Reduction of Pyrones with Complex Metal Hydrides[1]

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It has been known that α- and γ-pyrones have an aromatic character which is reflected on their physical properties—for example, their infrared spectra. The aromatic nature of γ-pyrone is also reflected on its chemical properties; in comparison with a normal ketone, carbonyl group of γ-pyrone is generally unreactive, which is illustrated by the fact that γ-pyrone does not form 2, 4-dinitrophenylhydrazone[2]. However, condensation of γ-pyrone with an active methylene compound was reported[3] and in this case γ-pyrone reacted as a normal ketone. α-Pyrone behaves as α, β-γ, δ-unsaturated lactone[2] in various reactions including ozonization, hydrolysis, catalytic hydrogenation[4] and Diels-Alder reaction. So far, little is known about the reduction of α- and γ-pyrones with various complex metal hydrides except for limited examples of benzo-α-[5,6], benzo-γ-pyrones[7] and xanthone[8]. In case of benzo-α-pyrones, the formation of diol expected for the usual reduction of a lactone was reported. An α-pyrone derivative was known to be unreactive towards sodium borohydride under mild condition[9]. As to benzo-

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1) Preliminary communication. K. Yamada, M. Ishizaka and Y. Hirata, This Bulletin, **34**, 1873 (1961).

2) R. C. Elderfield, "Heterocyclic Compounds", Vol. I, John Wiley, (1950), pp. 343—396.

3) a) L. L. Woods, *J. Am. Chem. Soc.*, **80**, 1440 (1958); b) M. Ohta and H. Kato, This Bulletin, **32**, 707 (1959).

4) In catalytic hydrogenation of α-pyrone derivative, it was reported that in addition to the formation of saturated δ-lactone, the hydrogenolytic cleavage of 1, 6-linkage of an α-pyrone ring took place to yield a saturated carboxylic acid[2]. The analogous result of the bond cleavage is found in the catalytic hydrogenation of β-alkoxy-α, β-unsaturated ketone.

5) a) F. A. Hochstein, *J. Am. Chem. Soc.*, **71**, 305 (1949); b) P. Karrer and P. Banerjea, *Helv, Chim. Acta*, 32, 1692 (1949).

6) J. P. Freeman and M. F. Hawthorne, *J. Am. Chem. Soc.*, **78**, 3366 (1956).

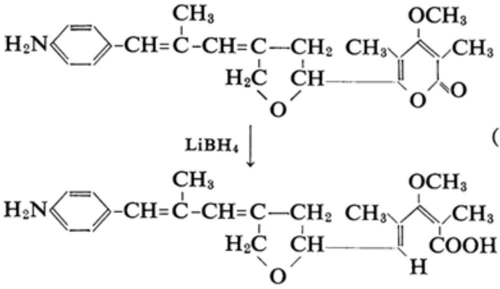
7) a) R. Robinson and R. Mirza, *Nature*, **166**, 929 (1950); b) R. Mirza and R. Robinson, ibid., **166**, 997 (1950).

8) A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, **1952**, 1343.

9) M. Bharucha, H. Jäger, K. Meyer, T. Reichstein and O. Schindler, *Helv. Chim. Acta*, **42**, 1395 (1959).

γ-pyrone derivatives⁷⁾, it was reported that the expected reduction of a ketone group to γ-pyranol took place.

In isoaureothamine (I) which is one of the derivatives of natural nitro compound aureothin¹⁰⁾, the presence of an α-pyrone ring was inferred from infrared and ultraviolet spectral data. Treatment of I with sodium borohydride or lithium borohydride led to a product aminol H, which was acidic and still showed a carbonyl band in the infrared spectrum¹¹⁾. Later, structure II was assigned to aminol H¹²⁾. This would be regarded as unusual reduction product if α-pyrone moiety of I is expected to behave like a lactone. Admitting the correctness of the structure II, there remained a problem whether or not this unexpected reduction occurred under the influence of other part of the molecule.

