REACTION OF SOME NUCLEOPHILES WITH 2,6-DI-TERT-BUTYLPYRYLIUM PERCHLORATE

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The title compound *IV* reacted with sodium borohydride to give the 4*H*-pyran *VIIa* and the dienone *VIIIa* whereas its reaction with sodium cyanide afforded exclusively the dienone *VIIIb*. Reaction of the salt *IV* with tert-butylmagnesium chloride or bromide gave a mixture of the 4*H*-pyran *VIIa* and the corresponding 4-tert-butyl derivative *V*. Upon treatment with hydrogen sulfide and hydrogen chloride, this mixture afforded 2,4,6-tri-tert-butyl-4*H*-thiopyran (*XI*) whereas aromatization with chloranil and subsequent reaction with ammonium acetate resulted in 2,4,6-tri-tert-butylpyridine (*X*). Analogously, the perchlorate *IV* reacted with ammonium acetate to give 2,6-di-tert-butylpyridine (*VI*). Addition of triphenylphosphine and potassium phthalimide to *IV* afforded exclusively the 4*H*-pyran derivatives *XII* and *XIII*. A similar reaction of nitromethyl anion led to the 4,4'-bis(4*H*-pyran) derivative *XIV*. Mechanism of the studied reactions and the reasons for the low reactivity of the sterically hindered pyridine derivative *VI* with electrophilic and nucleophilic reagents are discussed.

2,6-Disubstituted pyrylium ions are known to react with sufficiently nucleophilic anions X[-] to give 2*H*-pyrans *IIa*, tautomeric with 2,4-dienones *IIb*, and/or isomeric 4*H*-pyrans *III* which do not show any tautomerism[1,2] (Scheme 1).
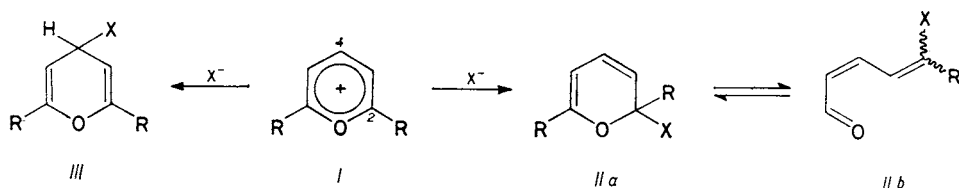

SCHEME 1

Investigating heterocyclic compounds with bulky substituents adjacent to the hetero atom, we were interested in the ion *I* in which the substituents R are tert-butyl groups. Only two reactions with nucleophiles have been described so far for the corresponding 2,6-di-tert-butylpyrylium perchlorate (*IV*). On treatment with tert-

-butylmagnesium bromide, compound *IV* was converted into an unidentified pyran which, although assigned[3] structure *V,* was aromatized[3] to the starting pyrylium salt *IV.* On the other hand, the perchlorate *IV* reacted with ammonia to give the expected 2,6-di-tert-butylpyridine (*VI*) (ref.[5]) in a low yield, in accord with the equimolar mixture of 2,6-di-tert-butyl-4H-pyran (*VIIa*) and 2,2,8,8-tetramethyl-4,6--nonadien-3-one (*VIIIa*), separable by preparative GLC. In this respect, the pyrylium salt *IV* behaves analogously to 2,4,6-trimethyl- (ref.[6]), 2,6-dimethyl-, 2,6-diphenyl-(ref.[7]), 2,4,6-triethyl- and 2,6-diisopropyl-4-ethylpyrylium perchlorate[8].

