solution were allowed to stand in a well-stoppered flask. In a few days the contents of the flask had become a solid mass of beautiful needles. On filtering and washing with anhydrous ether, the addition product was obtained in almost quantitative yield as white needles, m. p. 71–73°. Due to its tendency to dissociate, the substance was difficult to recrystallize. Satisfactory results were obtained, however, by dissolving in cold chloroform, adding petroleum ether, and allowing to stand in the ice-box, when long fine needles gradually separated, m. p. 73–74°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.2; H, 5.18. Found: C, 71.2; H, 5.3.

If this substance was dissolved in warm ligroin (b. p. 70–90°) and the resulting solution allowed to stand in the icebox, needles separated, which proved to be maleic anhydride, m. p. 57–59°, mixed m. p. 57–59°; orange color on heating with dimethyl- or diethylaniline.

Bromohydroxy Derivative (VIII, R = H).—The addition product (1.0 g.) was dissolved in excess sodium carbonate and the basic solution was exactly neutralized. This solution was shaken vigorously with a slight excess of bromine. Recation took place immediately with the quantitative precipitation of the bromohydroxy acid. After recrystallization from boiling water (Norit) the acid melted at 142–143°, with decomposition.

Anal. Calcd. for $C_{16}H_{15}O_5Br$: C, 52.4; H, 4.18. Found: C, 52.1; H, 4.4.

3-[β-(*m*-Methoxyphenyl)-ethyl]-3,6-endoxo-Δ^4-tetrahydro-*o*-phthalic Anhydride (VII, R = OCH_3) crystallized quantitatively in beautiful transparent rosets when 31.6 g. of 2-[β-(*m*-methoxyphenyl)-ethyl]-furan and 15.3 g. of pure maleic anhydride were dissolved in the least amount of anhydrous ether necessary for complete solution and allowed to stand for three days. After washing with anhydrous ether, drying and crystallizing by the chloroform–petroleum ether procedure, long, transparent needles were obtained, m. p. 78–80°.

Like the unsubstituted addition product, this methoxy derivative gave maleic anhydride on heating in ligroin, gave no color with dimethylaniline until heated, and was unstable to cold dilute alkaline permanganate.

Anal. Calcd. for $C_{17}H_{16}O_5$: C, 68.0; H, 5.33. Found: C, 68.0; H, 5.4.

Hydrogenation Experiments.—If 1 g. of 3-(β-phenylethyl)-3,6-endoxo-Δ^4-tetrahydro-*o*-phthalic anhydride dissolved in 30 cc. of glacial acetic acid was shaken with 0.2 g. platinum (palladium) oxide under 3 atmospheres of hydrogen for fifteen hours, succinic acid was obtained after washing the residue from the acetic acid (removed *in vacuo*) with dry benzene; m. p. 186–187°, mixed m. p. 185–187°.

All attempts to isolate other crystalline products from the reaction, or from numerous runs made in ethyl acetate or inert solvents, failed.

Summary

The synthesis of 2-(β-phenylethyl)-furan and 2-[β-(*m*-methoxyphenyl)-ethyl]-furan has been accomplished.

The Diels–Alder reaction has been applied with success to these substances.

CAMBRIDGE, MASS. RECEIVED MARCH 11, 1940

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. VI. The Preparation of Ketene Acetals from α-Bromo-orthoesters[1]

BY PHILIP M. WALTERS AND S. M. McELVAIN

The procedure which has been used in this Laboratory for the preparation of ketene acetals involves the removal of the elements of halogen acid from a halogenated acetal by means of potassium *t*-butoxide

$$XCH_2CH(OEt)_2 + KOC_4H_9(t) \longrightarrow CH_2{=}C(OEt)_2 + KX + t\text{-}C_4H_9OH$$

By this reaction ketene diethylacetal and various halogenated derivatives of it have been prepared.[2] It is obvious that attempts to apply this procedure to the acetals of the higher α-halogenoaldehydes, $R_2CHCHXCH(OEt)_2$, might be unsuccessful due to the preferential loss of halogen acid from the α- and β-carbon atoms with the resultant formation of the acetals of the unsaturated aldehydes.[3]

Another route to the ketene acetal structure that was partially explored when the problem first was undertaken is the elimination of the elements of ethyl hypohalite, EtOX, from an α-halogeno-orthoacetic ester in a manner similar to that used by Boord and co-workers[4] to prepare olefins. A

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[1] Paper V of this series is Barnes, Kundiger and McElvain, THIS JOURNAL, **62**, 1281 (1940).

[2] Beyerstedt and McElvain, *ibid.*, **58**, 529 (1936); **59**, 2266 (1937); Magnani and McElvain, *ibid.*, **60**, 2210 (1938).