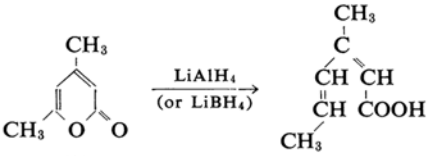


(I)

(II)

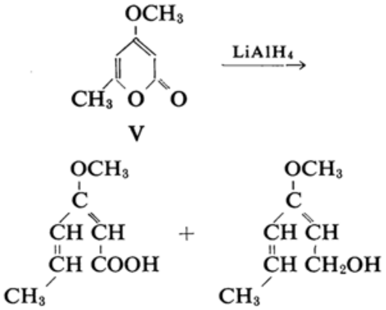
The result obtained in the reduction of isoaureothamine (I) is, thus quite different from those in benzo-α-pyrones, suggesting that the presence of the fused benzene ring in benzo-α-pyrone would account for this difference. From this viewpoint, monocyclic α-pyrones were prepared and their reductions with various complex metal hydrides were examined.

Reduction of α-Pyrones.—Firstly, reduction of 4, 6-dimethyl-α-pyrone (III) was carried out as a simple and standard α-pyrone. On treatment with sodium borohydride under various conditions (temperature, 20, 50, 70°C: solvent, ethanol or tetrahydrofuran) no reaction took place, though the reaction conditions employed in the present study were more drastic than that of Bharucha et al.⁹⁾ Lithium borohydride treatment of III in tetrahydrofuran, though a considerable amount of III was recovered, gave a reduction product identified as β-methylsorbic acid (IV) from the melting point and elemental analysis. When the more powerful reducing reagent, lithium aluminum hydride was used, the acid IV was obtained from III in fairly good yield (about 60%) and hence the recovery of III was decreased in amount (ca. 20%) as compared with lithium borohydride treatment.



III IV

Secondly, 6-methyl-4-methoxy-α-pyrone (V) was employed in the reduction reaction. The enhanced reactivity of V towards reducing reagents is evident from the following results. Even on treatment with sodium borohydride in ethanol, β-methoxysorbic acid (VI) was obtained from V, besides a large amount of starting material. Considerable amount of VI was produced from V in the reduction using lithium borohydride together with a small amount of starting material. Lithium aluminum hydride reduction of V afforded the acid VI in rather poor yield and the neutral product VII, which turned out to be a diene-alcohol derived from VI by further reduction of carboxyl group to hydroxymethyl group¹³⁾.



V VI VII

A large excess amount of lithium aluminum hydride (molar ratio, $V/LiAlH_4=1/2$) was used in the reduction of V, and the formation of VII becomes predominant with a raise of temperature (Table I).

Since the product ratio VII/VI is sensitive to the reaction conditions, it was necessary to carry out the experiments shown in Table I under the same concentrations and the same mode of addition, i. e., "inverse" addition method¹⁴⁾. In order to get an information on the product ratio VII/VI from the other point of view, the influence of the relative amount of lithium aluminum hydride to V was examined (Table II). As indicated in Table II, large excess amount of lithium aluminum hydride

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10) Y. Hirata, H. Nakata, K. Yamada, K. Okuhara and T. Naito, *Tetrahedron*, **14**, 252 (1961).

11) K. Yamada, Y. Hirata, K. Okuhara, H. Nakata, T. Naito and K. Iwadare, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 384 (1958).

12) K. Yamada, T. Naito, K. Okuhara, H. Nakata and Y. Hirata, This Bulletin, **33**, 1303 (1960).

13) The neutral product (VII) was independently prepared by reduction of VI with lithium aluminum hydride.

TABLE I. REDUCTION OF 6-METHYL-4-METHOXY-α-PYRONE (V). TEMPERATURE DEPENDENCE OF PRODUCTS

Temp. °C	Reactant V g.	Reactant $LiAlH_4$ g.	Product VI g.	Product VII g.	VII/VI[a]
0~3[b]	1.00	0.62	0.14	0.2	1.6
25~27	3.00	1.81	0.24	1.11	5.1
48~50	3.00	1.82	0.01	2.15	238

a) Molar ratio
b) Starting material V was partly recovered.

