the aforementioned. Undoubtedly the keto group is the site of attack by the base and is the key to the subsequent elimination of chloride



Experimental[18]

4-Methyl-1-naphthol. (a) **From 1-Methylnaphthalene.**—1-Methylnaphthalene was sulfonated by the method of Elbs and Christ,[8] and the sodium sulfonate was salted out according to the procedure of Fieser.[19] Fusion of the salt with a mixture of equal weights of sodium and potassium hydroxide[8,9] gave the naphthol in crude 20–50% yields.

(b) **From α-Naphthol.**—4-Hydroxy-1-naphthaldehyde, m.p. 170–172°, was prepared by the method of Adams and Levine.[12] Clemmensen reduction of the aldehyde using an ethanol–water medium[11] gave crude 4-methyl-1-naphthol in 40–45% over-all yield. Recrystallization from petroleum ether produced white crystals of pure naphthol, m.p. 83–84°.

4-Dichloromethyl-4-methyl-1(4H)-naphthalenone (II).—The procedure of Fuson and Miller[10] was used for the conversion of crude 4-methyl-1-naphthol into its Reimer–Tiemann product. The neutral fraction was purified by a distillation, by a passage of a 1:1 petroleum ether–benzene solution of the distillate through an alumina column and, finally, by recrystallization from petroleum ether. The pure substance consisted of white needles, m.p. 109–110°, whose 2,4-dinitrophenylhydrazone melted at 212–213°; spectra: infrared, C=O 1670 cm.$^{-1}$(s); ultraviolet, λ_{max} 232 mμ (ε 10,000), 267 mμ (ε 5500), λ_{min} 254 mμ (ε 3600).

Concentration of the petroleum ether filtrates from Reimer–Tiemann runs on crude 4-methyl-1-naphthol, prepared from 1-methylnaphthalene, yielded 3–4% of the isomeric 2-naphthalenone,[6b] m.p. 66–67°; ultraviolet spectrum: λ_{max} 239 mμ (ε 13,300) and 315 mμ (ε 9900).

Hydrogenation of the latter over Adams catalyst gave the known 1-dichloromethyl-1-methyl-2-tetralone,[6b] m.p. 71–72°.

Ethyl 3,5-Dihydroxy-6,7-benzo-8-dichloromethyl-8-methylbicyclo[3,3,1]non-2-ene-3-carboxylate (IV).—Ethyl acetoacetate (10.8 g., 83 mmoles) and the 1-naphthalenone II (20.0 g., 83 mmoles) were added to a sodium ethoxide solution, containing 0.64 g. (36 mmoles) of sodium in 240 ml. of absolute ethanol. After standing 5 days at room temperature, the solution was poured into 1 l. of water, neutralized with acetic acid and extracted with chloroform. The extract was washed with sodium bicarbonate solution and water, dried over magnesium sulfate, evaporated and the semi-solid residue taken up in petroleum ether. From this solution there crystallized 18.89 g. (61.4%) of the enol-ester IV, m.p. 114–116°. The filtrate was chromatographed on a Celite–silicic acid column and gave 4.31 g. (21.6%) of starting material II on elution with 32:1 petroleum ether–ether, and 3.81 g. (12.4%) of additional enol-ester, m.p. 114–116° on elution with a 9:1 mixture. Recrystallization from petroleum ether yielded white prisms, m.p. 116–117°; spectra: infrared, OH 3600 cm.$^{-1}$(w), C=O and C=C (enol) 1640 cm.$^{-1}$(s) and 1605 cm.$^{-1}$(s); ultraviolet, λ_{max} 258 mμ (ε 8300), λ_{min} 232 mμ (ε 2800).

Anal. Calcd. for $C_{18}H_{20}O_4Cl_2$: C, 58.23; H, 5.43; Cl, 19.10. Found: C, 58.13, 58.19; H, 5.63, 5.58; Cl, 19.2, 19.05.

The enol-ester IV also was obtained by the use of one mole of sodium ethoxide or 0.3 or one mole of potassium *t*-butoxide as base and carrying out the reaction at either room temperature or at reflux. However, the above procedure gave the best results.

