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REDUCTION OF PYRYLIUM SALTS WITH SODIUM BOROHYDRIDE

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Abstract—Sodium borohydride converts 2,4,6-trialkylpyrylium salts (I) into a mixture of dienones (III) and lower-boiling products, which are probably 4H-pyrans (IV). The latter products yield derivatives of 1,5-diones in acid medium, and are believed to be formed by addition of the hydride ion to the γ-position of the pyrylium salt, while the former dienones arise by addition to the α-position.

SINCE pyrylium salts react readily with practically all nucleophilic reagents (recent reviews[1,2]), it was expected that they would also react with the hydride ion. No such reduction of monocyclic pyrylium salts has been reported, although lithium aluminium hydride is known to reduce flavylium[3] and isochromylium[4] salts.

A cold aqueous suspension of 2,4,6-trimethylpyrylium perchlorate (Ia, $R = R' =$ Me) reacts smoothly with sodium borohydride yielding over 90 per cent of a liquid which was shown by vapour-phase chromatography and infra-red spectra to consist of three products: the two compounds IIIa and IVa described below and a small amount (ca. 5%) of an alcohol. Working rapidly at 0° in an aqueous-etheric mixture it was possible to diminish alcohol formation to a negligible proportion and to separate by fractional distillation a ketone (IIIa; ca. 75% yield) and a more volatile compound (IVa; ca. 20% yield).

The ketone (IIIa) yields a brick-red 2,4-dinitrophenylhydrazone, $C_{14}H_{16}N_4O_4$, m.p. 133°, which has $\lambda_{\max}$ 401 mμ and, therefore, has two double bonds conjugated with the carbonyl group.[5] This compound is considered to be 4-methyl-3,5-heptadien-2-one. It is not identical with Crisan and Normant's product (reported[6] m.p. of the 2,4-dinitrophenylhydrazone 172°) because our ketone must have a *cis* configuration of the double bond adjacent to the carbonyl group.

Compound (IVa) is more sensitive, darkening rapidly on standing; it reacts with Brady's reagent, yielding a yellow bis-2,4-dinitrophenylhydrazone, $C_{20}H_{22}N_8O_8$, shown by mixed m.p. to be identical with the bis-2,4-dinitrophenylhydrazone of 4-methyl-2,6-heptanedione.

These facts lead to the following representation of the reaction between 2,4,6-trialkylpyrylium salts (I–I″) and sodium borohydride.

Nucleophilic addition of the hydride ion may occur either in the α-position of the pyrylium salt giving rise to a dienone (III) or in γ-position leading to a 4H-pyran (IV) which hydrolyses to a 1,5-dienone (V) in acid medium.

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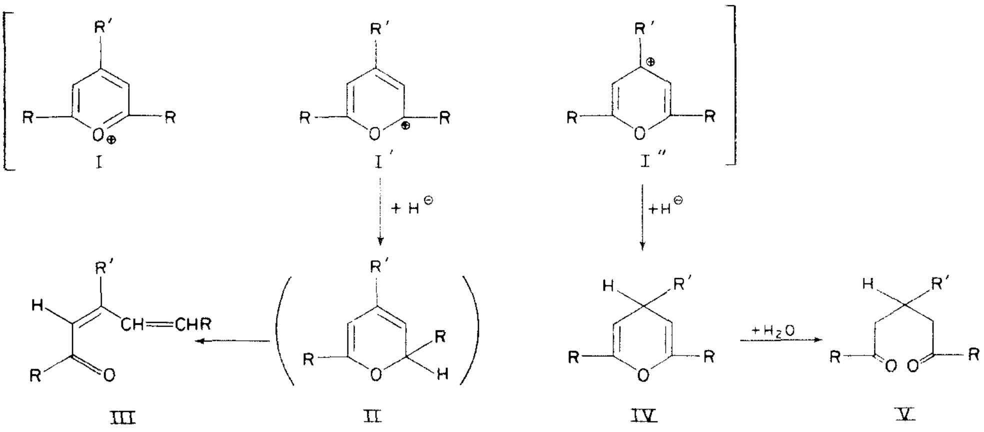