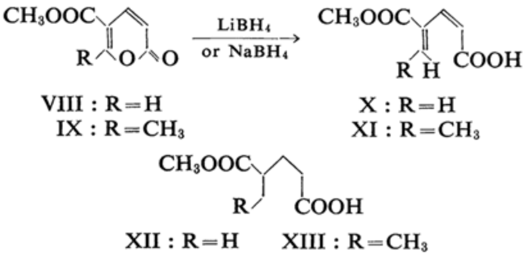
TABLE II. REDUCTION OF 6-METHYL-4-METHOXY-α-PYRONE. DEPENDENCE OF PRODUCT PROPORTIONS ON THE AMOUNT OF LITHIUM ALUMINUM HYDRIDE

Temp. °C	Reactant V mg.	Reactant $LiAlH_4$[a] mg.	Product VI mg.	Product VII mg.
10~12	280	45	90	—[b]
58~60	280	48	85	—[c]
10~12	280	110	84	(50)[d]
58~60	280	115	50	(60)[d]
10~12	280	220	65	140
58~60	280	220	Trace	205

a) The purity of $LiAlH_4$ was determined before use (Ref. 13, p. 8).
b) The formation of VII was very small in amount. As a neutral fraction, starting material (80 mg.) was recovered.
c) VII was detected by infrared spectrum, but the main part of the neutral fraction (110 mg.) was V.
d) In these cases, the neutral fraction was a mixture of VII and V and, on account of incomplete separation of two compounds, these figures would overestimate the amount of VII.

is markedly effective for the production of the alcohol VII even at rather low temperature. When the different mode of addition, normal addition[14] was applied in the reduction of V with lithium aluminum hydride, the acid VI and a neutral fraction were obtained. From the infrared analysis, this neutral fraction was shown to be a mixture of a ketonic compound[15] and the alcohol VII.

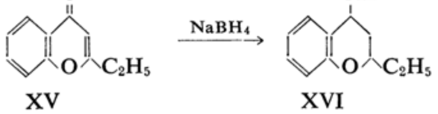
Further, methylesters of coumalic acid and 6-methylcoumalic acid, VIII, IX were treated with lithium borohydride and sodium borohydride. These α-pyrones showed enhanced reactivities and especially methyl coumalate VIII was so reactive as to form immediately a deeply colored complex near 0°C with lithium borohydride. The product was ester-carboxylic acid in each case. From the infrared and ultraviolet spectral evidence, structure X and XI were assigned to the products. These were further supported by the fact that the reduced products X, XI could by catalytic hydrogenation be led to XII and XIII, obtained[16] directly by catalytic hydrogenation of VIII and IX respectively (identification by comparison of infrared spectra).



VIII : R=H
IX : $R=CH_3$
X : R=H
XI : $R=CH_3$
XII : R=H XIII : $R=CH_3$

In order to avoid reduction of the ester group of the side chain, an experiment using lithium aluminum hydride was not undertaken.

Reduction of Benzo-γ-pyrone.—From the infrared evidence, a carbonyl group of monocyclic γ-pyrone in aureothin was reported[11] to be reduced with lithlum borohydride, but the structure of product is still uncertain. In connection with the reduction of aureothin, 2,6-dimethyl-γ-pyrone (XIV) was treated with complex metal hydrides ($LiAlH_4$, $LiBH_4$) to give a liquid mixture from which no definite compounds could be isolated[17]. While the monocyclic γ-pyrone (XIV) was inert to sodium borohydride, benzo-γ-pyrone showed an enhanced reactivity and was reduced with this reagent, as follows. Treatment of 2-ethylchromone (XV) with sodium borohydride under the same condition as employed in XIV, gave 2-ethyl-4-hydroxychroman (XVI).



XV XVI

When treated with lithium borohydride, XV afforded, in addition to XVI, an oily product, the formation of which increased further with lithium aluminum hydride reduction.

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[14] N. G. Gaylord, "Reduction with Complex Metal Hydrides", Interscience Publishers Inc., New York (1956), p. 1008.

