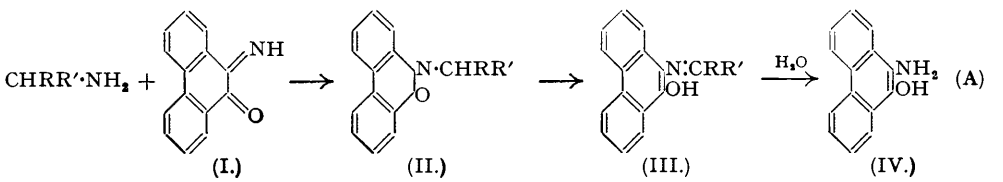
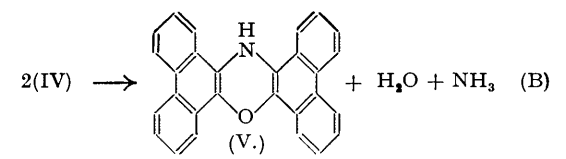
NOTES.

A Test for the Group $>CH\cdot NH_2$. By ALEXANDER SCHÖNBERG and WILLIAM IBRAHIM AWAD.

THIS characteristic and sensitive test is based on the fact that when a compound (or its salts) containing the group $>CH\cdot NH_2$ is warmed in aqueous alcohol, in the presence of ammonium chloride, with phenanthraquinoneimine (I) (Anschütz and Schultz, *Annalen*, 1879, **196**, 51), " phenanthroxazine " (tetrabenzophenoxazine) (V) separates; it is practically insoluble in low-boiling organic solvents and in water, but can be recrystallised from nitrobenzene. This compound, which forms characteristic crystals, gives a deep indigo-blue non-fugitive colour with concentrated sulphuric acid. The colour can be detected in a concentration of 1 mg. in 300 c.c. of concentrated sulphuric acid (thickness of layer, 1 cm.). The test can therefore be carried out as a micro-test.

The reaction sequence (A) and (B) is proposed for the formation of phenanthroxazine (R and R′ are alkyl or aryl groups or hydrogen); (A) is based on the observations of Schönberg, Moubacher, and Mostafa (*J.*, 1948, 176) who worked with phenanthraquinone, and (B) has been discussed by Schönberg and Awad (*J.*, 1947, 625).



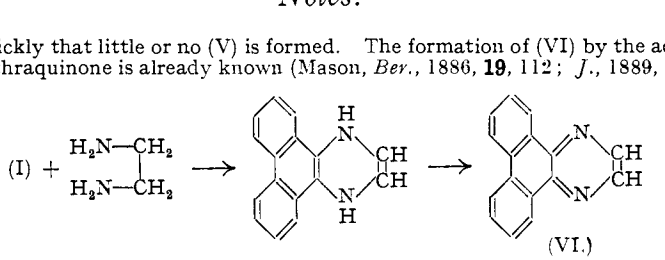


It is obvious from the above scheme that the presence of the aliphatic hydrogen atom (as in II) is essential and that it is derived from the group $>CH\cdot NH_2$. Substances not containing this group, listed below, do not show the reaction.

There is a great difference between the test now described and that with " ninhydrin " (triketoindane hydrate). The latter reagent gives a violet colour not only with substances containing the group $>CH\cdot NH_2$, but also with ammonia, potassium cyanide, and an alcoholic solution of aniline even in the cold (compare Ruhemann, *J.*, 1910, **97**, 1438, 2025).

A great variety of substances (listed below) containing the group $>CH\cdot NH_2$ give the test, and ethylenediamine is the only exception to the generalisation: the formation of " phenanthrapiazine "

(VI) proceeds so quickly that little or no (V) is formed. The formation of (VI) by the action of ethylenediamine on phenanthraquinone is already known (Mason, *Ber.*, 1886, **19**, 112; *J.*, 1889, **55**, 98).



(VI.)

We have found that a sample of technical diethanolamine contains, as impurity, traces of a substance containing the group $>CH\cdot NH_2$: it would be very difficult to prove the presence of such an impurity by any other method.

Substances that do not give a positive test. Urea, ethylenediamine, trimethylamine hydrochloride, dimethylglyoxime, DL-amino*iso*butyric acid, diethylamine hydrochloride, diethanolamine, uric acid, pyridine, aniline hydrochloride, phenylhydrazine hydrochloride, triethylamine hydrochloride, benzamide, toluene-*p*-sulphonamide, *o*-carboxyphenylglycine, ephedrine hydrochloride (as VII), azobenzene.