*IV*   *V*   *VI*
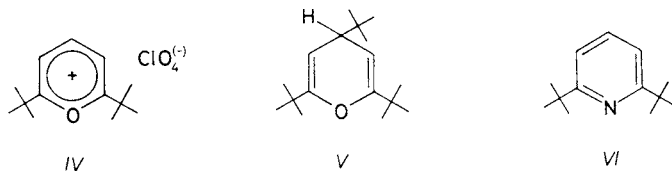
Contrary to the published assumption[3] we found that the reaction of tert-butyl-magnesium bromide with *IV* gives not only the reductive alkylation product 2,4,6--tri-tert-butyl-4H-pyran (*V*) but also the product of simple reduction, *i.e.* the 4H--pyran derivative *VIIa*. The presence of both compounds in the mixture was proved by ^{1}H NMR spectrum, the ratio *V* : *VIIa* being roughly 2 : 1 (according to the signal intensities). Since it is generally assumed that the reduction with sterically bulky Grignard reagents proceeds by a radical mechanism[9], we tried to suppress the formation of the 4-nonalkylated product *VIIa* by addition of a tertiary amine (tri-ethylamine) as radical scavanger. Although the molar ratio *V* : *VIIa* shifted into the expected direction (to about 3 : 1), the formation of the reduction product *VIIa* could not be completely eliminated, probably because the tert-butyl radicals in the reaction medium were too stable. Also replacement of tert-butylmagnesium bromide by the corresponding chloride did not suppress the simple reduction.

VIIa, X = H   *VIIIa,* X = H
VIIb, X = CN   *VIIIb,* X = CN
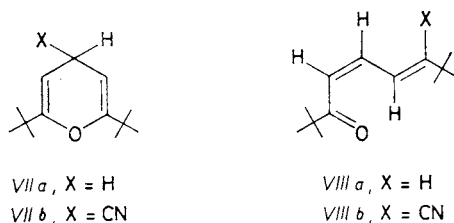
In connection with these results we checked the conclusion[3] that aromatization of the 4H-pyran derivative *V* is accompanied by oxidative elimination of the 4-tert--butyl group under formation of 2,6-di-tert-butylpyrylium ion. As mentioned already above, in the cited paper[3] the product of reaction of *IV* with tert-butylmagnesium bromide was not identified. Consequently, in the light of our results it is highly

probable that the aromatization reaction was performed with a mixture of the 4*H*-
-pyrans *V* and *VIIa* rather than with the individual compound *V*. In actual fact, we
found that aromatization of a mixture of *V* and *VIIa* with chloranil afforded a mix-
ture of 2,6-di-tert-butylpyrylium and 2,4,6-tri-tert-butylpyrylium salts (besides penta-
chlorophenol) from which either *IV* or *IX* could be isolated, according to the crystal-
lization conditions[3]. We treated the above-mentioned mixture also with ammonium
acetate in acetic acid and obtained a mixture of the expected pyridine derivatives *VI*
and *X* from which the latter was isolated as its perchlorate *XV*. Our assumption that
the pyridine derivative *VI* arises exclusively from the pyrylium salt *IV* was confirmed
by an independent experiment which gave *VI* in a high yield. Attempts to transform
the mixtures of *V* and *VIIa* directly to the pyridines *VI* and *X* by reaction of hydroxyl-
amine or its hydrochloride under conditions reported[10] for some analogous trans-
formations failed. On the other hand, we converted the mixture of *V* and *VIIa* into
2,4,6-tri-tert-butyl-4*H*-thiopyran *(XI)* by treatment with hydrogen sulfide and
hydrogen chloride according to the known[11] method of transforming 4*H*-pyrans
into their thia-analogues.

IX   X   XI
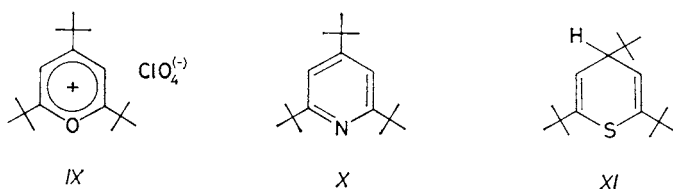
Reaction of the perchlorate *IV* with sodium cyanide afforded solely 7-cyano-2,2-
8,8-tetramethyl-4,6-nonadien-3-one *(VIIIb)*, analogously to the case of some 2,4,6-
-trisubstituted pyrylium ions[12]. It is noteworthy that, under analogous conditions,
2,6-diarylpyrylium ions afford 4-cyano-4*H*-pyrans in almost quantitative yields[13]
whereas in our case it was not possible to prove convincingly the corresponding
product *VIIb*. In contrast to this fact, all other nucleophiles studied by us gave the
expected products of this type. Thus, the perchlorate *IV* reacted with triphenyl-
phosphine or potassium phthalimide to afford the respective 4*H*-pyran derivatives
XII and *XIII*, as described for similar compounds[13,14]. From reaction with nitro-
methane in the presence of triethylamine we obtained the 4,4'-bis-(4*H*-pyran) deriva-
tive *XIV*, formed from the originally arising 4-nitromethyl-4*H*-pyran intermediate.
The reaction course was thus analogous to that found for 2,6-diphenylpyrylium[4].