[3] In the cases of the acetals of the α-halogeno-propionaldehyde, -butyraldehyde and -isobutyraldehyde the larger numbers of hydrogens on the β-carbon atoms makes the α,β-loss of halogen acid much more probable than that between the α-carbon and the aldehyde carbon atom. However in the case of the acetal of α-halogeno-isovaleraldehyde, $(CH_3)_2CHCHXCH(OEt)_2$, in which there is only one hydrogen on the β-carbon atom it seems that there should be some chance of loss of halogen acid from the α-carbon and the aldehyde carbon atom. But Jones (B.S. Thesis, University of Wisconsin, 1939), working along this line found that each of the above acetals (X is Br) gave the corresponding unsaturated acetal, through an α,β-loss of hydrogen bromide, when treated with potassium *t*-butoxide in *t*-butyl alcohol.

[4] Boord, *et al.*, THIS JOURNAL, **52**, 3396 (1930); **53**, 1505 (1931) **54**, 751 (1932); **55**, 3293, 4930 (1933).

study of the reaction of the various ethyl orthohalogenoacetates with both zinc and magnesium showed that the loss of EtOX was not intramolecular to form ketene acetal, but instead was poly-intermolecular to form non-volatile condensation products of high molecular weight.[5]

Wislicenus[6] reported the removal of the elements of ethyl hypochlorite from chloro-acetal by means of sodium to form vinyl ethyl ether according to the following reaction:

$$\mathrm{ClCH_2CH(OEt)_2 + 2Na \longrightarrow CH_2{=}CHOEt + NaCl + NaOEt}$$

The yield of the ether obtained was not reported by Wislicenus, but Lunsted[7] in this Laboratory has studied the reaction, using the bromo- instead of the chloro-acetal, and has found that vinyl ethyl ether is produced in yields of 75% of the theoretical.

Because of the success of this reaction with bromoacetal it seemed worth while to apply it to the preparation of ketene acetals from the α-bromo-orthoesters. It has proved to be most satisfactory for this purpose and the present paper reports the preparation of ketene diethylacetal and methylketene diethylacetal from ethyl orthobromoacetate and ethyl ortho-α-bromopropionate. Each of these bromo-orthoesters reacts smoothly with two equivalents of sodium to give the corresponding ketene acetal according to the following reaction:

$$\mathrm{RCHBrC(OEt)_3 + 2Na \longrightarrow RCH{=}C(OEt)_2 + NaBr + NaOEt}$$

Ketene acetal (R is H) and methylketene acetal (R is CH_3) were obtained from the above reaction in yields of 66 and 80% of the theoretical, respectively. Methylketene diethyl acetal boils at 133–134°[8] and shows no tendency to rearrange into the isomeric acrolein diethyl acetal, $CH_2{=}CHCH(OEt)_2$ (b. p. 123–124°). It reacts vigorously, with the evolution of heat, with both water and alcohol at room temperature and yields the corresponding esters, ethyl propionate and ethyl orthopropionate.

It seems that this method should be of general applicability. The elements, EtOBr, which are eliminated from the orthoester can only come from the carbon atoms that are to carry the double bond of the ketene acetal, and since it appears from the behavior of methylketene acetal that there is no rearrangement of the ketene acetal into an unsaturated aldehyde acetal, the reaction should be applicable to the preparation of any of the higher homologs of ketene acetal.

Experimental

Ketene Diethylacetal from Ethyl Orthobromoacetate.—To a stirred mixture of 9.2 g. (0.4 atom) of powdered sodium and 200 ml. of anhydrous benzene heated under gentle reflux was added dropwise 48.2 g. (0.2 mole) of ethyl orthobromoacetate[5] over a period of forty minutes. After the first few ml. of the bromo-ester had been added, the reaction mixture turned a characteristic deep blue in color. The reaction mixture was stirred for an additional two hours with continued refluxing. The clear supernatant liquid was then decanted from the precipitated blue salts, and the salts thoroughly washed by several triturations with anhydrous benzene. These washings were combined with the filtrate, and the benzene removed under atmospheric pressure with the heating bath temperature not exceeding 120°. The remaining material was distilled under diminished pressure (100 mm.). The yield of ketene diethylacetal was 15.4 g. (66%), b. p. 68° (100 mm.); n^{25}_{D} 1.4110; d^{25}_{25} 0.877.

Ethyl Orthopropionate.—This ester was prepared in yields of 48% of the theoretical from propioniminoethyl ether hydrochloride, m. p. 92°, by the procedure of Sah.[9] It was found advantageous to carry out the distillation of the reaction mixture under diminished pressure sufficient to keep its temperature below 85°. The ethyl orthopropionate obtained boiled at 44° (9 mm.); n^{25}_{D} 1.4000.

Ethyl Orthobromopropionate.—This ester was prepared by the procedure used for the preparation of ethyl orthobromoacetate.[5] The yields amounted to 67% of the theoretical. The product boiled at 73° (8 mm.); n^{25}_{D} 1.4338; d^{25}_{25} 1.181.

Anal. Calcd. for $C_9H_{19}O_3Br$: C_2H_5O, 52.95. Found: C_2H_5O, 53.05.

Methylketene Diethylacetal.—This acetal was prepared from ethyl ortho-α-bromopropionate and sodium in yields of 80% of the theoretical by the same procedure as that given above for the preparation of the lower homolog, ketene diethylacetal. The product obtained boiled at 133–134° or 77–78° (100 mm.); n^{25}_{D} 1.4083; d^{25}_{25} 0.8654.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.61; H, 10.72; C_2H_5O, 69.23. Found: C, 64.48; H, 10.57; C_2H_5O, 68.50.