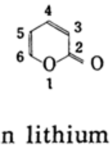
[15] In spite of the repeated experiments under various conditions, this compound was produced in poor yield. Though the structure is still ambiguous on account of difficulties in separation and purification, this would arise from the reduction of 1,2-linkage of V, which means the normal lactonic behavior of α-pyrone.

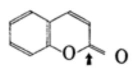
[16] J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 566 (1941).

[17] Main fraction of the products showed a strong band at 1710 cm^{-1}.

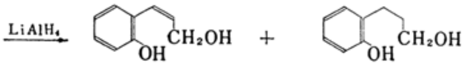
Discussion

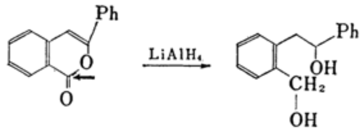
Reduction with complex metal hydride is considered as nucleophilic reaction involving hydride ions, though the active entity during the reduction process is still uncertain. Nucleophilic attack of hydride ion at 2-position of α-pyrone led to the same result as encountered in a usual lactone and, in fact, this mode of reaction is found in lithium aluminum hydride reductions (hydride ion as a nucleophile) and Grignard reactions (carbanion as a nucleophile) of benzo-α-pyrones XVII[5,6], XVIII[18].





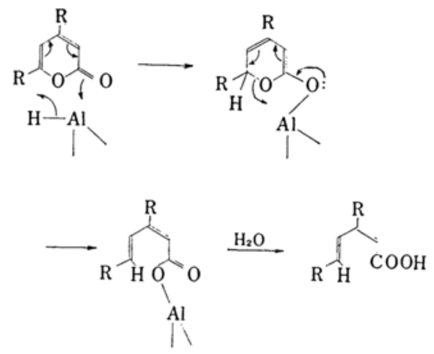
XVII





XVIII

A reaction of monocyclic α-pyrone with Grignard reagent involving an attack at 2-position of an α-pyrone was reported[19] recently, while, as described in this paper, the results of reduction of monocyclic α-pyrones with complex metal hydrides are unique, i. e., a general type of reduction of monocyclic α-pyrone with complex metal hydride reagent is a hydrogenolytic cleavage of 1, 6-linkage to afford an α, β-γ, δ-unsaturated carboxylic acid. This result is, at first sight, unexpected for the lactonic property of α-pyrone but can be explained as follows. According to the concept of vinylogy in reaction, possible points of attack by a nucleophile are 2-, 4- and 6-positions of an α-pyrone. In a complex metal hydride reduction, an attack of hydride to 6-position (1, 6-conjugate addition) occurs selectively and then the redistribution of electrons under the participation of metal ion takes place to afford a carboxylic acid, as shown in the scheme.



The difference of the reaction centers of monocyclic α-pyrone between hydride reduction and Grignard reaction[19] would be accounted for by considering the bulkiness of the reagent and/or a role of metallic ion involved in each reaction. Though a role of metallic ion in the hydride reduction is important, a precise mechanism of its participation during the reaction is not clear and hence aluminum is tentatively shown in the scheme as an electron acceptor. A high reactivity at 6-position of an α-pyrone is expected to be furthermore increased by introducing an electron-attracting substituent at 5-position[20], and this is encountered in the coumalic acid derivatives which were reduced under mild conditions.

In benzo-α-pyrone, carbon-carbon double bond of α-pyrone constitutes a part of benzene skeleton and the electronic displacement illustrated in the scheme would be accomplished with reluctance or prohibited[21], thus leading to a preferential attack of a nucleophile at a lactone-carbonyl carbon.

In the reduction of V, there were obtained an acid VI and an alcohol VII, and the amount of VII increased with a raise of temperature, when a large excess of hydride reagent was used—this is an expected result. The relative amount of the reducing reagent to V was found to have a more remarkable effect on the product proportions VI, VII, than temperature change. In the present case, reduction of COOH→CH_2OH is sensitive to the amount of the reagent (Table II).