Compounds that give a positive test. Methylamine hydrochloride, glycine, ethylamine hydrochloride, DL-alanine, cysteine, *n*-propylamine hydrochloride, 1 : 3-diaminopropane and its dihydrochloride, aspartic acid, DL-threonine (VIII), *n*-butylamine, *iso*butylamine, *sec.*-butylamine, putrescine dihydrochloride, histamine acid phosphate, D-glutamic acid, DL-valine, cadaverine dihydrochloride, L-histidine hydrochloride, cystine, *cyclo*hexylamine, leucine (synthetic), DL-*iso*leucine, DL-norleucine, glucosamine, L(+)-lysine monohydrochloride, L(+)-arginine monohydrochloride, benzylamine hydrochloride, *n*-octylamine, β-phenylalanine, L(−)-tyrosine, glutathione (IX), spermine tetrahydrochloride (X), DL-tryptophan, thyroxine sodium, insulin.

(VII.) $CHPh(OH)\cdot CHMe\cdot NHMe$ $CHMe(OH)\cdot CH(NH_2)\cdot CO_2H$ (VIII.)

$CO_2H\cdot CH_2\cdot NH\cdot CO\cdot CH(CH_2\cdot SH)\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$ (IX.)

$NH_2\cdot[CH_2]_3\cdot NH\cdot[CH_2]_4\cdot NH\cdot[CH_2]_3\cdot NH_2,4HCl$ (X.)

Experimental.—Experiments with reacting substances. These may be illustrated by the following example: Glycine (0·2 g.), phenanthraquinoneimine (0·2 g.), ammonium chloride (0·2 g.), alcohol (96%; 10 c.c.), and water (5 c.c.) were heated under reflux for 15 minutes, filtered while hot, and the residue washed with hot alcohol and then with hot water. The red-brown residue gave an intense indigo-blue colour with concentrated sulphuric acid and on crystallisation from nitrobenzene the characteristic crystals of "phenanthroxazine" (V) were obtained; m. p. >310° (Found: C, 87·3; H, 4·2; N, 3·4. Calc. for $C_{28}H_{17}ON$: C, 87·7; H, 4·4; N, 3·7%). With some substances (*e.g.*, ethylamine hydrochloride and insulin), the presence of ammonium chloride is not necessary.

Action of phenanthraquinoneimine on ethylenediamine hydrochloride. Under the same conditions as above, these compounds afforded a filtrate and a residue which was completely soluble in hot alcohol. The filtrate on cooling gave crystals which, recrystallised from alcohol, had m. p. 180° undepressed on admixture with phenanthrapiazine (Mason, *loc. cit.*). The substance dissolves with a brown colour in concentrated sulphuric acid.

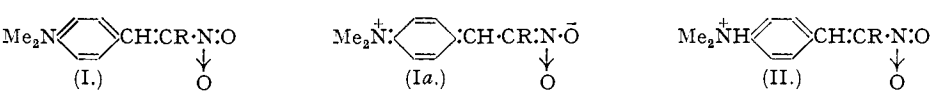
Action of phenylhydrazine hydrochloride on phenanthraquinoneimine. The standard conditions again being used, but with addition of hot alcohol (20 c.c.) before filtration, both the residue and the red crystalline product which separated out from the cold filtrate proved to be phenanthraquinone phenylhydrazone, m. p. and mixed m. p. 165° (Zincke, *Ber.*, 1883, **16**, 1563).

The authors are indebted to Hoffmann La Roche Co. (Basle) for the gift of putrescine dihydrochloride, cadaverine dihydrochloride, and spermine tetrahydrochloride.—FOUAD I UNIVERSITY, CAIRO. [*Received, May 20th*, 1948.]

The Condensation of p-*Dimethylaminobenzaldehyde with Nitroparaffins.* By DAVID J. DRAIN and WALTER WILSON.