a, R=R′=Me; b, R=Me, R′=Et; c, R=Et, R′=Me; d, R=iPr, R′=Me

The cyclic intermediate (II) is believed to possess only a transient existence: aromatic conjugation being no longer possible, it opens its ring yielding the conjugated dienone III (CO stretching at 1680 cm^{-1}). On the other hand, the 4H-pyran (IV) is possible; although in carbon tetrachloride it presents a CO stretching band at 1720 cm^{-1} like authentic 4-methyl-2,6-heptanedione (Va), the remainder of the spectra are not identical; indeed, it would otherwise be difficult to explain the greater volatility of 1,5-dione (V) as compared with the dienone (III): IVa, b.p. 72°/60 mm; IIIa, b.p. 104°/60 mm; authentic Va, b.p. 100/12 mm.

The reaction was applied to other symmetrical 2,4,6-trialkylpyrylium salts (Ib–d). In all cases the two products III and IV were obtained and characterized by conversion into 2,4-dinitrophenylhydrazones.

It was observed that the relative amounts of the α- and γ-addition products depend on the structure of the pyrylium salt: approximate proportions of III:IV are for Ia, 4·5; for Ib, 1; for Ic, 7; and for Id, 10. These figures indicate that localization of the positive charge in α (as I′) is favoured by increasing the bulk, hence the inductive effect, of the α-alkyl groups, while localization of the positive charge in γ (as I″) is favoured by an analogous increase of the γ-alkyl group. The usual site for nucleophilic attack is the α-position in pyrylium salts;[2,7] in fact, the present paper is the first report of γ-addition to a 2,4,6-trisubstituted monocyclic pyrylium salt; this is perhaps due to the great reactivity, hence small selectivity, of the hydride ion.

Another point which is deserving of mention, is the pronounced hypsochromic effect observed in the series of 2,4-dinitrophenylhydrazones IIIa — IIIb — IIIc $\simeq$ IIId. Similar hypsochromic effects were observed in the 2,4-dinitrophenylhydrazones of cyanodienones obtained from pyrylium salts Ia–d and alkali cyanides,[7] or of 2-acylfurans obtained from the same pyrylium salts and hydrogen peroxide.[8] Steric inhibition of conjugation, caused by bulky alkyl groups, is thought to be responsible for all these hypsochromic shifts. In the 2,4-dinitrophenylhydrazones of dienones III, steric hindrance causes the terminal double bond to be twisted and thus to be no longer conjugated with the —N—N=C—C=C— group. The twisting is complete in IIIc and IIId, and partial in IIIb.

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EXPERIMENTAL

Reduction of 2,4,6-*trimethylpyrylium perchlorate* (Ia). To perchlorate[9] (22·2 g, 0·1 mole) in 200 ml water and 100 ml ether stirred at 0°, 4–5 g sodium borohydride was added gradually, thereby preventing excessive foaming. After 1 hr, the cold ether layer was separated, washed several times with water, dried ($MgSO_4$) and fractionated *in vacuo*, yielding: 2 g IVa, b.p. 70–72°/60 mm, an orange-yellow liquid which rapidly darkens on standing but remains fluid, and 9 g IIIa, b.p. 100–105°/60 mm, a colourless liquid which on prolonged standing polymerizes, becoming more viscous but without darkening.

Fraction IVa yielded a slightly soluble yellow bis-2,4-dinitrophenylhydrazone m.p. 200° (from acetic acid) which did not depress the m.p. of authentic 4-methyl-2,6-heptanedione bis-2,4-dinitrophenylhydrazone (prepared by reduction with sodium and ethanol of 2,4,6-trimethylpyridine[10]). Reported m.p. 197–199°,[10] 197–198°,[11] 205°.[12] (Found: C, 48·06; H, 4·40; N, 21·85. Calc. for $C_{20}H_{22}N_8O_8$: C, 47·81; H, 4·41; N, 22·30%).

