SYNTHESIS OF 2, 6-DICYCLOHEXYL-SUBSTITUTED PYRYLIUM SALTS

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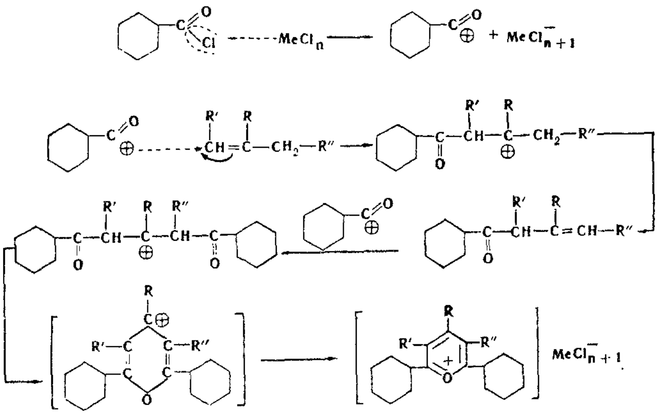
2, 6-Dicyclohexyl-substituted pyrylium salts are synthesized by condensing hexahydrobenzoyl chloride with isobutene, isomeric pentenes, diisobutene, and α-methylstyrene. Treatment of the resultant pyrylium salts with ammonia converts them into the corresponding pyridine salts.

One method of preparing pyrylium salts is to diacylate olefins [1–3], tertiary alcohols or alkyl halides [1, 4], or secondary alcohols [5, 6] with anhydrides or acid chlorides of carboxylic acids, in the presence of Lewis acids. 1, 5-Diketones are the intermediate compounds. The mechanism of cyclization of these compounds to pyrylium salts is considered in papers [7–12].

The present work aims to investigate the conditions for formation of pyrylium salts when hexahydrobenzoyl chloride is condensed with substituted olefins in the presence of $SnCl_4$, $AlCl_3$, and $ZnCl_2$. Isobutene, isomeric pentenes, diisobutene, and α-styrene were used. The formation of pyrylium salts then obtaining can be explained by the following scheme:



R=H, alkyl, C_6H_5. R′=H, CH_3; R″=H, alkyl
Me — Sn; Al; Zn. n — 4; 3; 2.

When hexahydrobenzoyl chloride was condensed with isobutene in the presence of $SnCl_4$, 2, 4-dicyclohexyl-4-methylpyrylium hexachlorostannate was isolated from the reaction products, and also the intermediate compound, the β, γ-unsaturated ketone of the chloro derivative of a 1,5-diketone.

As was previously pointed out [11], formation of pyrylium salts when olefins are diacylated with anhydrides of carboxylic acids passed unnoticed for a long time because of the solubility of the salts in water. Obviously the solubilities of these salts are largely dependent on the nature of the anion, and to some extent on the nature of the substituents in the pyrylium ring. Our work showed that 2, 6-dicyclohexyl-4-alkyl-(or 3, 4-dialkyl)pyrylium hexachlorostannate and trichlorostannate have low solubilities in water, ether, ethanol, benzene, n-hexane, etc. , but are readily soluble in dimethylformamide, nitromethane, and boiling acetic acid. Pyrylium tetrachloroaluminates and ferrates are soluble in water, and treatment of the aqueous solutions with the appropriate acid is a way of preparing the perchlorate, reineckate, and picrate.

Table 1

Effect of Amounts of Isobutene and $SnCl_4$ on the Yield of 2,6-Dicyclohexyl-4-methylpyrylium Hexachlorostannate*

Quantity of isobutene, *l* (mole)	Quantity of $SnCl_4$, g (mole)	Yield of pyrylium salt, %
1.5 (0.062)	8 (0.030)	7.5
3.0 (0.125)	8 (0.030)	18.8
6.0 (0.250)	8 (0.030)	26.3
6.0 (0.250)	4 (0.015)	23.0
6.0 (0.250)	16 (0.060)	23.0

*All runs were carried out with 19 g (0.125 mole) hexahydrobenzoyl chloride.

Diacylation of isobutene with hexahydrobenzoyl chloride in the presence of $SnCl_4$ results in partial polymerization of the former. Consequently, a certain excess of isobutene must be used to raise the yields of pyrylium salts (see Table 1).

