Tetrahedron, Supplement No. 7, pp. 1 to 8. Pergamon Press Ltd. Printed in Northern Ireland

REACTIONS OF PYRYLIUM SALTS WITH NUCLEOPHILES—IV[1]

ISOLATION OF AN INTERMEDIATE IN THE CONVERSION OF 2,4,6-TRIPHENYLPYRYLIUM PERCHLORATE INTO 2,4,6-TRIPHENYLPYRIDINE BY AMMONIA

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(*Received* 22 *July* 1965)

Abstract—In the reaction of 2,4,6-triphenylpyrylium perchlorate with aqueous ammonia, a crystalline intermediate was isolated, which is easily converted into 2,4,6-triphenylpyridine by dehydration. IR and UV spectroscopic evidence indicates that this intermediate is in solution an imino-enol (IIIb). A chelatic derivative (VII) with benzodioxaborole was isolated. UV and IR spectra evidence similar intermediates also in the reaction of NH_3 with 2,6-di-t-butyl-4-methylpyrylium and 2,4,6-trimethylpyrylium salts.

The reaction of pyrylium salts with ammonia leading to pyridines has been known since 1910[2] when Baeyer showed that the methiodide of 2,6-dimethylpyrone gives 4-methoxy-2,6-lutidine, establishing the structure of the methiodide. The reaction was applied subsequently to 2,4,6-trimethyl-[3] and 2,4,6-triaryl-pyrylium salts[4] and constitutes one of the most important reactions of pyrylium salts,[5,6] useful both in the synthesis of pyridines,[7] and in the characterization of pyrylium salts.[8] The generally admitted mechanism of this reaction involves the nucleophilic addition of ammonia to the α-position, which is the most electron-deficient as shown by the NMR spectra,[9] the site of electrophilic attack of α- and γ-phenyl substituents, (*meta* for the former, *para* for the latter[10]), isotopic exchange reactions of methyl groups,[11] and theoretical

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[1] Preceding parts in the series are to be considered: part I, A. T. Balaban and C. D. Nenitzescu, *J. Chem. Soc.* 3566 (1961); part II, A. T. Balaban, P. T. Frangopol, G. Mateescu and C. D. Nenitzescu, *Bull. Soc. Chim. Fr.* 298 (1962); part III, A. T. Balaban, G. Mihai and C. D. Nenitzescu, *Tetrahedron* **18**, 257 (1962).

[2] A. Baeyer, *Ber. Dtsch. Chem. Ges.* **43**, 2337 (1910).

[3] A. Baeyer and J. Piccard, *Liebigs Ann.* **384**, 208 (1911); **407**, 332 (1914).

[4] W. Dilthey, *J. Prakt. Chem.* [2], **94**, 53 (1916); **102**, 209 (1921); **104**, 28 (1922) and further papers.

[5] K. Dimroth and K. H. Wolf, *Newer Methods of Preparative Organic Chemistry* Vol. 3; p. 357. Academic Press, New York (1964).

[6] A. T. Balaban and C. D. Nenitzescu, *Rev. Chim. Acad. RPR* **6**, 269 (1964).

[7] F. Brody and E. Ruby, *Pyridine and Its Derivatives* Part I; p. 210. (Edited by E. Klingsberg) Interscience, New York (1960).

[8] A. T. Balaban and C. D. Nenitzescu, *Liebigs Ann.* **625**, 74 (1959).

[9] A. T. Balaban, G. R. Bedford and A. R. Katritzky, *J. Chem. Soc.* 1646 (1964).

[10] C. G. LeFèvre and R. J. W. LeFèvre, *J. Chem. Soc.* 2894 (1932).

[11] A. T. Balaban, E. Gîrd and C. N. Rentea, *Abh. Dtsch. Akad. Wiss., Kl. Chem., Geol., Biol.* 659 (1964).

calculations of the pyrylium[12] or thiopyrylium cation.[13] Although sensitive α- and γ-pyrans were recently isolated from the addition of C-nucleophiles to pyrylium salts,[5,14] and although the addition products of O-nucleophiles to pyrylium salts (pseudobases or their enol ethers) have been known for a long time,[3,4] N-nucleophiles seldom give intermediate addition products. Only in two instances were intermediates isolated from pyrylium salts and RNH_2 nucleophiles, namely in the reaction with phenylhydrazine (R = PhNH)[15,16] and with a few primary amines (R = cyclohexyl,[17] t-butyl, phenyl, etc.[18]).

Taking into account that, unlike alkylsubstituted pyrylium salts which form sensitive and unstable pseudobases,[3] 2,4,6-triphenylpyrylium perchlorate (I) forms a stable pseudobase (II), it could be expected by analogy that an intermediate could be most easily isolated in the reaction of 2,4,6-triarylpyrylium salts with N-nucleophiles. We studied therefore the reaction of 2,4,6-triphenylpyrylium perchlorate (I) with ammonia, and succeeded in isolating the amino-analogue (III) of the pseudobase (II), which is an intermediate product in the conversion of 2,4,6-triphenylpyrylium (I) into 2,4,6-triphenylpyridine (IV).