A 3-g. sample of methylketene diethylacetal was treated with the theoretical amount of water, and the reaction catalyzed with a trace of concentrated hydrochloric acid. The reaction mixture underwent almost spontaneous reaction and the temperature rose rapidly to 80–85°. The reaction mixture then was dried over anhydrous calcium chloride, and distilled under atmospheric pressure. The ethyl propionate so obtained boiled at 98–100°; n^{25}_{D}

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(5) Beyerstedt and McElvain, THIS JOURNAL, **59**, 1273 (1937).

(6) Wislicenus, *Ann.*, **192**, 106 (1879).

(7) Lunsted, M.S. Thesis, University of Wisconsin, 1940.

(8) Scheibler, Marhenkel and Nikolic, *Ann.*, **458**, 21 (1927), reported the formation of this acetal in 7% yield from the reaction of sodium ethoxide on ethyl propionate. They list the following physical properties, b. p. 78–81°; d^{18}_{4} 0.8002; n^{18}_{D} 1.36732 (*cf.* other properties given in the experimental part of this paper).

(9) Sah, THIS JOURNAL, **50**, 516 (1928).

1.3810; sap. equiv., 103 (calcd. 102); m. p. of the *p*-toluidide of the acid, 122–124°. When this experiment was repeated using absolute alcohol instead of water a decided evolution of heat was noticed and resulting ethyl orthopropionate boiled at 157–158° (752 mm.); $n^{25}\mathrm{D}$ 1.4000. The yields of ester in each of these cases were practically quantitative.

Summary

Ketene diethylacetal and methylketene diethylacetal have been prepared in excellent yields by the action of sodium on the corresponding α-bromo-orthoesters. This method appears to be of general applicability for the higher homologs of ketene acetal. The properties of methylketene diethylacetal are described for the first time.

MADISON, WISCONSIN RECEIVED APRIL 4, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Osage Orange Pigments. IV. Degree of Unsaturation and Flavone Nature[1]

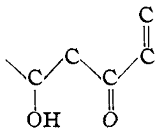
BY M. L. WOLFROM, P. W. MORGAN AND F. L. BENTON

The publication of the determination of the degree of unsaturation of osajin and pomiferin, the two pigments of the fruit of the osage orange (*Maclura pomifera* Raf.), has been withheld until enough data were obtained to warrant a satisfactory explanation. We believe that this can now be done.

Osajin could be hydrogenated catalytically at atmospheric pressure with platinum in a stepwise fashion. One double bond hydrogenated with great ease to yield dihydro-osajin. The second double bond also hydrogenated readily, although more slowly than the first, to yield tetrahydro-osajin. At this point further hydrogenation proceeded very slowly but a hexahydro-osajin was obtained. All of these hydrogenated derivatives showed the presence of the one easily acetylatable and of the one difficultly acetylatable hydroxyl group of the original osajin, a monoacetate and a diacetate of each hydrocompound being obtained. Hydrogenation thus produced no new hydroxyl groups and it was determined also that no carboxyl groups were formed. Similar results were obtained with pomiferin, except that the hexahydropomiferin has not yet been isolated. A diacetate and a triacetate of both dihydropomiferin and tetrahydropomiferin were obtained, this behavior on acetylation being identical with that of pomiferin. No carboxyl groups were produced.

Table I shows the results of the application of the perbenzoic acid titration procedure to the determination of the degree of unsaturation of the two pigments and of their reduction products. Osajin and pomiferin were found to undergo extensive general oxidation with perbenzoic acid, but when protected by acetylation, this effect was minimized, although not eliminated. If we consider the relatively low values given by the tetrahydro derivatives as a subtractable blank, it is seen that the data indicate the presence of two active double bonds in both osajin and pomiferin. The data indicate also that the third unsaturation, as represented by hexahydro-osajin, is of a different type and is not a simple aliphatic double bond. A negative Diels–Alder test with maleic anhydride denoted that the two active double bonds are not conjugated.

The nature of the unsaturation of this third double bond of osajin was therefore a presented problem. It was found that hexahydro-osajin gave a negative result with the boric acid test described by Wilson.[2] On the other hand, Table II shows that osajin and pomiferin and their dihydro and tetrahydro derivatives gave a positive color reaction. According to Wilson, flavanones give no color reaction with boric acid, and the grouping shown below is among those that do give a positive color reaction, the α,β-unsaturated carbonyl and a suitable *peri* auxochromic group, as the hydroxyl, being essential.



A phenolic group *peri* to a carbonyl group in osajin and pomiferin would be in harmony with the known fact of the presence of one hydroxyl group that is difficultly methylatable. This type of phenolic group is also frequently quite acidic and

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(1) Previous publications in this series: (a) THIS JOURNAL, **60**, 574 (1938); (b) **61**, 2832 (1939); (c) **62**, 651 (1940).

(2) C. W. Wilson, *ibid.*, **61**, 2303 (1939).