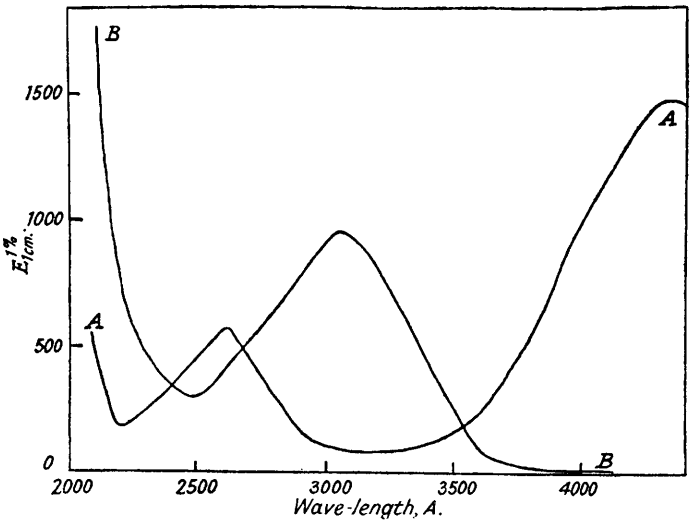
THE facile reaction by which ω-nitrostyrenes are produced from aromatic aldehydes and nitroparaffins, usually in the presence of a primary aliphatic amine catalyst (Knoevenagel and Walter, *Ber.*, 1904, **37**, 4502; Worrall, *J. Amer. Chem. Soc.*, 1934, **56**, 1556; Hass and Riley, *Chem. Reviews*, 1943, **32** 373), has not hitherto been applied to *p*-dimethylaminobenzaldehyde. Under the conditions mentioned, this aldehyde and nitromethane afforded a red crystalline *nitroethylene* (I; R = H) in high yield. A similar *nitropropylene* (I; R = Me) was obtained in lower yield from nitroethane, and although 1-nitropropane soon gave a red solution, no crystalline product could be isolated.

The two nitrostyrenes were intensely red compounds, soluble in hot nitromethane or glacial acetic acid, but very sparingly soluble in most organic solvents. The almost colourless solutions in concentrated (>4N) hydrochloric acid gave precipitates of the red bases on dilution with water.



Solutions of both compounds in 5N-hydrochloric acid and alcoholic solutions of ω-nitrostyrene (Braude, Jones, and Rose, *J.*, 1947, 1104) had similar ultraviolet absorptions. On the other hand,

alcoholic solutions of the two bases exhibited an entirely different type of absorption (see the two nitroethylene curves). These results are attributed to the existence of the ammonium ion (II), which is a true ω-nitrostyrene, in the acid solutions, whereas in neutral solutions the compounds probably exist in a resonance hybrid form related to the quinone (I*a*), derived from (I) by an electron transfer through the conjugated system.



1-*Nitro*-2-(4′-*dimethylaminophenyl*)*ethylene*. *Light absorption in* (A) *alcohol*, (B) 5N-HCl.

The absorption curves of the two compounds were very similar, the only notable difference being the lower intensity of the 4200 A. peak in alcoholic solutions of the nitropropylene. The reason for this difference was not established; possibly one compound has a *cis*- and the other a *trans*-configuration (cf. Stewart and Clark, *Canadian J. Res.*, 1948, **26**, *B*, 7).

Light-absorption data.

	In ethanol.		In 5N-HCl.	
	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{max.}$, A.	$\epsilon_{max.}$
$Me_2N{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}NO_2$	2620	10,250	3050—3080	18,500
	4350	28,500		
$Me_2N{\cdot}C_6H_4{\cdot}CH{:}CMe{\cdot}NO_2$	2640	10,500	3020—3080	13,100
	4200	15,900		
$C_6H_5{\cdot}CH{:}CH{\cdot}NO_2$ (in alcohol) *	—	—	2270	9,500
			3090	16,500
$C_6H_5{\cdot}CH{:}CMe{\cdot}NO_2$ (in alcohol) *	—	—	2260	10,300
			3050	12,400

* Braude, Jones, and Rose, *loc. cit.*

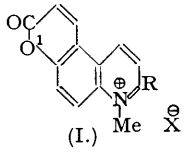
1-*Nitro*-2-(4′-*dimethylaminophenyl*)*ethylene* (I; R = H).—A mixture of nitromethane (4 g.), *p*-dimethylaminobenzaldehye (10 g.), 22% aqueous methylamine (1 c.c.), and methanol (20 c.c.) was kept at room temperature for 5 days. The red crystals (11·7 g.; 91%) were filtered off and recrystallised from nitromethane. The *nitroethylene* formed intense red glistening flakes, m. p. 181° (Found: N, 14·4. $C_{10}H_{12}O_2N_2$ requires N, 14·6%).