Agitation of a suspension of crystalline 2,4,6-triphenylpyrylium (I) with an excess of aqueous ammonia and ether at room temperature, leads to the coloration in orange of the solid and of the ethereal layer. The orange-yellow solid (III) melts, after filtration and washing with a small amount of ether, at 108–110° with foaming, then resolidifies and melts at 138–140°. When larger amounts of III were heated, the evolution of water was observed at 108–110°, and thermogravimetric analysis indicated a weight loss of 5%; the differential thermal curve shows that the process at 108–110° is exothermal and that the heat evolved is approximately equal to that absorbed on melting at 138–140°. The resolidified product is identical (by IR spectrum and mixed m.p.) with 2,4,6-triphenylpyridine (IV). On conservation, the product (III) is converted in a few days into IV.

Attempts to purify III were difficult because it dehydrates easily to IV under the action of heat, bases or acids, more easily in non-polar solvents. By dissolution in warm ethanol and rapid cooling, III can be recrystallized but longer heating causes the apparition of colourless crystals of the less soluble IV. Triphenylpyridine (IV) is, however, much more soluble in ether than III; this gives the possibility of obtaining simply product III of higher purity, by evaporating rapidly below 15° in a stream of air the ethereal layer separated from the reaction of perchlorate I with ammonia. Pure, almost white, crystals, are deposited first; the mother liquor is decanted and the product is washed with small portions of ether. When pure, colourless III melts at 115-116° and can be conserved longer.

[12] A. T. Balaban, C. Rentia, and Z. Simon, *Rev. Roumaine Chim.* in press.

[13] J. Koutecky, *Coll. Czech. Chem. Comm.* **24**, 1608 (1959).

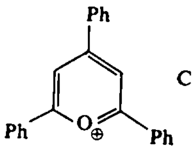
[14] K. Dimroth, K. Wolf and H. Kroke, *Liebigs Ann.* **678**, 183 (1964).

[15] W. Schneider and F. Seebach, *Ber. Dtsch. Chem. Ges.* **54**, 2285 (1921); W. Schneider and K. Weiss, *Ibid.* **61**, 2445 (1928); W. Schneider and W. Riedel, *Ibid.* **74**, 1252 (1941); W. Schneider and W. Müller, *Liebigs Ann.* **438**, 115, 147 (1924).

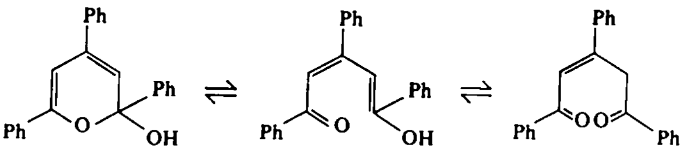
[16] A. T. Balaban, P. T. Frangopol, G. Mateescu and C. D. Nenitzescu, *Bull. Soc. Chim. Fr.* 298 (1962).

[17] R. Lombard and J. P. Stephan, *Bull. Soc. Chim. Fr.* 1458 (1958); R. Lombard and A. Kress, *Ibid.* 1528 (1960).

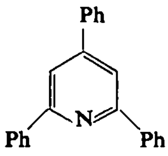
[18] C. Toma and A. T. Balaban, *Tetrahedron* **22**, Suppl. 1, 9 (1966).



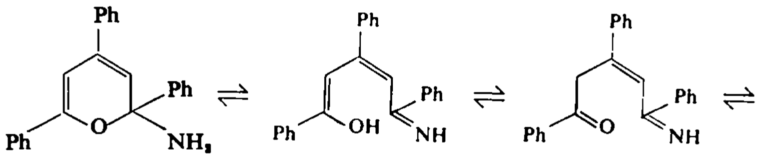
I



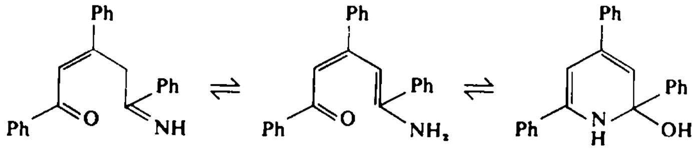
IIa IIb IIc



IV



IIIa IIIb IIIc



IIId IIIe IIIf

For the structure of the pseudobase II three formulas had to be taken into account (IIa, IIb, IIc); from these, Berson[19] showed that the 1,5-enedionic formula IIc is the real one on the basis of UV and IR evidence; 2,3,5,6-tetraphenylpyrylium pseudobase is, however, the ketoenol, corresponding to IIb, but is isomerizes thermally to a 1,5-enedione corresponding to IIc;[20] 2,3,4,6-tetraphenylpyrylium pseudobase is a *cis*-1,5-enedione which is converted by methanolic sodium methoxide into its *trans* isomer.[21]

For the structure of product III six formulas must be discussed: a 2-amino-2H-pyran formula IIIa, one of an iminopentadienol IIIb, two imino-pentanone formulas IIIc and IIId, one of an aminopentadienone IIIe, and a 2-hydroxy-1,2-dihydropyridine formula IIIf.

