identical with authentic[2] ketol (III) (m.p. 139.6–140.0°) by the criteria of mixture melting point and infrared spectra.

Attempted tosylation of 11 keto-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene (III). *11-Keto-12-methylene-9,10-dihydro-9,10-ethanoanthracene* (IV). A solution of crude ketol (III) (0.455 g., 1.82 mmoles) and *p*-toluenesulfonyl chloride (0.380 g., 1.99 mmoles) in dry pyridine (4 ml.) was kept at room temperature for 40 hr. The solution was then diluted with water, acidified, and extracted with ether.

From the ether extract after drying over magnesium sulfate, filtering, and removing ether, there was obtained an oil which was chromatographed on Florisil. The only identifiable material obtained from the chromatogram was 0.085 g. (20%) of crude methylene ketone (IV), which was eluted with benzene. This material, after one recrystallization from methanol, afforded methylene ketone (IV), m.p. 224.8–225.0°, which was identical with authentic[2] methylene ketone (IV) (m.p. 223.0–224.0°) by the criteria of mixture melting point and infrared spectra.

cis- and trans-11-Hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracenes (VIa *and* VIb). A solution of *cis* diol (IIa) (0.530 g., 2.10 mmoles) and *p*-toluenesulfonyl chloride (0.450 g., 2.36 mmoles) in a mixture of dry benzene (7 ml.) and dry pyridine (2 ml.) was kept at room temperature for 17 hr. The mixture was then diluted with water and extracted with ether, the ether extract being washed with dilute hydrochloric acid, then water, and finally being dried over magnesium sulfate. Filtration and removal of solvent yielded a glass which solidified on being triturated with carbon tetrachloride. Recrystallization of this solid from methanol gave 0.319 g. (37%) of the *cis*-hydroxy tosylate (VIa), m.p. 152°. An additional recrystallization from methanol afforded *cis-11-hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene* (VIa), m.p. 152.0–152.2°. In the infrared (chloroform solution) VIa exhibited absorption at 3540 and 3370 cm.$^{-1}$ (hydroxyl) and, among others, at 1365, 1192, and 1180 cm.$^{-1}$ (tosylate).

Anal. Calcd. for $C_{24}H_{22}O_4S$: C, 70.89, H, 5.46. Found: C, 70.72; H, 5.64.

For the preparation of *trans*-hydroxy tosylate (VIb), a solution of the *trans* diol (IIb) (0.177 g., 0.703 mmole) and *p*-toluenesulfonyl chloride (0.156 g., 0.817 mmole) in dry pyridine (6 ml.) was kept at room temperature for 41 hr. The reaction mixture was then processed as above to yield 0.243 g. of crude product which was chromatographed on Florisil. Elution of the column with 5% ether in benzene afforded 0.140 g. (49%) of *trans-11-hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene* (VIb) as a glass which could not be induced to crystallize. In the infrared (chloroform solution) this material exhibited absorption at 3540 cm.$^{-1}$ (hydroxyl) and, among others, at 1367, 1192, and 1178 cm.$^{-1}$ (tosylate); its spectrum was distinct from that of the *cis*-hydroxy tosylate (VIa) and indicated no contamination by VIa.

After elution of the *trans*-hydroxy tosylate (VIb) from the chromatographic column, there was obtained (with 3% methanol in benzene) 0.026 g. (34% recovery) of unchanged *trans* diol (IIb).

11-Keto-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene (VII). (A). *From cis-11-hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene* (VIa). A solution of *cis*-hydroxy tosylate (VIa) (0.199 g., m.p. 152°), *t*-butyl hypochlorite[6] (0.120 g.) and pyridine (0.139 g.) in chlorobenzene (4 ml.) was permitted to remain at room temperature for 9.5 hr. The solution was then diluted with ether, washed with aqueous sodium bisulfite, water, dilute hydrochloric acid, water, and then dried over magnesium sulfate. After filtration, solvent was removed under reduced pressure to yield the keto tosylate (VII) as a solid which, after one recrystallization from ethanol, melted at 149–150° dec., and amounted to 0.071 g. (36%). Two additional recrystallizations from ethanol afforded material, m.p. 151.0–151.8° dec., which was identical with authentic[2] keto tosylate (VII) (m.p. 152° dec., and 167° dec.) by the criteria of mixture melting point and infrared spectra.

