under vacuum. The crystalline residue was dissolved in 100 ml of warm methanol and diluted with 400 ml of ethyl acetate. The crystals which formed were collected by filtration and dried. They weighed 30.7 g (65%) and melted at 155–157°. The analytical sample, prepared by two recrystallizatios from methanol, melted at 157–159° and gave $[\alpha]_D$ +235° (MeOH).

Anal. Calcd for $C_{16}H_{25}NO_5S$: C, 55.95; H, 7.34; N, 4.08; S, 9.34. Found: C, 55.73; H, 7.31; N, 4.20; S, 9.52.

Methyl *N*-Benzyl-4,6-*O*,*N*-methylene-α-thiolincosaminide (7).—A solution of 11.6 g of *N*-benzyl sugar **6** and 4 ml of formalin in 200 ml of methanol was maintained at 26° for 30 min. Evaporation of the solvent gave a residue of 11.8 g which was chromatographed over 1.2 kg of silica gel using chloroform–methanol (4:1) for elution. A fraction of 11.8 g of oil was recovered. A portion was dissolved in acetone, clarified, and evaporated to a glassy solid, $[\alpha]_D$ +175° (MeOH).

Anal. Calcd for $C_{17}H_{25}NO_5S$: C, 57.44; H, 7.09; N, 3.94; M^+, 355. Found: C, 57.33; H, 6.92; N, 3.93; M^+, 355.

Methyl *N*-Methyl-α-thiolincosaminide (8).—**7** (6 g) was dissolved in 160 ml of methanol and the solution was acidified with 6 *N* hydrochloric acid. Pd/C (10%) (6 g) suspended in 40 ml of 95% ethanol was added. The resulting mixture was shaken for 5 hr under 2 atm of hydrogen pressure. A few drops of acid were added to acidify the solution and hydrogenation continued for 12 hr. The catalyst was removed by filtration and the solvent distilled *in vacuo* after the mixture was made basic with triethylamine. The residue, 7.1 g, was chromatogaphed over 700 g of silica gel. Elution with methanol afforded 1.2 g of dimethyl compound **2**, which was recrystallized from methanol to give 700 mg of crystals, mp 174–176°. The more polar fraction was recrystallized from methanol to yield 900 mg of monomethyl compound **8**, mp 187–189°. Stripping the column with methanol–ammonium hydroxide (5%) followed by recrystallization gave an additional 330 mg of **8**, mp 186–188°. A portion of **8** was recrystallized from methanol. It now melted at 180–182° and gave $[\alpha]_D$ +267° (H_2O).

Anal. Calcd for $C_{10}H_{21}NO_5S$: C, 44.92; H, 7.92; N, 5.24; S, 12.00. Found: C, 45.20; H, 7.54; N, 5.34; S, 11.62.

Methyl *N*-Benzyl-*N*-methyl-α-thiolincosaminide (9).—A mixture of 3 g of **6** and 100 ml of ethyl formate was heated for 2.5 hr at 100° in a stirred autoclave. After cooling, the solution was removed and evaporated to yield an oil. Tlc showed no starting amine **6**, while infrared data indicated stong amide and ester bands. The oil was dissolved in 60 ml of tetrahydrofuran and added to a mixture of 3 g of $LiAlH_4$ in 50 ml of tetrahydrofuran. The mixture was heated at reflux for 20 hr. Water was added and the supernant was decanted from the precipitated salts and evaporated. The residue was crystallized from methanol–acetone to give 200 mg of crude crystals, mp 155–175°. Recrystallization from the same solvent gave 120 mg of **9**, mp 165–175. The nmr spectrum in DMSO was satisfactory. This material was not purified further but used as described below.

Methyl *N*,*N*-Dimethyl-α-thiolincosaminide (2) and Methyl *N*-Methyl-4,6-*O*,*N*-methylene-α-thiolincosaminide (4).—A solution of 10.8 g of methyl α-thiolincosaminide and 4.9 ml of formalin (37%) in 50 ml of water was maintained at room temperature for 30 min. The solution was lyophilized. The amorphous solid was dissolved in 150 ml of methanol and shaken under hydrogen over 1 g of 10% Pd/C for 18 hr. Two grams of catalyst was added and shaking continued for 18 hr. The catalyst was removed by filtration and the filtrate evaporated *in vacuo*. The residue was dissolved in water, the solution was clarified, and the filtrate was lyophilized. Chromatography over silica gel using chloroform–methanol, 4:1, for elution gave chiefly two oily fractions which crystallized on standing. These fractions were triturated with ethyl acetate to yield the following crops of crystals. The less polar fraction afforded 2.6 g (18.9%) of crystalline **2**, mp 173–179°; the more polar fraction, 1.15 g (82%) of **4**, mp 166–176°. Each fraction showed only one spot on tlc.