The molecular structure of the prepared compounds *V*—*XIV* was confirmed by
their ^{1}H NMR spectral data (see Tables I and II and Experimental). The configuration
of the dienones *VIIIa,b* deserves a special notice. As follows from the mutual
coupling constants of protons at the sp^2-carbon atoms in *VIIIa* (Table III), one of
the double bonds has configuration Z ($^3J = 11 \cdot 4$ Hz) whereas the second one has
configuration E ($^3J = 15 \cdot 5$ Hz). The shifts calculated by the usual additive rules[15]

differed from those observed and led to the less probable conclusion that the double bond of E-configuration is that between the C(4) and C(5) atoms. Application of the Eu(fod)$_3$ shift reagent and attempted interpretation of the observed limiting induced shifts (LIS, ppm: 0·0, CH$_3$(8); 1·98, CH$_3$(2); 0·47, H7; 4·1, H6; 0·84, H5; 1·78, H4) did not give an unequivocal solution. The marked differences in the chemical shifts
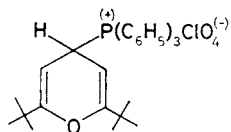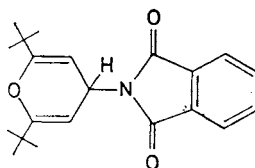
XII   *XIII*
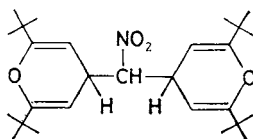
XIV

of the double bond carbon atoms led us to measurement of the "shift-correlated" ^{1}H − ^{13}C two-dimensional spectrum[16−18]. Its analysis determined unequivocally the relation between the ^{1}H and ^{13}C signals and proved the inadequacy of the individual increments for the structure *VIII*. On the basis of published carbon chemical shifts in structurally similar compounds[19], as well as of the 2D NMR experiment, we assigned the proton and carbon signals as given in Table II, the largest shift being ascribed to the H(6) atom (7·40 ppm). Consequently, the configuration of compound *VIIIa* is 4-Z and 6-E. A similar unusual order of olefinic proton signals has been already reported[20] for methyl 2Z,4E-hexadienoate. The assignment of the methyl signals follows from the limiting induced shifts. For *VIIIb* (Tables II and III) the spin–spin coupling constants ^3J(H4, H5) is 11·5 Hz and thus also in this compound the C(4)=C(5) double bond has the Z-configuration. In the proton-coupled ^{13}C NMR spectrum the nitrile carbon signal is split by the proton on C(6) and ^3J(HC) is 14·1 Hz, proving unequivocally that the H(6) proton is in E-relationship to the CN group (see ref.[21]).

The structure of the products *V−XIV* indicates regioselectivity of the nucleophilic attack at the 2,6-di-tert-butylpyrylium ion *I* (R = (CH$_3$)$_3$C) and stereoselectivity of the tautomerism *IIa* → *IIb*. As follows from the reaction conditions, the formation of isomeric pyrans *IIa* and *III* in the borohydride reduction (X$^-$ = BH$_4^-$ and X = H) is undoubtedly kinetically controlled and, according to the ratio of the isolated products

TABLE I

Proton magnetic resonance spectra of the synthesized compounds in deuteriochloroform (chemical shifts in ppm, internal standard tetramethylsilane)