(B). *From trans-11-hydroxy-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene* (VIb). A solution of *trans*-hydroxy tosylate (VIb) (0.126 g., as obtained from chromatography), pyridine (0.100 g.), and *t*-butyl hypochlorite[6] (0.054 g.) in chlorobenzene (3 ml.) was permitted to remain at room temperature for 16 hr. Isolation procedures as in (A) yielded, after one recrystallization from ethanol, 0.040 g. (32%) of keto tosylate (VII), m.p. 152–153° dec. This material was identical with that obtained in (A) by the criteria of mixture melting point and infrared spectra.

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[6] H. M. Teeter and E. W. Bell, *Org. Syntheses*, **32**, 20 (1952).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Chlorides Derived from 1-Ethynylcyclohexanol[1]

G. F. HENNION AND C. A. LYNCH, JR.[2]

Received February 8, 1960

The action of thionyl chloride on 1-ethynylcyclohexanol (I), under a variety of conditions, invariably led to a complex mixture only partially separable by fractional distillation. The following products were identified: unchanged carbinol (I), 1-ethynylcyclohexyl chloride (II), 1-ethynylcyclohexene (III), 1-(α-chlorovinyl)cyclohexene (IV), cyclohexylidenevinyl chloride (V), and 1-(β-chlorovinyl)cyclohexene (VI). The *t*-chloride (II) was always formed in minor amounts only. Cyclohexylidenevinyl chloride (V) is sensitive to thermal and prototropic rearrangement to the isomer (VI) and could not be isolated in high purity. Independent syntheses produced the isomers, II, IV, and VI in satisfactory yield and purity.

Various studies underway in this laboratory require assorted higher *t*-acetylenic chlorides, RR′C(Cl)—C≡CH. Where R and R′ are small alkyl groups, the preparations are easily accomplished by reaction of *t*-acetylenic carbinols with concentrated hydrochloric acid.[3] As this method has not proved satisfactory where R and (or) R′ are large, other preparative methods have been sought. We wish to summarize now a de-

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[1] Paper no. 72 on substituted acetylenes; previous paper by G. F. Hennion and R. S. Hanzel, *J. Am. Chem. Soc.*, (in press).

[2] Dow Chemical Company Fellow, 1957–58. Abstracted from the Ph.D. Dissertation of C. A. L., Jr.

TABLE I

PRODUCTS OF THE REACTION OF THIONYL CHLORIDE WITH 1-ETHYNYLCYCLOHEXANOL

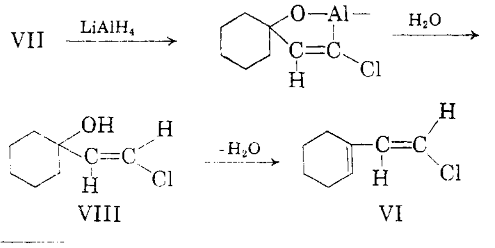
Conditions		Products Found (% of Total)					
Solvent	Temp.	I[a]	II[b]	III[c]	IV[d,e]	V[f]	VI[g]
Pyridine	50–60°	1.2	8.3	5.6	75.0	Absent	9.9
Ether	3°	6.2	6.6	8.9	54.7	Present	23.7
Ether	b.p.	3.2	4.3	16.3	52.5	Present	23.7
Ether	to 85°	30.9	6.4	18.0	31.5	Present	13.1
THF[h]	b.p.	6.7	5.4	4.0	57.6	Present	26.4
Ether-pyridine	3°	11.4	4.6	63.2	—	20.7	—

[a] 1-Ethynylcyclohexanol (recovered). [b] 1-Ethynylcyclohexyl chloride. [c] 1-Ethynylcyclohexene. [d] 1-(α-Chlorovinyl)-cyclohexene. [e] The figures cited include compound V, if present. [f] Cyclohexylidenevinyl chloride. [g] 1-(β-Chlorovinyl)cyclohexene. [h] Tetrahydrofuran.

tailed study of the reaction of 1-ethynylcyclohexanol (I) with thionyl chloride.

Fortunately, 1-ethynylcyclohexyl chloride (II) can be prepared from I in excellent purity and high yield[3c] by treatment with excess hydrochloric acid containing dissolved cuprous chloride. The yield is very poor in the absence of cuprous chloride.[3b] The reaction of I with thionyl chloride under widely varied conditions produced only minor amounts of *t*-chloride (II) and was more complex than was realized previously.[4,5] Products boiled over a wide range of temperature (*ca.* 40–90° at 12 mm.) and usually could not be separated cleanly by repeated fractional distillation. The infrared spectra of the total distillates were very complex and often revealed the structural features of unchanged carbinol (I), the enyne (III), and the isomeric chlorides (II, IV, V and VI) formulated in Fig. 1. Vapor phase chromatography confirmed the conclusion that the products contained four to six components, depending on experimental conditions.