The dimethyl compound (**2**) was recrystallized twice from methanol to afford an analytical sample, mp 177–179°, $[\alpha]_D$ +270° (MeOH).

Anal. Calcd for $C_{11}H_{23}NO_5S$: C, 46.95; H, 8.34; N, 4.98. Found: C, 46.96; H, 8.37; N, 5.02.

The more polar fraction after recrystallization from methanol melted at 184–186° and gave $[\alpha]_D$ +254° (MeOH).

Anal. Calcd for $C_{11}H_{21}NO_5S$: C, 47.29; H, 7.58; N, 5.01. Found: C, 47.46; H, 7.91; N, 4.93.

Methyl *N*-Methyl-α-thiolincosaminide (8) by Hydrogenolysis of 9.—The crude crystals of **9** from above were dissolved in 25 ml of methanol and shaken under hydrogen over 200 mg of 10% Pd/C for 7 hr. The catalyst was removed by filtration and the filtrate evaporated. The residue was crystallized from methanol–acetone to give 40 mg of **8**, mp 179–184°, whose infrared spectrum was identical with that of a known sample of **8**.

Methyl 4,6:6,7-Di-*O*,*N*-methylene-α-thiolincosaminide (3).—A solution of 10 g of methyl α-thiolincosaminide in 50 ml of water and 5 ml of formalin was stirred for 10 min. The solution was lyophilized. Chromatography over silica gel (chloroform–methanol, 4:1) gave a 5-g fraction of glassy solid, $[\alpha]_D$ +239° (H_2O).

Anal. Calcd for $C_{11}H_{19}NO_5S$: C, 47.63; H, 6.90; N, 5.05. Found: C, 47.58; H, 6.98; N, 5.21.

Methyl *N*,*N*-Dimethyl-α-thiolincosaminide (2). A. From Methyl 4,6:6,7-Di-*O*,*N*-methylene-α-thiolincosaminide (3).—Methyl 4,6:6,7-di-*O*,*N*-methylene-α-thiolincosaminide (**3**) (500 mg) was shaken over 200 mg of 10% Pd/C for 17 hr under hydrogen pressure. Tlc indicated about equal amounts of dimethyl compound **2** and monomethyl compound **4**. Fresh Pd/C (200 mg) was added and the mixture again shaken for 20 hr. A final addition of 150 mg of PtO_2 was made and shaking continued for 4 hr longer. The catalyst was removed by filtration and the solvent distilled *in vacuo*. The residue was crystallized from methanol to yield 145 mg of **2**, mp 169–172°, identical by infrared absorption with a known sample of **2**.

B. From Methyl *N*-Methyl-4,6-*O*,*N*-methylene-α-thiolincosaminide (4).—**4** (200 mg) was hydrogenolyzed over 100 mg of 10% Pd/C in the manner described above. Evaporation of the solvent after filtration afforded a crystalline residue which when recrystallized from methanol yielded 50 mg of **4**, mp 170–173°. This product was identical by infrared data with known **4**.

Chlorination of Methyl *N*-Methyl-4,6-*O*,*N*-methylene-α-thiolincosaminide (4).—A solution of 0.75 g of **4** and 2.2 g of triphenylphosphine in 10 ml of acetonitrile and 9 ml of carbon tetrachloride was stirred at ambient temperature for 17 hr. Methanol (2 ml) was added and the solvents were evaporated. Chromatography over silica gel afforded 400 mg of oily chlorination product showing only one spot on tlc ($CHCl_3$–MeOH, 6:1). The nmr spectrum in $CDCl_3$ showed a three-proton doublet centered at δ 1.5 (3 H-8). The nmr spectrum of **4** possessed a three-proton doublet centered at δ 1.2 (3 H-8).