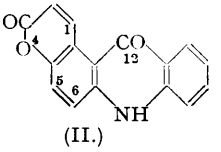
2-*Nitro*-1-(4′-*dimethylaminophenyl*)*propylene* (I; R = CH_3).—(*a*) Nitroethane (7·5 g.), *p*-dimethylaminobenzaldehyde (14·9 g.), 22% aqueous methylamine (1 c.c.), and methanol (20 c.c.) as above gave only 1·9 g. of crude product, m. p. 117—119°. The *nitropropylene* crystallised from benzene–petroleum in small red needles, m. p. 123—124° (Found: N, 13·7. $C_{11}H_{14}O_2N_2$ requires N, 13·6%). The compound was more soluble than the nitroethylene in benzene. (*b*) *n*-Butylamine (2 c.c.) was used as a catalyst in place of methylamine in an experiment similar to (*a*). After 4½ hours' boiling under reflux, the product (m. p. 117—119°) weighed 6·1 g. (30% yield). The mother-liquors contained much unchanged aldehyde.

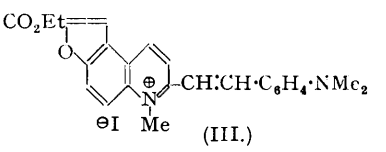
The authors are indebted to Mr. J. R. Rowlands, Head of the Science Department of this College, for facilities and encouragement, and to Dr. W. F. Elvidge and Mr. L. Brealy, of Boots Pure Drug Co. Ltd., for the light-absorption measurements.—Nottingham and District Technical College. [*Received*, *June 10th*, 1948.]

Some Derivatives of 2-Keto-1 : 2-dihydro-1-oxa-8-azaphenanthrene. By V. PETROW and E. L. REWALD.

SOME derivatives of 2-keto-1 : 2-dihydro-1-oxa-8-azaphenanthrene and of 3-oxa-6-aza-α-naphthindene were prepared following the observation by Dr. R. Wien (Biological Division, May and Baker Ltd., on behalf of the Therapeutic Research Corporation of Great Britain, Ltd.) that *2-keto-7-p-dimethylaminostyryl-1 : 2-dihydro-1-oxa-8-azaphenanthrene methoacetate* (I; R = $Me_2N{\cdot}C_6H_4{\cdot}CH{:}CH$; X = OAc) showed slight trypanocidal activity.


(I.)


(II.)


(III.)

Experimental. [M. p.s are corrected. Microanalyses are by Drs. Weiler and Strauss, Oxford. M. p.s and yields quoted by Dey and Goswami (*J.*, 1919, **115**, 536) are given in square brackets].—*2-Keto-1 : 2-dihydro-1-oxa-8-azaphenanthrene.* The following improved method was used: 6-Aminocoumarin (20 g.), arsenic pentoxide (22 g.), dry glycerol (46 g.), and concentrated sulphuric acid (25 g.) were carefully warmed to 175°, whereupon reaction occurred. After the temperature had been slowly raised to 220°, the mixture was heated for 3 hours at 180° (total time, 5 hours). The black product was poured into water (600 ml.), and the tarry residues extracted with hot water (total 500 ml.). The base, precipitated from the combined filtrates with sodium hydroxide, formed ivory needles (57%) from aqueous alcohol, m. p. 235—236° [232°; 36%], converted into the tetrahydro-derivative (52%), m. p. 148·5° [142°]. The methiodide, m. p. 263° (decomp.) [246°], was converted into *2-keto-1 : 2-dihydro-1-oxa-8-azaphenanthrene methochloride* (I; R = H, X = Cl), fine white needles from absolute alcohol, m. p. 267° (decomp.) (Found: Cl, 14·6. $C_{13}H_{10}O_2NCl$ requires Cl, 14·4%).

2-Keto-7-p-dimethylaminostyryl-1 : 2-dihydro-1-oxa-8-azaphenanthrene. An intimate mixture of 2-keto-7-methyl-1 : 2-dihydro-1-oxa-8-azaphenanthrene (2·0 g.) (Dey, Sarkar, and Seshadri, *J. Indian Chem. Soc.*, 1926, **3**, 187), *p*-dimethylaminobenzaldehyde (2·0 g.), and a little powdered anhydrous zinc chloride was heated at 170° for 35 minutes. The *product*, isolated from the powdered melt with spirit, separated from amyl alcohol in a felted mass of orange needles, m. p. 262—263° (Found: C, 76·7; H, 5·4; N, 8·6. $C_{22}H_{18}O_2N_2$ requires C, 77·2; H, 5·3; N, 8·2%).