Results of runs showed that when more than the stoichiometric amount of catalyst was present in the reaction mixture, the yield of pyrylium salt was low, a considerable quantity of unsaturated ketones and chloroketones being formed.

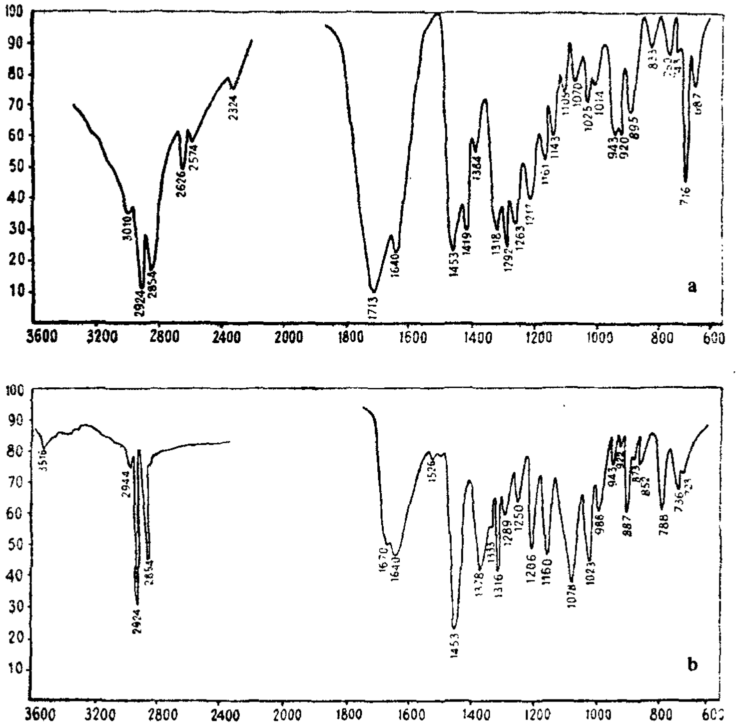
In the present work, a study was made of the effect of olefin structure in addition to a number of other factors on formation of pyrylium salts.

If an unsaturated 1, 5-diketone lacks a hydrogen atom at the position α to the carbonyl group, it cannot be cyclized to a pyrylium salt. In fact pyrylium salts were not obtained when hexahydrobenzoyl chloride was condensed with isopropylethylene.

The present experiments showed that when cis- and trans-pent-2-ene were condensed in the presence of $SnCl_4$ with hexahydrobenzoyl chloride, the cis isomer gave twice the yield of pyrylium salt of the trans one.

EXPERIMENTAL

2, 6-Dicyclohexyl-4-methylpyrylium salts. 16 g (0.06 mole) $SnCl_4$ was added in small portions to a constantly stirred mixture of 38 g (0.25 mole) hexahydrobenzoyl chloride and 70 ml nitromethane cooled to −20° C. Then the cooling bath was removed, and 8 *l* (0.333 mole)



IR spectra: a) first fraction; b) second fraction.

Table 2

Results of Runs with Isomeric Amylenes in the Presence of $SnCl_4$

R	R′	R″	Mp, °C	Found, %			Yield, %	Mp of picrate of the corresponding pyridine
				C	H	Cl		
C_2H_5	H	H	206—208	51.35	6.48	24.10	18.3	--
CH_3	H	CH_3	205—206	51.18	6.35	24.30	44.0	187—190
H	CH_3	CH_3	204—205	51.26	6.40	24.35	22.0**	193—194
H	CH_3	CH_3	204—205	51.10	6.45	24.40	44.0	192—193
CH_3	CH_3	H	206—207	51.42	6.50	24.15	40.0	210

*$C_{38}H_{58}Cl_6OSn$. Calculated: C 51.93; H 6.60; Cl 24.25%.