Compound	$CH_3(2, 6)$	$CH_3(4)$	H(3, 5)	H(4)	X(4)
IV^a	1·60 s	—	8·30 d	9·08 t	—
V	1·10 s	0·80 s	4·50 d	2·40 t	—
VI	1·37 s	—	7·04 d	7·46 t	—
VIIa	1·09 s	—	4·50 t	2·70 t	—
X^b	1·25 s	1·23 s	6·95 s	—	—
XI	1·18 s	0·90 s	5·50 d	2·50 t	—
XII	1·05 s	—	7·60— 7·80 m		7·64 s^c
XIII	1·12 s	—	3·38 d	6·86 t	6·40— 7·04 m^c
XIV	1·10 s	—	4·48 dd	3·50 t	4·11 t^d

^{a} In hexadeuterioacetone; ^{b} in tetrachloromethane; ^{c} signal of C_6H_5; ^{d} signal of $CHNO_2$.

TABLE II

NMR spectral data for VIIIa and VIIIb

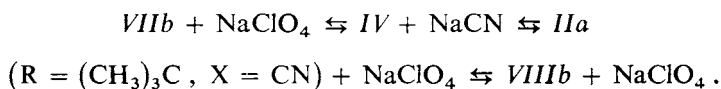| Compound (solvent)	NMR	3	4	5	6	7	2	$CH_3(2)$	8	$CH_3(8)$
VIIIa	^1H	—	6·21	6·49	7·40	6·10	—	1·17	—	1·08
(C^2HCl_3)	^{13}C	206·06	118·56	144·74	122·76	157·06	43·61	26·36	33·87	29·07
VIIIb	^1H	—	6·04	6·95	8·10	—	—	0·96	—	0·96
$(C_6{}^2H_6)$	$^{13}C^a$	205·06	126·00	137·34	135·25	133·42	43·85	26·11	35·56	28·54

^{a} In addition, the spectrum contains a CN signal at 166·24 ppm.

TABLE III

Coupling constants ^3J(H—X, H—Y), in Hz, for compounds VIIIa and VIIIb

X—Y	4—5	4—6	4—7	5—7	5—6	6—7
VIIIa	11·4	0·9	0·8	0·9	11·4	15·5
VIIIb	11·5	<1	—	—	11·5	—

VIIa/VIIIa ($\sim$1), the attack in position 4 of the ion *I* is about twice as fast as in the sterically hindered positions 2 and 6. With the bulky Grignard reagents $(X = (CH_3)_3C)$ both the reductive alkylation and simple reduction are regiospecific, taking place solely in position 4; the formation of the corresponding transition states in positions 2 and 6 is sterically impossible. All the other reactions of *I* with bulky nucleophiles, leading exclusively to addition in position 4 (*i.e.* 4*H*-pyrans *XII – XIV*) can be explained in an analogous way. The quite opposite reaction course with sodium cyanide $(X^- = CN^-$ and $X = CN)$, which leads specifically to the dienone *VIIIb*, apparently reflects the energetic preference of this ketone in a rapidly established thermodynamically controlled equilibrium system

$$VIIb + NaClO_4 \leftrightarrows IV + NaCN \leftrightarrows IIa$$

$$\left(R = (CH_3)_3C, X = CN\right) + NaClO_4 \leftrightarrows VIIIb + NaClO_4.$$

According to the quantum-chemically simulated reaction coordinate for an electrocyclic cleavage of the 2*H*-pyran ring[22], the alternative steric pathways for the unisolated intermediates *IIa* $(R = (CH_3)_3C$ and $X = H$ or CN) are described by Scheme 2. It is obvious that the *endo-* or *exo*-opening of the heterocycle can be for-
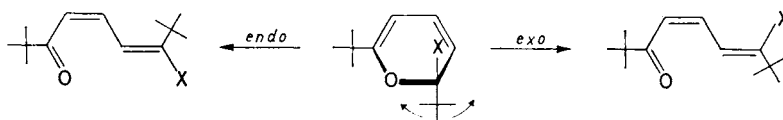
SCHEME 2

mally distinguished by rotation of the bulky tert-butyl group to or from the hetero-cyclic oxygen atom. The found structure of *VIIa* and *VIIIb* thus agrees with the *exo*-course and the complete stereospecificity of the process is probably due to the bulky tert-butyl group in position 2 of the pyran ring.