The isomeric chlorides (II, IV, V and VI) were then prepared by alternative methods as shown in Fig. 1. Pure II was made[3c] from I with hydrochloric acid and cuprous chloride; authentic IV was prepared[6] from the enyne (III) by addition of hydrochloric acid across the triple bond; VI was obtained by the sequence I→VII→VIII→VI. It is noteworthy that VI must have the *trans*-configuration with respect to the exocyclic double bond in view of the scheme shown below.[7] Preparation of pure chloroallene (V) was troublesome, however. The reaction of I with thionyl chloride in cold ether containing pyridine gave a four component product (see Table I, last line) notably rich in V and free of the isomers IV and VI. Removal of unchanged carbinol (I) from this material by percolation through alumina followed by fractional distillation *in vacuo* yielded V in 86% purity as determined by VPC. The distilled sample now contained VI, even though originally absent. It was observed repeatedly throughout this work that the facile thermal and (or) prototropic rearrangement of V to VI virtually precludes the possibility of obtaining V in high purity.



With the exception of V, the compounds listed in Fig. 1 and Table I were thus obtained in excellent purity, permitting characterization by infrared spectroscopy and VPC (retention times). The analysis of the total distilled products of the reaction of 1-ethynylcyclohexanol (I) with thionyl chloride was thus possible. In some instances, however, the presence of *both* IV and V could be established only by infrared examination, as these substances have identical boiling points and VPC retention times (see Table II).

The reaction of 1-ethynylcyclohexanol with thionyl chloride appears to be useful only for the preparation of 1-(α-chlorovinyl)cyclohexene (IV). When the reaction is carried out in warm pyridine, the major product is IV, isolable in acceptable yield and purity as observed earlier[4] (see Table I, line 1). Hurd and Jones[4] postulated that under these conditions I is dehydrated to enyne (III), which adds hydrochloric acid across the triple bond. This mechanism has now been supported by the observation that when thionyl chloride is added to a warm solution of enyne (III) and water (1:1 ratio) in pyridine, IV is indeed produced (70% yield, once distilled, 85% purity by VPC).

The various reaction products are all believed

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(3)(a) G. F. Hennion, J. J. Sheehan, and D. E. Maloney, *J. Am. Chem. Soc.*, **72**, 3542 (1950); (b) G. F. Hennion and E. G. Teach, *J. Am. Chem. Soc.*, **75**, 1653 (1953); (c) G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.*, **79**, 2142 (1957).

(4) C. D. Hurd and R. N. Jones, *J. Am. Chem. Soc.*, **56**, 1924 (1934).

(5) Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, **24** (1959).

(6) W. H. Carothers and D. D. Coffman, *J. Am. Chem. Soc.*, **54**, 4071 (1932).

(7) R. A. Raphael, *Acetylenic Compounds in Organic Synthesis*, Academic Press, Inc., New York, 1955, p. 30.

TABLE II

VAPOR PHASE CHROMATOGRAPHY, 1-ETHYNYLCYCLOHEXANOL AND REACTION PRODUCTS

Compound	B.P., °C/Mm.	Retention Time, Min.[a]
1-Ethynylcyclohexene (III)	39/12	14
1-Ethynylcyclohexanol (I)	68/11	21
1-Ethynylcyclohexyl chloride (II)	58/12	24
1-(α-Chlorovinyl)cyclohexene (IV)	73/11	45
Cyclohexylidenevinyl chloride (V)	72/11	45
1-(β-Chlorovinyl)cyclohexene (VI)	82/12	49

[a] Silicone oil, G. E. SF-96, 3.05 meter column, 134°, flow rate of 40 ml. of helium per minute.

to originate from the chlorosulfite ester of I as follows: II by the usual S_Ni mechanism; III by elimination of sulfur dioxide and hydrogen chloride; IV by addition of hydrochloric acid to III; V by the S_Ni' mechanism; and VI by prototropic rearrangement of V.

