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HETEROCYCLIZATION OF TRIKETONES OF THE 2-(3-OXOPROPYL)-
CYCLOHEXANE-1,3-DIONE SERIES

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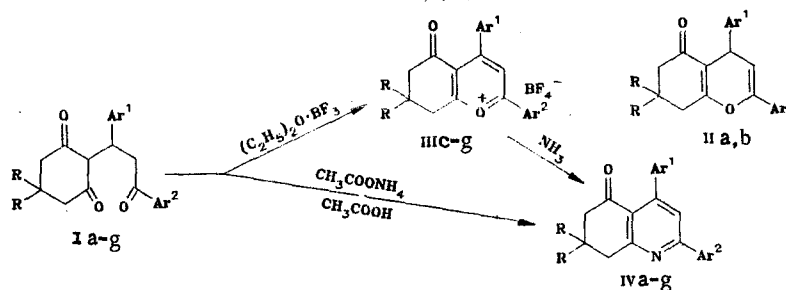
Triketones of the 2-(3-oxopropyl)cyclohexane-1,3-dione series have been shown for the first time to react with boron trifluoride etherate to give the novel 5-oxo-5,6,7,8-tetrahydrochromylum fluoroborates, which in turn react with ammonia to give 5-oxo-5,6,7,8-tetrahydroquinolines. These were also obtained directly from ammonium acetate and 2-(3-oxopropyl)cyclohexane-1,3-diones.

Treatment of 1,5-diketones with acid affords the corresponding pyrilium salts [1-3]. There have, however, been no reports of the reaction of acids with oxo-1,5-diketones, namely, 2-(3-oxopropyl)cyclohexane-1,3-diones.

We have examined the behavior of the oxo-1,5-diketones (Ia-g) with boron trifluoride etherate in glacial acetic acid and acetic anhydride.

Under these conditions, 2-(3-oxopropyl)cyclohexane-1,3-diones (Ia, b), which contain phenyl substituents, cyclize smoothly to give the 5-oxo-5,6,7,8-tetrahydro-4H-chromenes (IIa, b) only, in 70-72% yield.

A feature of phenyl-substituted oxo-1,5-diketones (Ia, b) is their inability to form salts, which is a characteristic of "ordinary" 1,5-diketones, since the initially formed 5-oxotetrahydrochromenes (IIa, b), like their sulfur analogs, are distinguished by the low hydride lability of the hydrogen at C(4). The introduction of electron-donor substituents at this position results in an increase in electron density and the lability of this hydrogen



I, II, IV a, c, e, f R=H; b, d, g, R=CH₃; a, b Ar¹=Ar²=C₆H₅; c, d Ar¹=C₆H₄-OCH₃-4, Ar²=C₆H₅; e Ar¹=C₆H₅, Ar²=C₆H₅-OCH₃-4; f, g Ar¹=Ar²=C₆H₄-OCH₃-4; III c, e, f R=H; d, g R=CH₃; c, d, f, g Ar¹=C₆H₄-OCH₃-4; e Ar¹=C₆H₅; c, d Ar²=C₆H₅; e-g Ar²=C₆H₄-OCH₃-4

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TABLE 1. Properties of (IIIc-g) and (IVa-g)

Com- pound	Mp, °C	IR spectrum, cm ⁻¹			Found, %			Empirical formula	Calculated, %			Yield, %
		ν_{cat}	ν_{anion}	$\nu_{\text{C=O}}$	C	H	N		C	H	N	
IIIc	154-156	1590	1060	1710	63,2	4,8	—	C ₂₂ H ₁₉ BF ₄ O ₃	63,1	4,5	—	44
III d	59-60	1592	1065	1708	63,8	5,3	—	C ₂₄ H ₂₄ BF ₄ O ₃	64,4	5,4	—	97
III e	201-203	1590	1063	1710	63,4	4,9	—	C ₂₂ H ₁₉ BF ₄ O ₃	63,1	4,5	—	24
III f	175-178	1595	1060	1710	60,6	5,1	—	C ₂₃ H ₂₁ BF ₄ O ₄	60,6	4,7	—	26
III g	103-107	1595	1065	1708	62,9	5,1	—	C ₂₅ H ₂₆ BF ₄ O ₄	62,9	5,4	—	19
IV a	110-111	—	—	1685	84,5	5,8	4,7	C ₂₁ H ₁₇ NO	84,3	5,7	4,7	10
IV b	125-126	—	—	1680	85,0	6,5	4,5	C ₂₃ H ₂₁ NO	84,7	6,4	4,3	58
IV c	160-161	—	—	1685	80,5	6,2	4,5	C ₂₂ H ₁₉ NO ₂	80,2	5,2	4,3	38
IV d	134-136	—	—	1682	80,1	6,7	4,2	C ₂₄ H ₂₃ NO ₂	80,5	6,4	3,9	63
IV e	116-117	—	—	1686	80,5	6,2	4,5	C ₂₂ H ₁₉ NO ₂	80,2	5,8	4,3	12
IV f	113-114	—	—	1680	76,8	6,0	4,6	C ₂₃ H ₂₁ NO ₃	76,9	5,8	4,0	10
IV g	138-139	—	—	1685	77,4	6,5	3,9	C ₂₅ H ₂₅ NO ₃	77,5	6,3	3,6	22