2-Keto-7-methyl-1 : 2-dihydro-1-oxa-8-azaphenanthrene methochloride (I; R = Me, X = Cl), needles from alcohol–ether, m. p. 258° (decomp.) (Found: Cl, 13·0. $C_{14}H_{12}O_2NCl$ requires Cl, 13·6%), was prepared from the corresponding methiodide, m. p. 248° (decomp.) (Found: I, 36·0. Calc. for $C_{14}H_{12}O_2NI$: I, 36·0%) (Dey, Sarkar, and Seshadri, *loc. cit.*, give m. p. 245°).

2-Keto-7-p-dimethylaminostyryl-1-oxa-8-azaphenanthrene methiodide (I; R = $Me_2N{\cdot}C_6H_4{\cdot}CH{:}CH$, X = I). Finely powdered (I; R = Me, X = I) (2·5 g.) was suspended in acetic anhydride (250 ml.), and *p*-dimethylaminobenzaldehyde (1·5 g.) added to the rapidly boiling solution. Heating was continued for 30 minutes. After standing overnight, the *product* (93%) was collected and crystallised from a large volume of boiling spirit, from which it separated in nearly black needles having a dark green reflex, m. p. 265—266° (decomp.) (Found: N, 5·8; I, 26·0. $C_{23}H_{21}O_2N_2I$ requires N, 5·8; I, 26·2%). The *methochloride* separated from methyl alcohol in scarlet needles having a deep green reflex, m. p. 269—270° (decomp.) (Found: Cl, 9·0. $C_{23}H_{21}O_2N_2Cl$ requires Cl, 9·0%). The *methoacetate* separated from absolute alcohol in nearly black needles having a deep green reflex, m. p. 155—156° (decomp.) (Found: N, 6·3. $C_{25}H_{24}O_4N_2$ requires N, 6·7%).

p-*Dimethylaminoanil* (I; R = $Me_2N{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}$; X = Cl) *from 2-keto-7-formyl-1-oxa-8-azaphenanthrene methochloride.* (I; R = Me, X = I) (3·5 g.), dissolved in alcohol (60 ml.) and water (15 ml.), was treated with *p*-nitrosodimethylaniline (1·8 g.), and piperidine (1 ml.) added to the warm solution. After 5 minutes' heating under reflux, the product (2·8 g.; m. p. 230—231°) was collected, and, as it proved to be extremely insoluble in the usual solvents, converted directly into the *methochloride*, black needles having a green reflex from methyl alcohol, m. p. 234—235° (Found: N, 9·6; Cl, 7·7, $C_{22}H_{20}O_2N_3Cl$,MeOH requires N, 9·9; Cl, 8·7%). The compound underwent fairly rapid decomposition when heated in alcoholic solution.

2-Keto-7-p-acetamidostyryl-8-methyl-1-oxa-8-azaphenanthrene methosulphate (I; R = $NHAc{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}$, X = $MeSO_4$), prepared by heating (I; R = Me, X = $MeSO_4$) (2 g.), *p*-acetamidobenzaldehyde (1·1 g.), alcohol (25 ml.), water (3 ml.), and 3 drops of piperidine under reflux for 1 hour, separated (yield 90%) in very sparingly soluble yellow crystals, m. p. 308° (decomp.) (Found: S, 6·5. $C_{24}H_{22}O_7N_2S$ requires S, 6·6%).

N-(6-*Coumarino*)*anthranilic acid.* *o*-Chlorobenzoic acid (6 g.), anhydrous potassium carbonate (6 g.), 6-aminocoumarin (10 g.), and copper bronze (1 g.) were heated in amyl alcohol (130 ml.) under reflux for 3 hours. The amyl alcohol was removed in steam, and the aqueous-alkaline filtrate rendered acid with acetic acid. The product was collected and purified from spirit giving the *acid*, faintly-coloured prisms from spirit, m. p. 250—251° (Found: C, 68·4; H, 3·8; N, 5·3. $C_{16}H_{11}O_4N$ requires C, 68·3; H, 3·9; N, 5·0%).