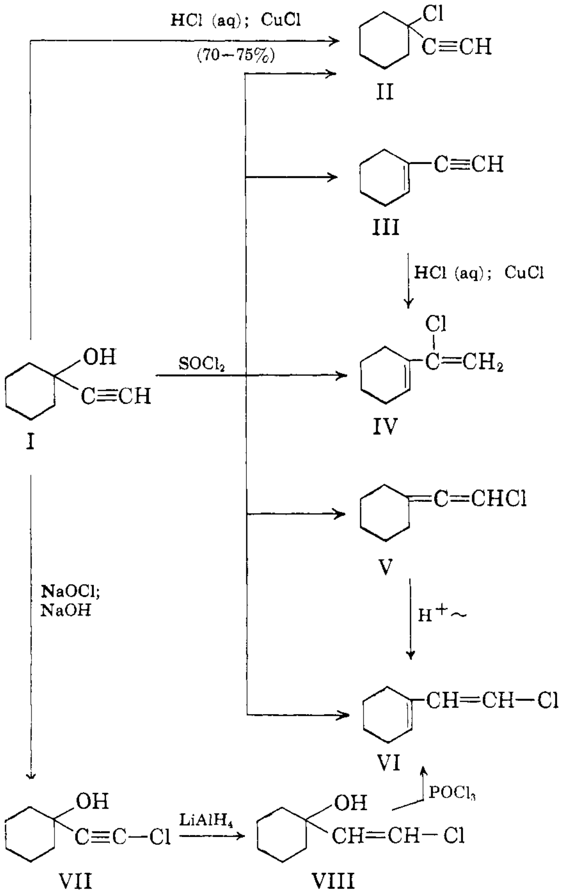

Fig. 1. Preparation of the isomeric chlorides

EXPERIMENTAL

1-Ethynylcyclohexanol (I) was used as received from Air Reduction Company, New York, New York.

1-Ethynylcyclohexene (III), b.p. 39° at 12 mm., n_D^{25} 1.4940, was prepared from I in 75–80% yields.[8] Infrared absorption bands (μ) were observed at 3.05 (vs), 3.40 (vs), 4.77 (m), 6.16 (w), 6.95 (s), 8.80 (s), 10.92 (vs), 11.70 (s), 11.85 (vs), 12.50 (s) and 15.00–15.50 (s).

1-Ethynylcyclohexyl chloride (II), b.p. 58° at 12 mm., n_D^{25} 1.4782, d^{25} 1.009, was prepared in 70–75% yields as previously described.[3c] Infrared bands (μ) were observed at 3.04 (vs), 3.40 (vs), 4.70 (w), 6.90 (vs), 7.74 (s), 7.97 (s), 8.85 (s), 9.95 (s), 11.14 (s), 11.50 (s), 12.40 (vs), 12.80 (vs), 15.00–15.50 (s).

Anal.[9] Calcd. for $C_8H_{11}Cl$: Cl, 24.86. Found: Cl, 24.48, 24.56.

1-(α-Chlorovinyl)cyclohexene (IV), b.p. 73° at 11 mm., n_D^{25} 1.5240, d^{25} 1.041, was prepared from III (60% yield) as described by Carothers and Coffman.[6] Infrared bands (μ) at 3.40 (vs), 6.02 (m), 6.11 (s) 6.25 (vs) 6.93 (s), 8.30 (vs), 9.37 (s), 10.85 (s), 11.50 (vs), 11.69 (vs), 13.70 (s), 14.15 (vs).

1-Chloroethynylcyclohexanol (VII), m.p. 50–51°, was prepared from I in 95% yield by the method of Strauss, Kolleck, and Heyn.[10]

1-(β-Chlorovinyl)cyclohexanol (VIII), b.p. 103–105° at 12 mm., was prepared in 55% yield by minor modification of the procedure of Julia and Surzur.[11] A standardized solution of lithium aluminum hydride in ether (25% excess) was added dropwise with stirring to a solution of 1-chloroethynylcyclohexanol (VII) in cold ether. Stirring was continued for 5 hr. after addition was completed. Hydrolysis was then accomplished with water and aqueous sodium potassium tartrate.