Reduction of 2-ethylchromone (XV) takes place under milder conditions, than in case of

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[18] S. Siegel and S. Coburn, *J. Am. Chem. Soc.*, **73**, 5494 (1951).

[19] R. Gompper and O. Christmann, *Chem. Ber.*, **94**, 1784 (1961).

[20] Electropositive property of 6-position is increased by an addional effect of electronic displacement in B besides A.

(A) (B)

[21] In other words, an electropositive character at 6 position of monocyclic α-pyrone is weakened in benzo-α-pyrone system by supply of electrons from a benzene ring.

monocyclic γ-pyrone (XIV), indicating that a carbonyl group of XV loses an inert character of γ-pyrone carbonyl and instead has a property of a usual conjugated ketone. In case of XV, the first stage of the reaction is, of course a conjugate addition (1, 4-addition) of hydride ion, followed by further reduction of the ketone group.

Experimental

The infrared spectra were measured with a Hilger H 800 Model and Nihonbunko model IR-S. The ultraviolet spectra were measured with a Beckmann DK-2 spectrophotometer.

4, 6-Dimethyl-α-pyrone. — Prepared from ethyl acetoacetate[22]. M. p. 48~49°C.

Reduction of 4, 6-Dimethyl-α-pyrone.—*a) Sodium Borohydride*.—To an ethanolic solution (10 ml.) of 500 mg. of sample was added 300 mg. of sodium borohydride. The mixture was kept at 70°C for 2.5 hr. After cooling, a small amount of hydrochloric acid was added, and on removal of the solvent at reduced pressure, the residue was extracted with ether. The ethereal solution was dried with anhydrous sodium sulfate and after filtration, ether was removed to afford colorless crystals (460 mg.), m. p. 45~48°C which were identified as starting material. To the residue was added hydrochloric acid until the solution became strongly acidic and the aqueous solution was extracted with ether. From this ethereal solution, the expected carboxylic acid IV could not be obtained. The same procedure was repeated at 50 and 20°C only to recover a starting material. When tetrahydrofuran was employed as solvent, sodium borohydride was suspended in it.

b) Lithium Borohydride.—A suspension of lithium borohydride in tetrahydrofuran (240 mg./10 ml.) was added to a solution of a sample in tetrahydrofuran (720 mg./10 ml.) and the mixture was kept under reflux for 3 hr. The solution became yellow and turbid. After removal of the solvent under reduced pressure, 5 ml. of water was added to decompose the formed complexes and excess reagent. The aqueous solution was extracted with ether (50 ml.). From this ethereal layer, starting material was recovered. On acidification of the aqueous layer with hydrochloric acid, a white precipitate appeared, was collected and recrystallized from benzene, 120 mg. M. p. 97~98°C (reported 98~99°C)[23]: this acid proved to be β-methylsorbic acid.

Found: C, 67.00; H, 8.10. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99%.

UV: $\lambda_{\max}^{\mathrm{EtOH}}$, 260 m$\mu$ (log ε, 4.22).

c) Lithium Aluminum Hydride.—To a solution of 5.0 g. of a sample in tetrahydrofuran (15 ml.) was gradually added a suspension of 1.0 g. of lithium aluminum hydride in tetrahydrofuran (30 ml.). The mixture was stirred at 40°C for 4 hr. After cooling, the solvent was removed under reduced pressure and water was added to decompose complexes and excess reagent. The aqueous solution was extracted with ether and starting material (1 g.) was recovered from this ethereal layer. After filtration, the aqueous layer was acidified with hydrochloric acid to afford white crystals which was identical with an acid obtained with lithium borohydride treatment, yield 3 g.

6-Methyl-4-methoxy-α-pyrone.—Triacetic lactone was prepared from dehydroacetic acid with concentrated sulfuric acid at 130°C. Treatment of triacetic lactone with ethereal diazomethane gave 6-methyl-4-methoxy-α-pyrone contaminated with a small amount of isomeric γ-pyrone.