Ethyl 2-(1-Dichloromethyl-1-methyl-4-keto-1,2,3,4-tetrahydro-2-naphthyl)-3-ketobutyrate (V).—A solution of 15.0 g. (62 mmoles) of the 1-naphthalenone II, 15.0 g. (0.115 mole) of ethyl acetoacetate and 1.2 ml. of piperidine in 120 ml. of benzene was shaken and allowed to stand at room temperature for 52 days. The solution then was washed with dilute acetic acid and water, dried over magnesium sulfate and evaporated. The solid residue was dissolved in hot petroleum ether and, on cooling, deposited 5.86 g. (39.1%) of starting ketone II, m.p. 107–108°. On chromatography of the filtrate on a Celite–silicic acid column and elution with 19:1 petroleum ether–ether, an additional 5.80 g. (38.7%) of starting material, m.p. 108–109°, was obtained. Further elution of the column with 9:1 petroleum ether–ether gave 0.24 g. (1%) of enol-ester IV, while the 4:1 eluate yielded 4.2 g. (18.3%) of white crystals, m.p. 98–100°. Recrystallization of this substance with petroleum ether gave white prisms, m.p. 102–103°; spectra: infrared, C=O 1715 cm.$^{-1}$(s), 1680 cm.$^{-1}$(s); ultraviolet, λ_{max} 252 mμ (ε 10,000), 290 mμ (ε 1400).

Anal. Calcd. for $C_{18}H_{20}O_4Cl_2$: C, 58.23; H, 5.43; Cl, 19.10. Found: C, 58.32; H, 5.62; Cl, 19.18.

When the reaction mixture was left standing at room temperature for 20 days, a 15% yield of the diketoester V was realized. Refluxing the reactants for 3 days in the same proportion as above resulted in a 0.3% yield of V and a 96% recovery of starting material. When a solution of 2.75 g. of ethyl acetoacetate, 5.0 g. of II and 0.40 ml. of piperidine in 60 ml. of ethanol was refluxed for 3 days, a 0.4% yield of enol-ester IV was obtained and 94% of starting ketone was recovered.

The diketoester V (300 mg., 0.81 mmole) was left standing for 30 hours at room temperature in 10 ml. of absolute alcohol containing 0.35 mmole of sodium ethoxide. The mixture then was poured into 100 ml. of water, neutralized with acetic acid and extracted with chloroform. The extract was washed with water, dried over magnesium sulfate, evaporated and a petroleum ether solution of the residue placed on a Celite–silicic acid column. Elution with 19:1 petroleum ether–ether gave 120 mg. (61.5%) of the naphthalenone II, m.p. 107–108°, and the 9:1 eluate produced 105 mg. (35%) of the enol-ester IV, m.p. 114–116°.

4-Dichloromethyl-4-methyl-3-acetonyl-1-tetralone (VI) and its Aldol (VII).—Fifteen grams of the enol-ester IV was added to a solution of 300 ml. of concentrated hydrochloric acid and 300 ml. of 95% ethanol and the mixture refluxed on the steam-bath for 9 hr. After the addition of 1.2 l. of water to the cooled solution, it was extracted with chloroform, the extract was washed with sodium bicarbonate solution and water, dried over magnesium sulfate and evaporated. Crystallization of the gummy residue in 95% ethanol yielded 7.88 g. (65.2%) of a compound, m.p. 145–146°. Recrystallization from petroleum ether–benzene gave hard white crystals, m.p. 147–148°; spectra: infrared, C=O 1715 cm.$^{-1}$(s), 1680 cm.$^{-1}$(s); ultraviolet, λ_{max} 252 mμ (ε 10,700); λ_{min} 227 mμ (ε 2000), 280 mμ (ε 1050).

Anal. Calcd. for $C_{15}H_{16}O_2Cl_2$: C, 60.21; H, 5.39; Cl, 23.70. Found: C, 60.29, 60.34; H, 5.40, 5.47; Cl, 23.6, 23.5.

Evaporation of the ethanolic filtrate under reduced pressure and recrystallization of the residue five times from benzene gave 0.77 g. (6.4%) of white prisms, m.p. 187–188°; spectra: infrared, OH 3570 cm.$^{-1}$(w), C=O 1705 cm.$^{-1}$(s); ultraviolet, λ_{max} 265 mμ (ε 200); λ_{min} 250 mμ (ε 100).

Anal. Calcd. for $C_{15}H_{16}O_2Cl_2$: C, 60.21; H, 5.39; Cl, 23.70. Found: C, 60.14; H, 5.48; Cl, 23.8.