Registry No.—**2**, 22939-47-5; **3**, 27093-10-3; **4**, 27093-11-4; **5**, 22939-44-2; **6**, 22939-45-3; **7**, 27141-08-8; **8**, 22939-46-4; **9**, 27093-15-8.

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The Photochemical Acid Type II Reaction of Organic Esters[1a]

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The recent report by Nicholls and Leermakers[2] which established the occurrence of a type II photochemical elimination reaction in butyric and valeric acids, and the absence of such a reaction for butyramide, valeramide, and *N*,*N*-dimethylbutyramide prompts us to communicate our results concerning a closely related reaction. The reaction to which we refer is a type II elimination in the alkyl group of the acid portion of organic esters (acid type II reaction). The

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (b) National Science Foundation Undergraduate Research Participant, 1969.

(2) C. H. Nicholls and P. A. Leermakers, *J. Org. Chem.*, **35**, 2754 (1970).

TABLE I
COMPETITIVE TYPE II REACTIONS OF ORGANIC ESTERS

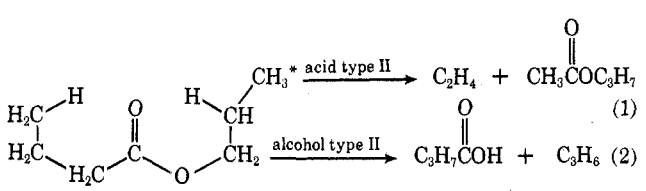
Ester	Acid type II: No.[b]	Acid type II: Type H	Acid type II: Olefin	Alcohol type II: No.	Alcohol type II: Type H	Alcohol type II: Olefin	Φ(acid type II)/[a] Φ(alcohol type II)
Isopropyl butyrate	3	1[c]	C_2H_4	6	1[c]	C_3H_6	0.129 ± 0.006
n-Propyl butyrate	3	1	C_2H_4	2	2[d]	C_3H_6	0.058 ± 0.002
Isobutyl butyrate	3	1	C_2H_4	1	3[e]	*i*-C_4H_8	0.022 ± 0.001
Ethyl valerate	2	2[d]	C_3H_6	3	1	C_2H_4	2.80 ± 0.12
n-Butyl valerate	2	2	C_3H_6	2	2	1-C_4H_8	0.200 ± 0.011
Isobutyl valerate	2	2	C_3H_6	1	3	*i*-C_4H_8	0.140 ± 0.008

[a] A minimum of three determinations for each value. [b] The number of γ-hydrogen atoms available. [c] Primary. [d] Secondary. [e] Tertiary.

type II elimination in the alkyl group of the alcohol portion of organic esters (alcohol type II reaction) is well established.[3] The acid type II reaction of organic esters was first postulated by Ausloos[4] in 1958 based upon the experimental observation that, in the gas-phase photolysis of methyl butyrate, the yield of ethylene, which is a major product, is only slightly reduced by the presence of molecular oxygen, while essentially all of the other hydrocarbon products disappear. Norrish, *et al.*,[5,6] later reached the same conclusion based upon a similar experimental observation. The experiments described here not only put the occurrence of the acid type II reaction of organic esters on a firmer basis but also provide additional insight into this reaction.

Results

When methyl butyrate vapor undergoes mercury ($^3P_1$) sensitized decomposition in the presence of 10% nitric oxide, the yields of ethylene and methyl acetate are identical within experimental error (±10%). In order to eliminate the analytical difficulties associated with the relative analysis of two substances of very different boiling points and polarities, we have examined the acid type II reaction relative to the alcohol type II reaction in esters which are capable of undergoing both reactions. This competition is shown in reactions 1 and 2 for *n*-propyl butyrate. In the absence of products originating from free radicals, the ratio of C_2H_4/C_3H_6 may be equated to the ratio of the quantum yield of reaction 1 relative to that of reaction 2. In the mercury sensitized photolysis of the esters shown in Table I, in the presence of nitric oxide and at conversions of 0.5%, saturated hydrocarbons and olefins, other than those expected from reactions 1 and 2, constitute less than 0.1% of the total yield of the expected olefins. The last column in Table I gives the ratio of the quantum yield for the acid type II reaction relative to that for the alcohol type II reaction for each of the six esters.



(3) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 435.
(4) P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958).
(5) P. Borrell and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **262**, 19 (1961).
(6) R. G. W. Norrish and R. P. Wayne, *ibid.*, **284**, 1 (1965).