After separation[24] of γ-isomer, 6-methyl-4-methoxy-α-pyrone melted at 83~85°C.

Reduction of 6-Methyl-4-methoxy-α-pyrone.—*a) Sodium Borohydride*.—To a solution of 500 mg. of sample in ethanol (10 ml.) was added a solution of 300 mg. of sodium borohydride. The mixture was worked up in a manner identical with that used for 4, 6-dimethyl-α-pyrone. From the ethereal layer, starting material was recovered (350 mg.). To the residue was added 5 ml. of water and after filtration, aqueous solution was acidified with hydrochloric acid to give a white solid. Recrystallization from benzene gave colorless prisms (β-methoxysorbic acid), 25 mg., m. p. 146~148°C (reported 152°C (decomp.)[25]).

Found: C, 59.17; H, 7.13. Calcd. for $C_7H_{10}O_3$; C, 59.14; H, 7.09%.

UV: $\lambda_{\max}^{\mathrm{EtOH}}$, 264 m$\mu$ (log ε, 4.1).

b) Lithium Borohydride.—To a solution of 500 mg. of sample in tetrahydrofuran (10 ml.) was added 300 mg. of lithium borohydride in tetrahydrofuran (10 ml.) and the mixture was kept under reflux for 1 hr.

After removal of the solvent, 5 ml. of water was added to decompose yellow complexes. The aqueous solution was extracted with ether (40 ml.). From the ethereal layer was obtained an oily product, which gradually solidified and was identified as starting material (80 mg.). The aqueous solution was acidified to give a white precipitate which was collected, dried and recrystallized from benzene, m. p. 147~149°C (β-methoxysorbic acid), 305 mg.

c) Lithium Aluminum Hydride. — To a solution of 4.5 g. of sample in anhydrous tetrahydrofuran (60 ml.) was added with stirring a solution of lithium aluminum hydride (2.6 g.) in tetrahydrofuran (50 ml.) gradually. The mixture was kept at 30°C for 2 hr. Greenish precipitates appeared and the solution became yellow. Water was added carefully and the precipitates were removed by filtration.

The filtrate was concentrated to give an aqueous solution (an alcohol VII separated from the aqueous layer).

The aqueous solution was extracted with 150 ml. of ether. From the aqueous layer, β-methoxysorbic acid was obtained, 820 mg. The ethereal solution was dried with anhydrous sodium sulfate and the

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[22] R. H. Wiley and N. R. Smith, *J. Am. Chem. Soc.*, **73**, 3531 (1951).

[23] R. Kuhn and M. Hoffer, *Ber.*, **65**, 651 (1932).

[24] S. Janiszewska-Drabarek, *Roczniki Chem.*, **27**, 456 (1953).

[25] a) E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, **1949**, 1423; b) H. B. Henbest and E. R. H. Jones, ibid., **1950**, 3628.

solvent was removed to give a yellow liquid, of 3.1 g. This was fractionally distilled under reduced pressure in a small apparatus. Almost the whole part of the liquid was distilled between 100～104°C 16 mmHg. This was again distilled, yielding a colorless liquid, b. p. 102～104°C/16 mmHg.

IR, 3600, 3470(br.), 1665, 1605 $\mathrm{cm^{-1}}$ ($CHCl_3$) : UV, $\lambda_{\max}^{\mathrm{EtOH}}$, 239 mμ (log ε, 3.9).

Found: C, 65.92; H, 9.60. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44%. Methoxyl analysis (Zeisel) : 0.93 group.

This liquid was obtained also from β-methoxysorbic acid (500 mg.) and lithium aluminum hydride (200 mg.) in tetrahydrofuran (20 ml.) at 40°C for 30 min. This substance is 3-methoxy-2, 4-hexadienol and is rather unstable when exposed to air and light and becomes colored and viscous.

d) Experiment on Table II.—When reduction of V was carried out using various amounts of lithium aluminum hydride, it was sometimes necessary to separate V from VII in a mixture of neutral fraction. Though complete separation was difficult, a small difference of solubility of carbon tetrachloride was used for the separation. The extent of separation was checked by infrared spectrum.

e) Reduction using a Normal Addition. — To a solution of 800 mg. of lithium aluminum hydride in 20 ml. of tetrahydrofuran was added 2.0 g. of a sample of tetrahydrofuran (40 ml.). The mixture was kept at 30°C with stirring for 2 hr. The reaction mixture was worked up in the same manner as described in the inverse addition method and β-methoxysorbic acid (280 mg.) was obtained.