**The upper numbers are for pyrylium salts from trans-pent-2-ene; the lower ones for those from the cis isomer.

dry isobutene added over a period of 1 1/2 hr. The reaction mixture was stirred at room temperature for 2 hr, washed with 30 ml cold 10% HCl, then with twice the volume of water, and treated with n-hexane. Addition of ether to the organic layer precipitated 2,6-dicyclohexyl-4-methylpyrylium hexachlorostannate as a white powder, yield 11 g (20%), mp 216–217.5° (decomp, ex glacial AcOH). Found: C 50.10; H 6.65; Cl 24.83%, calculated for $C_{36}H_{54}Cl_6O_2$: C 50.82; H 6.35; Cl 25.06%.

The aqueous layer obtained by washing the reaction products with water was steam distilled to remove nitromethane and then treated with 42% $HClO_4$, or a 2% aqueous solution of Reinecke's salt, to give an insignificant amount of 2,6-dicyclohexyl-4-methylpyrylium perchlorate or reineckate. Perchlorate mp 135°. Found: C 60.45; H 7.42; Cl 9.76%, calculated for $C_{18}H_{27}ClO_5$: C 60.68; H 7.52; Cl 9.88%. Reineckate, mp 140°. Found: C 58.23; H 7.12%, calculated for $C_{22}H_{33}CrN_6OS_4$: C 58.79; H 7.35%.

The ether solution obtained after cooling 2,6-dicyclohexyl-4-methylpyrylium hexachlorostannate was treated with 25% NH_4OH. After 24 hr the ether layer separated off and dried over KOH. After removing the ether, the residue was vacuum distilled, to give 3.5 g 2,6-dicyclohexyl-4-methylpyridine, bp 210–212° (8 mm); n_d^{20} 1.5250; d_4^{20} 0.9875. Found: C 84.25; H 10.56%; MR_d 79.57, calculated for $C_{18}H_{27}N$: C 84.78; H 10.59%; MR_d 80.47. Picrate, yellow needles, mp 213.5–214° (ex EtOH). Found: C 59.21; H 5.98%, calculated for $C_{18}H_{27}N \cdot C_6H_3N_3O_7$: C 59.50; H 6.19%.

After 3 days, 2.82 g colorless crystalline substance, mp 160°, was isolated from the hexane extract. Its elementary analysis corresponded to 3-chloro-1,5-dicyclohexyl-3-methylpenta-1,5-dione.

The hexane was distilled off from the solution obtained after removing the chloroketone. The residue was vaccum distilled at 10 mm, to give a cut 133–139°, n_d^{20} 1.4750, mass 4.5 g, and another bp 139–145°, mass 4.0 g (the second fraction crystallized, mp 23°).

The fraction with bp 133–139° (10 mm) gave a 2,4-dinitrophenylhydrazone mp 126°. Found: C 58.14; H 6.60%, calculated for $C_{17}H_{21}N_4O_4$: C 59.13; H 6.86%.

The figure shows the IR spectra of the two fractions. The spectrograms show that the first fraction is mainly β,γ-unsaturated ketone, and the second fraction α,β-unsaturated ketone.

2,6-Dicyclohexyl-4-methylpyrylium trichlorozincate. 25 g (0.18 mole) $ZnCl_2$, ground to a powder, was added to a mixture of 38 g (0.25 mole) $C_6H_{11}COCl$ and 50 ml nitromethane cooled to 5°. Then 7 *l* dry isobutene was passed in over a period of 2 1/2 hr, after which the reaction mixture was stirred for 2 hr more at room temperature. The products were worked up as described above, to give 1.5 g 2,6-dicyclohexyl-4-methylpyrylium trichlorozincate, mp 175–176° (ex glacial AcOH). Found: C 50.47; H 6.42; Cl 24.53%, calculated for $C_{18}H_{27}Cl_3Zn$: C 50.23; H 6.28; Cl 24.77%.

Treatment of the aqueous layer with a 2% aqueous solution of Reinecke's salt gave the reineckate mp 139–140°. Found: C 58.56; H 7.29%, calculated for $C_{22}H_{33}CrN_6OS_4$: C 58.79; H 7.35%.

The ether layer obtained after precipitating the pyrylium salt, was treated with 25% NH_4OH, to give 2,6-dicyclohexyl-4-methylpyridine, bp 210° (10 mm); n_d^{20} 1.5220. Picrate mp 215°.