Discussion

The observation of ethylene and methyl acetate in equivalent yields from the photolysis of propyl acetate substantiates the occurrence of the alcohol type II reaction. The data presented in Table I indicate that the alcohol type II reaction is the favored reaction. This is most clearly demonstrated by the ratio of 0.200 obtained for *n*-butyl valerate. In this ester both the number and type of γ hydrogens are the same for each reaction. The remainder of the data also support this conclusion. The only case in which the ratio observed is greater than 1 is that of ethyl valerate. In this particular ester a secondary hydrogen atom is transferred in the acid type II reaction while a primary hydrogen atom is transferred in the alcohol type II reaction. The data in Table I indicate that, although the number of γ-hydrogen atoms available for each reaction has a slight effect upon the competition, the major factor is the strength of the C–H bond which is broken. The importance of this factor in the alcohol type II reaction has been recognized previously by Ausloos, *et al.*,[7,8] who observed a primary isotope effect in the photolysis of ethyl acetate-d_4 and also a preferential transfer of a secondary rather than a primary hydrogen atom in the photolysis of *sec*-butyl acetate and formate. Similar effects have also been recognized by Ausloos, *et al.*,[9,10] and Nichol and Calvert[11] among others, in the type II reaction of ketones. These observations are perhaps not unexpected if one makes the reasonable assumption that C–H bond breaking is occurring in the transition state. This assumption is supported by the molecular orbital calculations of Boer, *et al.*,[12] who concluded that, although olefin formation is not important in the transition state, C–H bond breaking is occurring in the transition state.

The observation that the competition between the alcohol type II and the acid type II reactions of organic esters is dependent upon structural differences in the alkyl groups is, we believe, presumptive evidence that the same excited state is involved in both reactions. Therefore it appears that the relative quantum yields are related directly to the relative rate constants for the partitioning of that excited state between the alternate paths indicated by reactions 1 and 2. Since spin conservation normally holds for Hg($^3P_1$) sensitized

(7) P. Ausloos and R. E. Rebbert, *J. Phys. Chem.*, **67**, 163 (1963).
(8) R. P. Borkowski and P. Ausloos, *J. Amer. Chem. Soc.*, **83**, 1053 (1961).
(9) P. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961).
(10) P. Ausloos, *ibid.*, **65**, 1616 (1961).
(11) C. H. Nichol and J. G. Calvert, *J. Amer. Chem. Soc.*, **89**, 1790 (1967).
(12) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *ibid.*, **90**, 7239 (1968).

reactions, the excited state involved in the present system is most likely a triplet, presumably n–π^*.

Experimental Section

Each of the six esters used in this study was synthesized by the reaction of the appropriate acid chloride and alcohol. After being refluxed for 24 hr, the reaction mixture was distilled through a Vigreux column. After a number (usually three to four) of careful distillations in which only the middle half of the distillate was taken, no impurities were observed by gas chromatography using both diisodecyl phthalate and Hallcomid columns.

Mercury sensitized photolyses were conducted in a cylindrical quartz cell containing a drop of mercury. The light source was a Hanovia 87A-45 low-pressure mercury vapor lamp. Since the envelope of this lamp is Vycor, the radiation is pure 253.7 nm and contains none of the 184.9-nm mercury line. The reaction is entirely mercury sensitized since the long wavelength cutoff of absorption by aliphatic esters is 240 nm. The pressure of the esters was generally 2–5 Torr and nitric oxide was added to remove products of free-radical reactions. The data given in Table I were determined at conversions of 0.5% in the presence of 10% nitric oxide.

Hydrocarbon products were analyzed using a 30 ft long, 0.25 in. o.d. column packed with 20% squalane on 60–80 mesh Chromosorb P, operated at ambient temperature and a helium flow of 70 ml/min. Methyl acetate was analyzed using a 10 ft long 0.25 in. o.d. column packed with 10% diisodecyl phthalate on 60–80 mesh Chromosorb P, operated at 80° and a helium flow of 30 ml/min.

Registry No.—Isopropyl butyrate, 638-11-9; *n*-propyl butyrate, 105-66-8; isobutyl butyrate, 539-90-2; ethyl valerate, 539-82-2; *n*-butyl valerate, 591-68-4; isobutyl valerate, 10588-10-0.