Fraction IIIa yielded a brick-red 2,4-*dinitrophenylhydrazone* m.p. 133° from benzene–ethanol. (Found: C, 55·00; H, 5·41; N, 18·01. $C_{14}H_{16}N_4O_4$ requires: C, 55·25; H, 5·31; N, 18·01%). Absorption maxima in ethylene dichloride:* 401 (4·14); 344 (4·11); 258 (4·20). Fraction IIIa is believed to consist in 2,5-cis-4-*methyl*-3,5-*heptadien*-2-*one*.

Reduction of 4-*ethyl*-2,6-*dimethylpyrylium perchlorate* (Ib). The perchlorate[13] was similarly reduced. Fractionation gave the following two fractions:

IVb, b.p. 80–85°/55 mm, yielding 4-*ethyl*-2,6-*heptanedione bis* -2,4-*dinitrophenylhydrazone*, yellow, m.p. 185° from acetic acid. (Found: C, 49·17; H, 4·68; N, 21·68; $C_{21}H_{24}N_8O_8$ requires: C, 48·83; N, 4·68; N, 21·70%). A different orange-coloured form m.p. 150° was obtained by repeated recrystallizations from acetic acid, and it reverted to the higher-melting yellow form on boiling in benzene. The orange form is soluble in hot benzene while the yellow form is not.

IIIb, 2,5-cis-4-*ethyl*-3,5-*heptadien*-2-*one*, b.p. 90–95°/55 mm, yielding a red 2,4-*dinitrophenylhydrazone* m.p. 87° from benzene–ethanol. (Found: C, 56·56; H, 5·88; N, 17·47. $C_{15}H_{18}N_4O_4$ requires: C, 56·59; H, 5·70; N, 17·60%). Absorption maxima: 388 (4·38), 297 (3·70) (appearing as shoulder; data obtained by graphical subtraction of extrapolated adjacent bands), 260 (4·16).

Reduction of 2,6-*diethyl*-4-*methylpyrylium perchlorate*[13] (Ic). The mixture obtained as previously gave on fractionation:

IVc, b.p. 110°/55 mm, yielding 5-*methyl*-3,7-*nonanedione bis*-2,4-*dinitrophenylhydrazone* yellow m.p. 172° from benzene–ethanol. (Found: C, 49·90; H, 5·33; N, 21·07. $C_{22}H_{26}N_8O_8$ requires: C, 49·81; H, 4·94; N, 21·13%).

IIIc, 3,6-cis-5-*methyl*-4,6-*nonadien*-3-*one*, b.p. 125°/55 mm, yielding an orange 2,4-dinitrophenylhydrazone which after chromatography on alumina from benzene and recrystallization from ethanol had m.p. 86°. Absorption maximum 376 (4·40).

Reduction of 2,6-*diisopropyl*-4-*methylpyrylium perchlorate*[13] (Id). Fractionation was not efficient in the separation of IIId and IVd, therefore the mixture b.p. 120°/40 mm was converted as such into the 2,4-dinitrophenylhydrazone, which was then fractionally crystallized from dil acetic acid, giving:

2,5,8-*trimethyl*-3,7-*nonanedione bis*-2,4-*dinitrophenylhydrazone*, yellow, m.p. 178° from aqueous acetic acid. (Found: C, 51·57; H, 5·60; N, 19·73. $C_{24}H_{30}N_8O_8$ requires: C, 51·60; H, 5·41; N, 20·07%).

3,6-cis-2,5,8-*trimethyl*-4,6-*nonadien*-3-*one* 2,4-*dinitrophenylhydrazone*, yellow, m.p. 91° readily soluble and recrystallized from aqueous ethanol. (Found: C, 59·42; H, 6·61; N, 15·81. $C_{18}H_{24}N_4O_4$ requires: C, 59·58; H, 6·71; N, 15·55%). Absorption maxima: 375 (4·37), 246 (4·36).

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* This and following spectra are in ethylene dichloride; lower limit of the spectrum 240 mμ, wave lengths in mμ, and in parentheses lg ε.

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