We can thus summarize that the observed selectivity of the reactions investigated is determined mainly by the steric effect of the tert-butyl groups. In this context it appeared interesting to what extent steric hindrance of the lone electron pair can influence the reactivity of the pyridine derivative *VI* which is protonated with hydrogen chloride to dihydrochloride containing the HCl_2^- anion[23] and is quaternized with methyl iodide only at an extremely high pressure[23]. We converted the base *VI* easily into the corresponding perchlorate *XV* but attempted alkylation or acylation of *VI* in the presence of Lewis acids failed. These results indicate that the known unreactivity of pyridine bases in Friedel–Crafts reactions cannot be related with coordination of the catalyst with the heterocyclic nitrogen atom because, for steric

reasons, in *VI* such coordination is not possible. On the other hand, an analogous coordination of the reagent seems to be necessary for the attack of the pyridine nucleus by complex hydrides and organometallic compounds. This assumption is supported by our negative results in the attempted reaction of the base *VI* with lithium aluminium hydride, methyllithium and n-butyllithium, although unsubstituted pyridine reacts easily with these reagents[24,25]. In accord with these facts we can explain the finding that, in addition to the 2,4,6-trialkyl product X (arising after alkylation in positions 2 and 4) the reaction of pyridine with an excess of tert-butyl-lithium affords[26,27] invariably the 2,6-dialkyl derivative *VI* which does not undergo further alkylation.

EXPERIMENTAL

The NMR spectra were measured at 30°C in deuteriochloroform or hexadeuteriobenzene with tetramethylsilane as internal standard, proton spectra at 100 and 200 MHz, ^{13}C spectra at 25·14 and 50·31 MHz. Digital resolution for ^{1}H 0·23 Hz, for ^{13}C 0·93 Hz, flip angle 30°. The heterocorrelated 2 D spectrum was measured at 200 MHz for ^{1}H and at 50 MHz for ^{13}C on a Varian XL-200 instrument, matrix 2 048 × 64 points. LIS values were determined for Eu(fod)$_3$ by extrapolation of the linear plot shift *vs* R_p (mol LSR/mol substrate) in the region $R_p = 0·05$ to 0·40. The shifts and coupling constants were obtained by analysis of the first order. Mass spectra were measured (at 70 eV) on an LKB 9000 and a JEOL D 300 instrument. Melting points were determined on a Boetius block, the temperature data are uncorrected.

2,6-Di-tert-butyl-4*H*-pyran (*VIIa*) and 2,2,8,8-Tetramethyl-4,6-nonadien-3-one (*VIIIa*)

Sodium borohydride (0·4 g) was added in several portions at 5°C under nitrogen to a stirred mixture of pyrylium salt *IV* (ref.[3]; 2·5 g), benzene (15 ml) and water (25 ml). After stirring at 10°C for 2 h, benzene (20 ml) was added and the organic layer was dried over magnesium sulfate. The solvent was evaporated *in vacuo* and the residue (1·5 g; 90%) was distilled at 60—70°C (bath)/66 Pa. The obtained mixture of *VIIa* and *VIIIa* was separated by preparative gas–liquid chromatography (Carlo Erba, 150 × 3 cm column packed with 15% Carbowax 20 M on Chroma-ton N, AV DMCS, column temperature 160°C, injection at 280°C, nitrogen flow rate 100 ml/min), yielding 2,6-di-tert-butyl-4*H*-pyran (*VIIa*) as a yellowish liquid (0·4 g; 24%) and 2,2,8,8-tetra-methyl-4,6-nonadien-3-one (*VIIIa*) as crystals (0·3 g; 18%), m.p. 41—42°C. Mass spectra, *m/z* (rel. intensity, %): *VIIa*: 194 (38), 193 (84), 178 (8), 137 (100), 122 (38), 109 (23), 57 (77), 42 (68), 29 (38). *VIIIa*: 194 (4), 166 (4), 151 (3), 137 (100), 109 (82), 95 (10), 81 (9), 67 (30), 57 (23), 42 (17).