Condensing hexahydrobenzoyl chloride with isobutene in the presence of $AlCl_3$. 10 g (0.073 mole) $AlCl_3$ was dissolved in a mixture of 19 g (0.125 mole) $C_6H_{11}COCl$ and 40 ml nitromethane, and 4 *l* (0.167 mole) isobutene passed into the mixture, after which stirring was continued for 3 hr more. Then the products were washed with 10% HCl. Pyrylium salt was not precipitated by treating the oily reaction product with ether. Treatment of the product with 60 ml 25% NH_4OH gave 2,6-dicyclohexyl-4-methylpyridine. Treatment of an aqueous solution (obtained by washing the reaction products with water) with 57% $HClO_4$ gave 2,6-dicyclohexyl-4-methylpyrylium perchlorate.

Condensing hexahydrobenzoyl chloride with pentenes. Table 2 gives the results of runs with isomeric pentenes in the presence of $SnCl_4$. In this series of runs, 10 g (0.143 mole) olefin and 8 g (0.030 mole) $SnCl_4$ were taken for 19 g (0.125 mole) $C_6H_{11}COCl$. The condensation of hexahydrobenzoyl chloride with trimethylethylene in the presence of $SnCl_4$ was also run with the mole ratios of those 3 reactants changed. With olefin:acid chloride: $SnCl_4$ = 1 : 1 : 0.25, the pyrylium salt yield was almost twice what it was with the ratios 0.5 : 1 : 0.25 and 0.5 : 1 : 0.125.

The condensation of hexahydrobenzoyl chloride with isopropylethylene run in the presence of $SnCl_4$ using the above method, showed that, as was to be expected, pyrylium salt was not obtained.

2,6-Dicyclohexyl-3,5-dimethylpyrylium trichlorozincate. 5 g (0.037 mole) powdered fused $ZnCl_2$ was added to a stirred solution of 19 g (0.125 mole) $C_6H_{11}COCl$ in 40 ml dry nitromethane, after which, continuing stirring, 10 g (0.143 mole) trimethylethylene was added dropwise. The pyrylium salt was isolated as described above, yield 7 g (50%), mp 137–138°. Found: C 51.00; H 6.60; Cl 23.78%, calculated for $C_{19}H_{29}Cl_3OZn$: C 51.23; H 6.52; Cl 23.93%.

2,6-Dicyclohexyl-4-methyl-5-tert-butylpyrylium hexachlorostannate. 8 g (0.030 mole) $SnCl_4$, followed by 14 g (0.125 mole) diisobutene (bp 102–104°, n_d^{20} 1.4110), were added dropwise to a mixture of 19 g (0.125 mole) $C_6H_{11}COCl$ and 40 ml nitromethane at 10°. After stirring for 3 hr, the products were worked up as described above, to give 12 g (45%) pyrylium salt, mp 201–202°. Found: C 54.10; H 7.12; Cl 21.95%, calculated for $C_{44}H_{70}Cl_6O_2Sn$: C 54.88; H 7.28; Cl 22.14%. Dicyclohexyl-4-methyl-5-tert-butylpyridine picrate mp 185–186°.

2,6-Dicyclohexyl-4-phenylpyrylium hexachlorostannate. 8 g (0.030 mole) $SnCl_4$ was added to a mixture of 19 g (0.125 mole) $C_6H_{11}COCl$ in 40 ml nitromethane, with cooling to 10°, after which 15 g (0.127 mole) α-methylstyrene was added dropwise. The whole was stirred for 3 hr, and the products then worked up as described above, to give 2,6-dicyclohexyl-4-phenylpyrylium hexachlorostannate, yield 6 g (18%), mp 221–222°. Found: C 56.00; H 5.95; Cl 21.53%, calculated for $C_{46}H_{58}Cl_6O_2Sn$: C 56.67; H 6.05; Cl 21.87%.

Treatment of the hexachlorostannate with 25% NH_4OH gave the corresponding pyridine derivative, bp 240–260° (10 mm); n_d^{20} 1.5552 and 260–265° (10 mm); n_d^{20} 1.5732. When treated with an ethanol solution of picric acid, both cuts gave a picrate mp 207–209°.

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