The neutral fraction (1.1 g.) showed a carbonyl band at 1710 $\mathrm{cm^{-1}}$ in addition to the bands at 1665 and 1605 $\mathrm{cm^{-1}}$ of VII and is positive for iodoform test.

Methyl Coumalate.—Coumalic acid was treated with 1.5 equivalent amount of ethereal diazomethane, m. p. 71～72°C.

Methyl 6-Methylcoumalate.—Coumalic acid was treated with a large excess amount of diazomethane (3～4 mol. equiv.) at room temperature. M. p. 83～85°C.

Reduction of Methyl Coumalate.—To a solution of 460 mg. of sample in 10 ml. tetrahydrofuran was added 100 mg. of lithium borohydride in 10 ml. tetrahydrofuran under cooling. The solution immediately turned yellow and then became brown. After 20 min., the mixture became dark-red and brown complexes appeared. After removal of the solvent, water (20 ml.) was added and the brown solution was extracted with ether. From the colorless ethereal layer nothing could be obtained. Yellow aqueous solution was acidified with 4 N sulfuric acid. The solution was tubid and extracted with ether (40 ml.). From the ethereal solution, a slightly yellow liquid was obtained (420 mg.). Infrared spectrum, 1725(sh), 1705, 1650(w), 1610 (w) $\mathrm{cm^{-1}}$ (film). UV, $\lambda_{\max}^{\mathrm{EtOH}}$, 263 mμ.

Neutralization of the liquid with sodium bicarbonate (or triethylamine) gave a solid, which showed bands at 1720, 1590(s) $\mathrm{cm^{-1}}$. Catalytic hydrogenation (PtO_2 as catalyst) of this liquid in methanol, gave, after uptake of about two equivalent moles of hydrogen, a liquid which was chromatographed on silicic acid. The main fraction thus obtained was identical with liquid obtained[16] by direct hydrogenation of methyl coumalate by infrared comparison. The same result was obtained, when the sample (500 mg.) was treated with sodium borohydride (200 mg.) in ethanol (20 ml.) at room temperature.

Reduction of Methyl 6-Methylcoumalate.—To a solution of 670 mg. of sample in 10 ml. of tetrahydrofuran was added 110 mg. of lithium borohydride in 10 ml. of tetrahydrofuran at room temperature (10～15°C). The solution became yellow and then orange red. The same procedure as described in methyl coumalate was employed.

Reduction of 2-Ethylchromone.—To an ethanolic solution (200 ml.) of 1.04 g. of sodium borohhydride was added 2.06 g. of 2-ethylchromone[26] in ethanol (50 ml.) and the mixture was kept under reflux for 3 hr. The solvent was removed under reduced pressure, and the extraction with ether was repeated. Concentration of ethereal solution gave an oil which gradually solidified. The solid was recrystallized from petroleum ether to give white feathery needles, 1.3 g., m.p. 77～78°C (reported for 2-ethyl-4-hydroxychroman, 78～79°C[27]).

Found: C, 74.19; H, 7.83. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

Summary

Reduction using complex metal hydrides was carried out on monocyclic α-pyrones and benzo-γ-pyrone. It was established that generally the hydrogenolysis of the 1, 6-linkage of an α-pyrone ring occurred. In benzo-γ-pyrone, carbon-carbon double bond and ketone were reduced. The effects of the substituents on the reactivity of α-pyrone were discussed.

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[26] "Organic Syntheses", Coll. Vol. III, p. 387.

[27] R. Mozingo and H. Adkins, *J. Am. Chem. Soc.*, **60**, 669 (1938).