The combined filtrates from all above recrystallizations were evaporated under reduced pressure, and a benzene solution of the residue was chromatographed on an alumina column. Elution with 9:1 benzene–chloroform gave an additional 560 mg. (4.6%) of the diketone VI, m.p. 144–146°, while 100:1 benzene–methanol yielded 1.15 g. (9.5%) of more ketol VII, m.p. 186–187°.

Five hundred milligrams of diketoester V was added to a mixture of 10 ml. of concentrated hydrochloric acid and 10 ml. of 95% ethanol, and the solution refluxed on the steam-bath for 7 hr. The mixture then was poured into 100 ml. of water, partially neutralized with a 10% sodium hydroxide solution and extracted with chloroform. The extract was washed with sodium bicarbonate solution and water, dried over magnesium sulfate and evaporated. A benzene solution of the solid residue was chromatographed on an alumina column, yielding 235 mg. (58.4%) of diketone VI, m.p. 146–147°, on elution with 9:1 benzene–ether, and 80 mg. (19.8%) of ketol VII, m.p. 184–186°, on continued elution with 100:1 benzene–methanol.

1-Dichloromethyl-1-methyl-2-acetonyl-1,2,3,4-tetrahydronaphthalene (VIII).—A mixture, containing 690 mg. of the tetralone VI, 200 mg. of 5% palladium-on-charcoal catalyst and 1 ml. of 80% sulfuric acid in 60 ml. of ethyl acetate, was hydrogenated at one atmosphere. Hydrogen absorption ceased after 90 minutes and a two-mole hydrogen uptake. The mixture was filtered, washed with sodium bicarbonate solution and water and on evaporation yielded white crystals, m.p. 75–77°. Recrystallization from aqueous ethanol gave white platelets, m.p. 82–83°; spectra: infrared, C=O

(18) The use of the Baird infrared spectrophotometer of the Institute of Atomic Research, Ames, Iowa, is hereby gratefully acknowledged.

(19) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 139.

1705 cm.$^{-1}$ (s); ultraviolet, λ_{max} 265 mμ (ϵ 400); λ_{min} 240 mμ (ϵ 200).

Anal. Calcd. for $C_{15}H_{18}OCl_2$: C, 63.17; H, 6.35; Cl, 24.87. Found: C, 63.50; H, 6.56; Cl, 24.4.

Its 2,4-dinitrophenylhydrazone crystallized from ethanol–ethyl acetate as yellow plates, m.p. 169–170°.

Anal. Calcd. for $C_{21}H_{22}O_4N_4Cl_2$: C, 54.20; H, 4.77; N, 12.04. Found: C, 54.06; H, 4.72; N, 12.2.

The ketone VIII was isolated sometimes as prisms melting at 93–94°. The mixed m.p. of the two crystalline modifications was 92–94°. Their infrared spectra were identical, and their 2,4-dinitrophenylhydrazones had the same m.p. (169–170°) and showed no depression on admixture.

A mixture of 200 mg. of ketol VII, 100 mg. of 5% palladium-on-charcoal catalyst and 1.25 ml. of concentrated sulfuric acid in 25 ml. of ethyl acetate was hydrogenated at atmospheric pressure. After 24 hr. a two-mole hydrogen uptake was attained. The mixture was filtered, washed with sodium bicarbonate solution and water and evaporated. Recrystallization of the residue in petroleum ether yielded white crystals, m.p. 80–81°, whose lack of mixed m.p. depression and identity of infrared spectrum with the ketone VIII proved its identity with the latter.

4a-Methyl-4a,9,10,10a-tetrahydro-2(1H)-phenanthrone (IX).—A 200-ml. ether solution of 28.6 mmoles of sodium triphenylmethyl was added under a nitrogen atmosphere to 1.00 g. (3.5 mmoles) of ketone VIII. The solution was left standing at room temperature for 3 days with occasional shaking. After a final 5 hr. reflux on the steam-bath, the deep red mixture was cooled, hydrolyzed with water containing a little acetic acid and extracted 5 times with ether. The organic extract was washed with sodium bicarbonate solution and water, dried over magnesium sulfate and evaporated. The residue was extracted five times with hot petroleum ether and the cooled extract placed on a Celite–silicic acid chromatography column. The 19:1 petroleum ether–ether eluate gave 230 mg. of solid, m.p. 98–100°. Rechromatography under identical conditions of the noncrystalline fractions, whose infrared spectra made them appear to contain more unsaturated ketone, led to an additional 90 mg. of product. Three recrystallizations from petroleum ether yielded white crystals, m.p. 103–104°; spectra: infrared, C=O 1670 cm.$^{-1}$(s); ultraviolet, λ_{max} 228 mμ (ϵ 14,000).