1-(β-Chlorovinyl)cyclohexene (VI) was prepared from VIII by dehydration with phosphorus oxychloride. The latter (40 ml., 0.44 mole) was added dropwise to a well-stirred solution of 32 g. (0.2 mole) of β-chlorovinylcyclohexanol (VIII) in 200 ml. of dry pyridine. The mixture was stirred for 4 hr., poured over crushed ice, and the organic layer was separated. The aqueous layer was extracted with three 100-ml. portions of petroleum ether. The original product and the extracts were combined, washed with dilute hydrochloric acid, with water, finally with saturated sodium bicarbonate solution, and dried over anhydrous potassium carbonate. Distillation yielded three fractions: (a), 0.70 g., b.p. 76–80° at 12 mm.; (b) 7.8 g., b.p. 80–82° at 12 mm., n_D^{25} 1.5304; (c) 3.2 g., b.p. 82–118° at 12 mm. Redistillation of fraction (b) gave 5.7 g., b.p. 82° at 12 mm., n_D^{25} 1.5307, d^{25} 1.036. Infrared bands (μ) were observed at 3.40 (vs), 6.13 (w), 6.27 (s), 6.95 (s), 10.70 (vs), 11.75 (s), 12.0 (vs), 12.80 (vs), 13.1 (vs), and 15.20 (s).

Anal.[9] Calcd. for $C_8H_{11}Cl$: Cl, 24.86. Found: Cl, 24.49.

Cyclohexylidenevinyl chloride (V). Thionyl chloride (purified by the method of Cottle[12]) (39.2 g., 0.33 mole) was added to a stirred solution of 37.2 g. (0.3 mole) of 1-ethynylcyclohexanol (I) and 27.6 g. (0.35 mole) of dry pyridine in 150 ml. of anhydrous ether at 3–5°. Water (100 ml.) was added and the etheral layer was separated, washed with dilute hydrochloric acid, with saturated sodium bicarbonate, and then dried with anhydrous potassium carbonate. Distillation gave 22 g. of crude product, b.p. 40–71° at 12 mm., n_D^{25} 1.4983. Sixty-four grams of this material (obtained from three runs) was redistilled partially, all material boiling below 46° at 11 mm. discarded (30 g., mostly 1-ethynylcyclohexene). The still residue was dissolved in 50 ml. of petroleum ether and percolated through a column of alumina

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[8] J. C. Hamlet, H. B. Henbest, and E. R. H Jones, *J. Chem. Soc.*, 2652 (1951).

[9] Analyses by Midwest Microlab, Inc., Indianapolis, Ind.

[10] F. Strauss, L. Kolleck, and W. Heyn, *Ber.*, **63**, 1868 (1930).

[11] M. Julia and J. M. Surzur, *Bull. soc. chim. France*, 1615 (1956).

[12] D. L. Cottle, *J. Am. Chem. Soc.*, **68**, 1380 (1946).

(80 g., "Alcoa F-20"). The column was washed with petroleum ether and 15-ml. fractions were collected. Each fraction was examined by infrared. The desired product (V) was detected in fractions 7–11, inclusive, free of starting material (I). These fractions were then distilled to yield 3.1 g., b.p. 72° at 11 mm., n^{25}_{D} 1.5229. Redistillation gave 1.04 g. of cyclohexylidenevinyl chloride (V), 86% pure by VPC, b.p. 72° at 11 mm., n^{25}_{D} 1.5235, d^{25} 1.025. The contaminents proved to be III (5.2%), II (1.4%), and VI (7.2%). Infrared bands (μ) at 3.40 (vs), 5.12 (vs), 6.93 (vs), 7.23 (s), 8.15 (vs), 10.28 (vs), 11.17 (s), 11.70 (s), 13.10–13.50 (vs), and 13.90–14.10 (vs). Notably significant are the bands at 5.12 and 13.10–13.50 μ, characteristic of the group C=C=CHCl.[5]

Anal.[9] Calcd. for $C_8H_{11}Cl$: Cl, 24.86. Found: Cl, 24.46. After redistillation, Cl found: 24.70.

Reaction of thionyl chloride with 1-ethynylcyclohexanol in pyridine. The procedure is essentially that of Hurd and Jones.[4] Purified[12] thionyl chloride (108 g., 0.9 mole) was added dropwise to a stirred mixture of 99 g. (0.81 mole) of 1-ethynylcyclohexanol and 78 g. (0.99 mole) of dry pyridine at 50–60°. After addition was complete the mixture was heated at 50–60° for 3 hr. and then cooled to room temperature. Water and petroleum ether (100 ml. of each) were added and the organic layer was separated. After washing and drying with anhydrous potassium carbonate, distillation gave 72 g., b.p. 39–75° at 12 mm., n^{25}_{D} 1.5178. Analysis of the total distillate by VPC (see Table I, line 1) showed that it contained 0.86 g. of recovered I, 5.98 g. of II, 4.04 g. of III, 7.14 g. of VI, and 54.0 g. (47% yield) of 1-(α-chlorovinyl)cyclohexene (IV).