3-Keto-3 : 4-dihydro-4-oxa[3 : 4]*benzacridone* (II), a pale yellow powder insoluble in the usual solvents, m. p. >320° (Found: N, 5·8. $C_{16}H_9O_3N$ requires N, 5·3%), was obtained when the foregoing compound (1·0 g.) was heated with concentrated sulphuric acid (6 ml.) for 30 minutes on the water-bath, and the product poured into water. Attempts to convert it into the corresponding chloroacridine were not successful.

2-Carbethoxy-7-methyl-3-oxa-6-aza-α-naphthindene derivatives. 2-Carbethoxy-7-methyl-3-oxa-6-aza-α-naphthindene, m. p. 119° (Found: C, 70·0; H, 5·1. Calc. for $C_{15}H_{13}O_3N$: C, 70·6; H, 5·0%) (Dey and Seshadri, *J. Indian Chem. Soc.*, 1926, **3**, 166, give m. p. 107°), was prepared from the corresponding

acid by the silver salt method. The *methiodide*, prepared *via* the methosulphate in benzene solution, formed light yellow crystals from alcohol, m. p. >300° (Found: I, 31·9. $C_{16}H_{16}O_3NI$ requires I, 32·0%). The *methochloride* formed very unstable platelets from absolute alcohol which decomposed on recrystallisation, m. p. *ca.* 250° (decomp.) (sinters 210°) (Found: Cl, 10·1. $C_{16}H_{16}O_3NCl$ requires Cl, 11·8%).

When the above finely powdered methiodide (1 g.) was dissolved in boiling acetic anhydride (50 ml.), and the solution treated with *p*-dimethylaminobenzaldehyde (1 g.) under reflux for 10 minutes, brilliant green needles of 2-*carbethoxy*-7-p-*dimethylaminostyryl*-3-*oxa*-6-*aza*-α-*naphthindene methiodide* (III) were obtained, m. p. 263° (decomp.) (Found: I, 24·1. $C_{25}H_{25}O_3N_2I$ requires I, 24·1%) after crystallisation from spirit. The corresponding *methochloride* was again obtained with difficulty, forming deep-red microcrystals from alcohol, m. p. 273° (decomp.) (with previous sintering) (Found: Cl, 7·2. $C_{25}H_{25}O_3N_2Cl$ requires Cl, 8·1%).

The authors thank the Therapeutic Research Corporation of Great Britain Limited for grants and for certain facilities.—QUEEN MARY COLLEGE (UNIVERSITY OF LONDON), E. 1. [*Received, June 4th*, 1948.]

"α-*Methylenic Reactivity in Olefin Systems. Part III. The Prins Reaction with Ethylene and* α-*Methylstyrene.*" By J. W. BAKER.

SINCE the publication of a paper with the above title (*J.*, 1948, 89) an abstract of a paper by Olsen (*Z. Naturforsch.*, 1946, **1**, 676) has become available in which the reaction of ethylene with formaldehyde in concentrated acetic–sulphuric acid medium at 130—140°/73 atm. is discussed. The high temperature and pressure necessary to obtain reasonable yields of the condensation products confirm the lack of reactivity under atmospheric pressure previously noted. The products of the reaction under the two sets of conditions appear to be identical, *viz.*, trimethyleneglycol diacetate (I) and "pentaglyceryl triacetate", $CMe(CH_2{\cdot}OAc)_3$ (II), b. p. 151·5—151·8°/11 mm., hydrolysed to 2-methyl-2-hydroxymethylpropane-1 : 3-diol (III), m. p. 199—200°. The unidentified fraction, b. p. 123—126°/0·8 mm., which could not be freed from a formaldehyde impurity, was almost certainly an impure specimen of (II) (Found: C, 52·6; H, 7·2. Calc. for $C_{11}H_{18}O_6$: C, 53·6; H, 7·4%), for which (as found) the acetyl content approximates very closely to that of (I) and which, on hydrolysis, gave a crystalline alcohol, m. p. 197°, which must similarly be identified with (III) (Found: C, 50·25; H, 9·6. Calc. for $C_5H_{12}O_3$: C, 50·0; H, 10·0%).

If the structure assigned by Olsen to (II) is correct, the mechanism of its formation in the reaction is rather obscure.—THE UNIVERSITY, LEEDS. [*Received, June 25th*, 1948.]