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.96, 85.21; H, 7.38, 7.61.

Its 2,4-dinitrophenylhydrazone crystallized as red platelets from ethanol–ethyl acetate; m.p. 205–206°.

Anal. Calcd. for $C_{21}H_{20}O_4N_4$: C, 64.27; H, 5.14; N, 14.28. Found: C, 63.94; H, 5.20; N, 13.8.

The chromatographic fractions immediately preceding the hydrophenanthrone contained considerable amounts of unreacted acetonyl compound VIII, as indicated by their infrared spectra.

***trans*-4a-Methyl-3,4,4a,9,10,10a-hexahydro-2(1H)-phenanthrone (X).**—A mixture of 200 mg. of tricyclic ketone IX and 50 mg. of 5% palladium-on-charcoal catalyst in 20 ml. of ethanol was hydrogenated at one atmosphere. Hydrogen absorption ceased after 15 minutes and an uptake of one mole. The mixture was filtered, evaporated and the residue crystallized in petroleum ether, yielding white plates, m.p. 107–108°. Its m.p., mixed m.p. and infrared spectrum and those of its semicarbazone and *p*-nitrophenylhydrazone showed it to be the previously reported[6] *trans*-hydrophenanthrone X.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Isomerism of Dithiolphthalates

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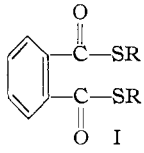
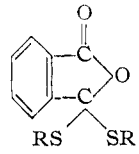
Both of the possible isomeric structures (symmetrical and unsymmetrical) for diphenyl dithiolphthalate and for di-(*p*-nitrophenyl) dithiolphthalate have been obtained in pure form and structures assigned on the basis of infrared spectra. *sym*-Diphenyl dithiolphthalate was prepared in 94% yield by interaction of *sym*-phthaloyl chloride, thiophenol and sodium methoxide in methanol solution. By treatment of a mixture of phthalic anhydride and thiophenol with phosphorus pentoxide, there was produced a mixture of isomers from which the pure *unsym*-diphenyl dithiolphthalate was isolated. *sym*-Di-(*p*-nitrophenyl) dithiolphthalate, synthesized from *sym*-phthaloyl chloride and *p*-nitrothiophenol in the presence of pyridine, was isomerized to the unsymmetrical form in basic solution. Treatment of glycine and of ethyl glycinate with *sym*-di-(*p*-nitrophenyl) dithiolphthalate at room temperature afforded phthaloylglycine and ethyl phthaloylglycinate (ethyl phthalimidoacetate), respectively.

Two isomeric structures may be written for dithiolphthalates: symmetrical isomer I and unsymmetrical isomer II.[2-4] Troeger and Hornung, after treating lead thiophenolate with phthaloyl chloride, obtained a compound, m.p. 84–85°, to which they assigned structure I in which R = C_6H_5. Two compounds[3] were isolated after heating a mixture of phthalic anhydride, thiophenol and phosphorus pentoxide, m.p. 84–85° and m.p. 101°.



I



II

It was stated, "neither of these could be hydrolyzed by boiling with aqueous alkali, which indicates that neither has the lactone structure adopted for one of them by Troeger and Hornung. These two compounds are isomeric and the difference between them is not clear." Similar results were observed by heating thiophenol and phthaloyl chloride in benzene.

Knapp,[4] by treatment of phthaloyl chloride and phenyl thiolacetate with aluminum chloride, obtained a compound, m.p. 101°, which was designated as the lactone structure II (R = C_6H_5). This assignment was based on the well-known conversion by aluminum chloride[5] of symmetrical phthaloyl chloride into unsymmetrical phthaloyl chloride, which could then react with phenyl thiolacetate to give unsymmetrical diphenyl dithiolphthalate. In the present investigation the procedure of Chakravarti and Saha[3] was repeated and two compounds

(1) This work was aided by a contract from the Office of Naval Research.

(2) J.Troeger and V. Hornung, *J. prakt. Chem.*, **66**, 345 (1902).

(3) G. C. Chakravarti and J. M. Saha, *J. Indian Chem. Soc.*, **4**, 141 (1927).

(4) W. Knapp, *Monatsh.*, **58**, 176 (1931).

(5) E. Ott, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 528.