2,2,8,8-Tetramethyl-7-cyano-4,6-nonadien-3-one (*VIIIb*)

A mixture of pyrylium salt *IV* (2·92 g), sodium cyanide (1 g), diethyl ether (150 ml) and water (150 ml) was stirred until the solid dissolved (2 h). The ethereal layer was separated, dried over magnesium sulfate, filtered and the solvent was evaporated. The residue was cooled in a carbon dioxide–ethanol mixture and the obtained yellow crystals were crystallized from hexane, affording 2 g (90%) of compound *VIIIb*, m.p. 31—33°C. For $C_{14}H_{21}NO$ (219·0) calculated: 76·7% C, 9·6% H, 6·4% N; found: 76·7% C, 9·5% H, 6·4% N.

2,6-Di-tert-butyl-4*H*-pyranyl-4-triphenylphosphonium Perchlorate (*XII*)

A mixture of pyrylium salt *IV* (2·9 g), triphenylphosphine (2·9 g) and nitromethane (10 ml) was heated with stirring until the solid material dissolved and then boiled for 3 min. Ethyl acetate (40 ml) was added and, after standing at 5°C for 24 h, the white crystals were collected and washed with diethyl eter. Yield 2·9 g (53%) of compound *XII*, m.p. 149—152°C. For $C_{31}H_{35}ClO_5P$ (553·5) calculated: 67·3% C, 6·3% H, 6·3% Cl, 5·6% P; found: 67·4% C, 6·2% H, 6·7% Cl, 5·5% P.

N-(2,6-Di-tert-butyl-4-4*H*-pyranyl)phthalimide (*XIII*)

A mixture of pyrylium salt *IV* (2·9 g), potassium phthalimide (5·5 g), diethyl ether (300 ml) and water (300 ml) was vigorously stirred until the solids dissolved. The ethereal layer was separated, dried over magnesium sulfate and the solvent was evaporated. The residue was repeatedly extracted with cyclohexane (to remove phthalic acid monoamide) and allowed to crystallize at 5°C. Crystallization from light petroleum afforded 2·6 g (76%) of crystals, m.p. 45—46°C. For $C_{21}H_{25}NO_3$ (339·4) calculated: 74·3% C, 7·4% H, 4·1% N; found: 74·1% C, 7·6% H, 4·2% N.

Bis-(2,6-di-tert-butyl-4-4*H*-pyranyl)nitromethane (*XIV*)

Triethylamine (4·1 ml) was added dropwise to a stirred mixture of pyrylium salt *IV* (5 g), nitromethane (1·4 g) and ethanol (40 ml). After refluxing for 3 h, the mixture was concentrated to half of the original volume and set aside at 5°C. The obtained crystals were crystallized from ethanol; yield 2·8 g (73·6%) of needles, m.p. 101—102°C. For $C_{27}H_{43}NO_4$ (445·0) calculated: 3·1% N; found: 3·3% N. Mass spectrum, m/z (rel. intensity, %): $M^+ —NO^{28} = 415$ (1), 399 (1), 341 (<1), 315 (<1), 259 (<1), 206 (<1), 193 (100), 178 (2), 137 (<1), 107 (<1), 57 (20).

2,4,6-Tri-tert-butyl-4*H*-pyran (*V*)

A solution of tert-butylmagnesium chloride (0·063 mol) in ether (100 ml) was added dropwise during 30 min to a stirred suspension of pyrylium salt *IV* (5 g) in diethyl ether (40 ml). After the exothermic reaction had ceased, the mixture was heated to 40°C for 30 min and decomposed with aqueous solution of ammonium chloride. The organic layer was separated, the aqueous one was shaken with ether (2 × 30 ml) and the combined ethereal solutions were dried over magnesium sulfate. After evaporation of ether *in vacuo*, the residue (3·6 g) was distilled at 65 to 70°C (bath)/65 Pa. According to ^{1}H NMR spectrum (Table I), the product was a 1 : 2 (molar) mixture of 2,6-ditert-butyl-4*H*-pyran (*VIIa*) and 2,4,6-tri-tert-butyl-4*H*-pyran (*V*). The structure of *VIIa* was confirmed by mass spectrometry.