TABLE 2. PMR Spectra of 5-Oxo-5,6,7,8-tetrahydroquinolines (IVa-c, f, g)

Com- pound	Chemical shifts, ppm						
	Ar ¹ ; Ar ²	3-H*	6-H (2H)	7-H (2H)	CH ₃ -7 (6H)	8-H (2H)	-OCH ₃
IV a	8,10-7,16	—	3,24	2,20	—	2,64	—
IV b	8,16-7,22	—	3,19	—	1,15	2,53	—
IV c	8,11-6,84	—	3,27	2,22	—	2,67	3,83
IV f	8,08-6,85	7,41	3,22	2,19	—	2,64	3,83
IV g	8,08-6,90	7,41	3,13	—	1,12	2,50	3,82

*In the cases of compounds (IVa-c), multiplets for the aromatic substituents were also present.

atom. As shown by the ability of (Ic-g) to form salts. For instance, diketones (Ic-g) react with boron trifluoride etherate in a 1:1 mixture of acetic acid and acetic anhydride to give 5-oxo-5,6,7,8-tetrahydrochromylum tetrafluoroborates (IIIc-g) in yields of 19-97% depending on the structure of the starting material.

In the absence of acetic anhydride, the formation of salts (IIIc-g) is very slow, the yields of products after this time being no greater than 8-9%. This is in accordance with the function of acetic anhydride as a hydride ion acceptor in the oxidation of pyrans to give the pyrilium cation.

In the absence of acetic anhydride, the hydride ion acceptor could be the double bond in 5-oxotetrahydrochromene, although no disproportionation products have yet been found.

Treatment of salts (IIIc-g) with ammonia in absolute ethanol gives high yields of the 5-oxo-5,6,7,8-tetrahydroquinolines (IVc-g). The presence of an oxo-group at C(5) has no noticeable effect on the reactions of the salts (IIIc-g) with ammonia. The 2-(3-oxopropyl)-cyclohexane-1,3-diones (Ia-g) react less smoothly than the "usual" 1,5-diketones with ammonium acetate. Varying the reaction conditions (ratio of reactants, temperature) did not result in any increase in the yields of the hydroquinoline bases.

The structures of the compounds obtained were confirmed by their elemental analyses and their IR and PMR spectra (Tables 1 and 2).

In the IR spectra of the tetrahydrochromylum tetrafluoroborates (IIIc-g), absorption was present at 1380-1595 cm⁻¹. In the presence of phenyl substituents, however, the absorption due to these overlapped with that due to the tetrahydrochromylum ion. Of the peaks in the spectra of the tetrafluoroborates (IIIc-g), those at 1590-1595 cm⁻¹ are of the greatest intensity, and we assign these to vibrations of the tetrahydrochromylum cation.

The absorption at 1060-1065 cm⁻¹ in (IIIc-g) corresponds to the BF₄⁻ anion. The spectra of salts (IIIc-g) show strong absorption for the carbonyl group at 1710 cm⁻¹.

Assignment of the absorptions in the IR spectra of the 5-oxotetrahydroquinolines (IVa-g) is complicated by the presence of aryl substituents. The absorption at 1680-1685 cm⁻¹ in-

dicates that the carbonyl group is still present, and the bands at 1240 and 1540 cm^{-1} correspond to pyridine ring vibrations.

The types of signals and the chemical shifts of the protons in (IVa-c, e, g) are in good agreement with those reported in [5, 6], and they confirm the structures of the 5-oxotetrahydroquinolines (Table 2). The formation of the pyridine ring is shown by the signals for the 4-H proton at 7.41 ppm distinguishable in the PMR spectra of (IVf, g) (Table 2). In the other compounds (IVa-c), the signal for this proton is masked by the multiplets for the aromatic substituents.

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrometer in Vaseline oil and perchloro-1,3-butadiene, and PMR spectra on a Varian 80FTA, solvent CDCl_3 , temperature 30°C, concentration 0.1 m/liter, internal standard HMDS. The reactions were followed by TLC on Silufol UV-254 plates in the system hexane-ether-chloroform 2:1:1, developer - iodine vapor.

5-Oxo-2,4-diphenyl-5,6,7,8-tetrahydro-4H-chromene (IIa). To a suspension of 5 g (15 mmole) of 2-(1,3-diphenyl-3-oxopropyl)-1,3-cyclohexanedione (Ia) in 30 ml of glacial acetic acid was added dropwise with constant stirring 6.6 g (46 mmole) of boron trifluoride etherate. The mixture was stirred until the ketone had reacted completely (followed by TLC). The reaction mixture was then treated with 200 ml of ether, and the ether layer was washed with water, 10% aqueous potassium hydroxide, and again with water, followed by drying over calcined sodium sulfate. The ether was removed, and the resulting crystalline 5-oxotetrahydrochromene (IIa) was isolated and recrystallized from alcohol. Yield 2.1 g (44%).