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The Preparation and Certain Reactions of 3-Formyl-4*H*-flavene

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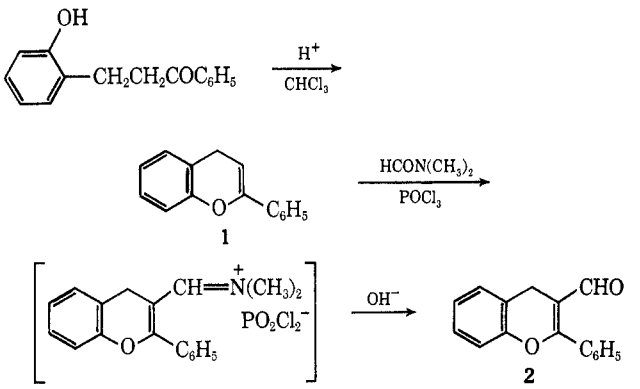
Recently we described[1] a convenient method for the preparation of 4*H*-flavene (2-phenyl-4*H*-1-benzopyran) (**1**). The present paper describes the formylation of **1** to give 3-formyl-4*H*-flavene (**2**) and the reaction of **2** with some active methyl compounds.

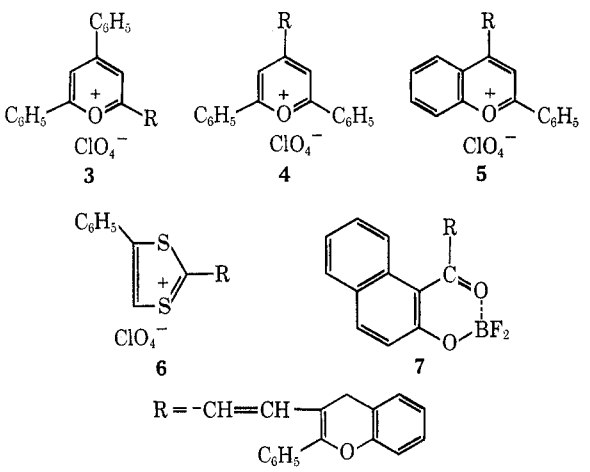
The Vilsmeier reagent reacts with **1** to give an intermediate iminium salt (not characterized) which was hydrolyzed to give **2**, as shown in Scheme I. It is interesting that the aldehyde **2** is stable, in contrast to **1**, which is quite unstable and decomposes to a tar in several hours. We have found that it is not necessary to isolate **1** but, instead, to treat the chloroform reaction mixture containing **1** directly with the Vilsmeier reagent.

The aldehyde **2** was allowed to react with some charged heterocyclic compounds which contained active methyl groups to give the compounds listed in Scheme II. Only compounds which contain very reactive methyl groups react with **2**. No reaction took place between **2** and 1-ethyl-2-methylquinolinium perchlorate or 1,2-dimethylnaphtho[1,2-*d*]thiazolium perchlorate under the conditions employed for the preparation of the compounds in Scheme II.

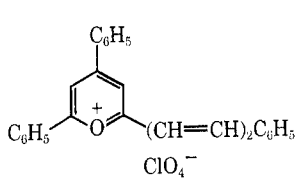
Scheme I



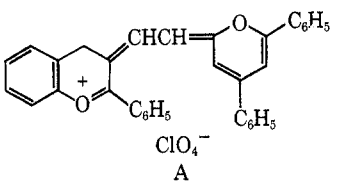
Scheme II



The dyes listed in Scheme II show absorption at longer wavelengths than the corresponding simple styryl dyes. For example, in acetonitrile solution, 2,4-diphenyl-6-(4-phenyl-1,3-butadienyl)pyrylium perchlorate[2] (**8**) shows absorption at λ_{max} 490 mμ (ϵ 30,200)



while **3** shows λ_{max} 539 mμ (ϵ 28,900). It is evident that the oxygen atom of the flavene nucleus has affected the absorption of **3**, and therefore canonical forms such as A must be considered. However, comparison of the



(1) J. A. VanAllan, G. A. Reynolds, and T. H. Regan, *J. Org. Chem.*, **32**, 1897 (1967).

(2) R. Wizinger and K. Wagner, *Helv. Chim. Acta*, **34**, 2290 (1951).