2,4,6-Tri-tert-butylpyrylium Perchlorate (*IX*)

Chloranil (5·4 g) and concentrated sulfuric acid (2 ml) were added to a solution of the above--prepared mixture of pyrans *V* and *VIIa* (2·6 g) in ethanol (70 ml). The mixture was refluxed for 2 h, the unreacted chloranil was filtered off, ethanol was evaporated and the residue was diluted with water (100 ml). The separated red-brown precipitate was filtered, mixed with ethanol (20 ml) and allowed to crystallize. The obtained yellow crystals were identified as pentachlorophenol. The aqueous solution was concentrated to a half and the colourless perchlorate *IX*, m.p. 255—257°C (0·5 g; 14%) was precipitated by adding 70% perchloric acid (1·4 ml). For $C_{17}H_{29}ClO_5$ (348·5) calculated: 58·6% C, 8·3% H, 10·2% Cl; found: 58·5% C, 7·7% H, 10·2% Cl. For pentachlorophenol C_6HCl_5O (266·5) calculated: 27·0% C, 0·37% H, 66·6% Cl; found: 28·1% C, 0·41% H, 67·1% Cl.

2,4,6-Tri-tert-butylpyridine (X)

The mixture of pyrans V and VIIa (1·5 g) was converted into the pyrylium salts as described in the preceding experiment, the unreacted chloranil was filtered off and the solvent was evaporated. The residue was mixed with 100% acetic acid (30 ml) and ammonium acetate (3·3 g) and heated to 140°C for 30 h. The mixture was made alkaline (pH 12) with aqueous sodium hydroxide and extracted with diethyl ether (4 × 150 ml). The combined ethereal extracts were dried over calcium chloride, the solvent was evaporated *in vacuo* and the residue was distilled at 130—140°C (bath)/1·85 kPa; yield 0·4 g (36%) of X, m.p. 68—69°C (reported[26] m.p. 70·9—71·2°C). Mass spectrum, m/z (rel. intensity, %): for $C_{17}H_{29}N$ calculated M = 247·43, found M^+ 247 (59·3), 232 (100), 216 (16·6), 205 (80·2), 190 (39·5), 162 (4·1), 94 (8·3), 78 (4·1), 67 (3·1), 57 (28·8), 42 (27), 29 (18·7).

2,4,6-Tri-tert-butyl-4H-thiopyran (XI)

Hydrogen sulfide was introduced for 2 h into a solution of the mixture of pyran V and VIIa (3 g) in acetic acid (40 ml), then a 1 : 1 mixture of hydrogen sulfide and hydrogen chloride was introduced for further 2 h. After standing for 24 h, the mixture was diluted with ether (100 ml), repeatedly shaken with water and 15% solution of potassium hydrogen carbonate to neutral reaction and dried over magnesium sulfate. The solvent was evaporated *in vacuo* and the residue was mixed with a few drops of ethanol; yield 0·6 g (19%) of XI, m.p. 59—61°C. For $C_{17}H_{30}S$ (266·0) calculated: 76·7% C, 11·3% H, 12·0% S; found: 76·1% C, 11·3% H, 12·0% S.

2,6-Di-tert-butylpyridinium Perchlorate (XV)

A solution of pyridine VI (0·5 g) in diethyl ether (5 ml) was mixed with 70% perchloric acid (0·5 ml). The precipitate was filtered and washed with diethyl ether; yield 0·7 g (98%) of perchlorate XV, m.p. 229—232°C. For $C_{13}H_{21}ClNO_4$ (290·5) calculated: 53·7% C, 7·2% H, 12·2% Cl, 4·8% N; found: 53·6% C, 7·4% H, 12·3% Cl, 4·8% N.

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