5-Oxotetrahydro-4H-chromene (IIb) was obtained similarly, from 5 g (15 mmole) of 5,5-dimethyl-2-(1,3-diphenyl-3-oxopropyl)-1,3-cyclohexanedione (Ib) and 6.6 g (46 mmole) of boron trifluoride etherate. Yield 2.4 g (51%).

Compounds (IIa, b) were identified by their mixed melting points with samples obtained by an earlier method [7].

5-Oxo-2-phenyl-4-(4-methoxyphenyl)-5,6,7,8-tetrahydrochromylum Tetrafluoroborate (IIIc). To a suspension of 5 g (15 mmole) of 2-[1-phenyl-3-(4-methoxyphenyl)-3-oxopropyl]-1,3-cyclohexanedione (Ic) in 30 ml of a 1:1 mixture of acetic anhydride and acetic acid was added dropwise with constant stirring 3.9 ml (25 mmole) of boron trifluoride etherate. The mixture was stirred until the triketone starting material had reacted completely (TLC). The mixture was then poured into 300 ml of dry ether, and the solid tetrafluoroborate (IIIc) which separated was isolated, washed several times with dry ether, and reprecipitated from chloroform with dry ether. Yield 1.72 g (44%).

Obtained similarly were the 5-oxotetrahydrochromylum tetrafluoroborates (IIIId-g) (Table 1).

5-Oxo-2-phenyl-4-(4-methoxyphenyl)-5,6,7,8-tetrahydroquinoline (IVc). A. A mixture of 0.19 g (0.4 mmole) of (IIIc) and 30 ml of absolute ethanol saturated with 6 g of ammonia was heated in a sealed ampul at 50-60°C for 20 h, until the starting material (IIIc) had reacted completely (TLC). The mixture was then partially evaporated, and added dropwise to 200 ml of water. The solid 5-oxotetrahydroquinoline (IVc) which separated was isolated, dried, and recrystallized from alcohol. Yield 0.14 g (38%).

Obtained similarly were the 5-oxotetrahydroquinolines (IVd, g) (Table 1).

B. A mixture of 3 g (0.01 mole) of (Ic), 2.3 g (30 mmole) of ammonium acetate, and 30 ml of glacial acetic acid was heated on a boiling water bath for 48 h. When the reaction was complete, the mixture was poured into 200 ml of ether. The ether solution was washed with water until neutral, dried over calcined sodium sulfate, and the ether removed. The crystals of 5-oxotetrahydroquinoline (IVc) obtained were isolated and recrystallized from alcohol. Yield 0.68 g (23%).

Obtained similarly were the 5-oxotetrahydroquinolines (IVb, d) (Table 1).

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FREE-RADICAL REACTIONS OF 2-ETHOXY-1,3-OXATHIOLANE

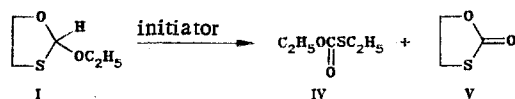
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Homolytic reactions of 2-ethoxy-1,3-oxathiolane in the presence of benzoyl peroxide and tert-butyl peroxide in chlorobenzene have been studied. The principal reaction products are diethyl monothiocarbonate and 1,3-oxathiolane-2-one. The yields and ratios of the products are temperature-dependent.

It has previously been shown that straight-chain and cyclic orthoesters and their nitrogen analogs are converted in the presence of radical initiators into straight-chain and cyclic carbonates and dialkylcarbamate esters, respectively [1, 2].

We have examined for the first time the liquid-phase homolytic reactions of the analogous 2-ethoxy-1,3-oxathiolane (I) on treatment with benzoyl peroxide (II) and tert-butyl peroxide (III) in chlorobenzene. Under these conditions, (I) affords in parallel diethyl monothiocarbonate (IV) and 1,3-oxathiolan-2-one (V).



In the absence of an initiator, (IV) and (V) were not formed.

The experimental results on the conversion and yields of the products of the free-radical reactions of 2-ethoxy-1,3-oxathiolane are given in Table 1.

TABLE 1. Yields of Products of Free-Radical Reactions of (I) [concentration of (I) 4.0, (II) 0.1, and (III) 0.3 mole/liter; solvent chlorobenzene]

Reaction conditions			Concentration, mole/liter			Conversion of (I), %	Yield on (I) reacted, %	
temperature, °C	initiator	time, h	I	IV	V		IV	V
80	II	5	3,2	0,45	0,15	20	56	20
100	II	4	2,0	1,30	0,4	50	65	20
120	III	2	2,4	1,05	0,20	40	60	12

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