Reaction of thionyl chloride with 1-ethynylcyclohexanol in ether. The procedure is essentially that of Bhatia, Landor, and Landor.[5] A solution of 37.2 g. (0.3 mole) of ethynylcyclohexanol and 39.3 g. (0.33 mole) of purified[12] thionyl chloride in 300 ml. of anhydrous ether was stirred for 1 hr. Most of the ether was then removed by distillation and the residue was heated on the steam bath for 3 hr. After cooling, the mixture was stirred with 100 ml. of saturated sodium bicarbonate solution, dried with anhydrous potassium carbonate, and distilled to give 30 g. of crude product, b.p. 34–82° at 11 mm., n^{25}_{D} 1.4992. Analysis of the total distillate by VPC (see Table I, line 4) indicated the composition to be 9.27 g. of I, 1.92 g. of II, 5.40 g. of III, 3.93 g. of VI, and 9.45 g. of a mixture of IV and V. The infrared spectrum revealed absorption bands for each of these substances.

Acknowledgment. The authors express their thanks to Air Reduction Company, New York, for generous gifts of 1-ethynylcyclohexanol and to the Dow Chemical Company, Midland, Michigan, for financial assistance. The gas chromatography unit used in this work was acquired under National Science Foundation Grant G-4058.

NOTRE DAME, IND.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

Studies on 3-Acylcatechols. II.[1] A New Synthesis of 8-Hydroxyflavone

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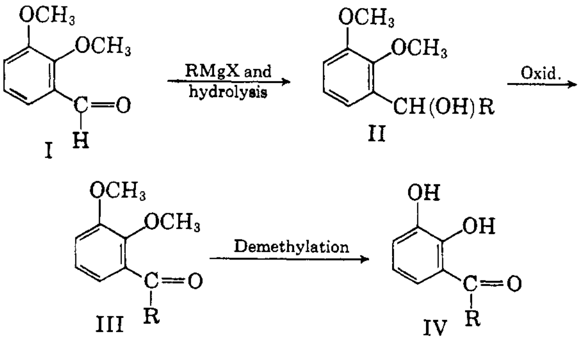
Received November 10, 1959

Some 3-acylcatechols are synthesized by an orthodox method. Their infrared spectra are recorded. 2,3-Dihydroxyacetophenone is utilized in the preparation of some chalcones, flavanones, and 8-hydroxyflavone. The latter has also been prepared *via* Claisen condensation of 2,3-dimethoxyacetophenone with ethyl benzoate followed by demethylation and cyclization.

In a previous publication,[1] we used the method described by Krannichfeldt,[2] for the preparation of some 3-acylcatechols[2], according to the following scheme:



In the present work we have prepared 2,3-dihydroxyisovalerophenone (IV. R = —$CH_2CH(CH_3)_2$) 2,3-dihydroxybenzophenone (IV. R = C_6H_5), 2,3,4′-trihydroxybenzophenone (IV. R = p-OHC_6H_4), and 2,3-dihydroxy-4′-chlorobenzophenone (IV. R = p-ClC_6H_4). The first of these compounds (m.p. 48°) is not identical with that reported by Miller, Hartung, Rock, and Crossley[3] (m.p. 93–95°) which they obtained as a by-product of a Fries rearrangement. The structure of our product cannot be questioned on account of the unambiguous method used in its preparation. Furthermore, our product gives a green color with ferric chloride that changes to red by the addition of sodium carbonate solution, a characteristic color test for catechols.[4,5] Moreover, the infrared data (*inter alia*) provides additional proof for the structure of 3-acylcatechols described here. The second

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(1) W. I. Awad, M. F. El-Neweihy, and S. F. Selim, *J. Org. Chem.* **23,** 1783 (1958).

(2) H. V. Krannchfeldt, *Ber.,* **46,** 4017–4018 (1913).

(3) Ellis Miller, Walter H. Hartung, Henry J. Rock and Frank S. Crossley, *J. Am. Chem. Soc.,* **60,** 7 (1938).

(4) Compare Paul Karrer, *Organic Chemistry,* Fourth English Edition, Elsevier Publ. Co., Inc., New York, N. Y., p. 435.

(5) A. Schönberg, W. I. Awad, and G. A. Mousa, *J. Am. Chem. Soc.,* **77,** 3850 (1955).