The IR spectra of I–IV in potassium bromide pellets are presented in fig. 1. The striking features of the IR spectrum of III are the presence of strong bands at 1643, 1569, 1556 and 1105 cm^{-1} and weak bands at 2960, 2905 and 1600 cm^{-1}. The broad absorption at 3050–3180 cm^{-1} indicates hydrogen bonding. In CCl_4 solution (5 mm cell), III presents a quite different spectrum in the range 2800–3700 cm^{-1} (Fig. 2): weak sharp bands at 3592, 3092, 3070 and 3040 cm^{-1} and very weak bands at 3112 and 2892 cm^{-1}. The band at 1643 cm^{-1} appears in the same position in solution as in KBr wafer. No evidence of saturated CH stretching at 2900–2980 cm^{-1} can be seen. On slow gradual precipitation with D_2O from ethanol solution, III presents in CCl_4 a new band at 2652 cm^{-1}. These data indicate in CCl_4 solution the presence of an OH group (stretching vibrations νOH at 3592 cm^{-1} and νOD at 2652 cm^{-1}). Thus

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[19] J. A. Berson, *J. Amer. Chem. Soc.* **74**, 358 (1952).

[20] J. J. Basselier, *Ann. Chim.* [13], **6**, 1131 (1961).

[21] G. Rio and Y. Fellion, *Tetrahedron Letters* 1213 (1962).

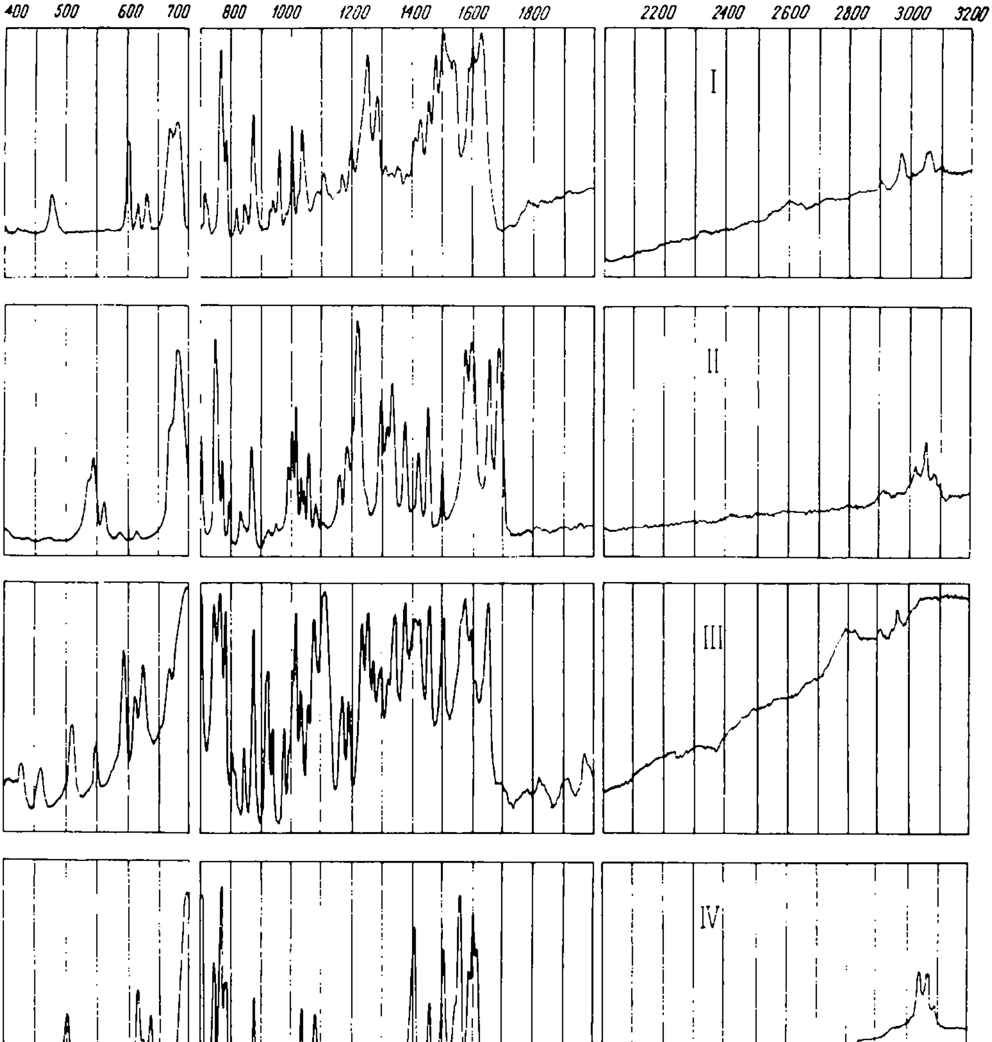

FIG. 1. IR absorption spectra in KBr pellets of I–IV (I as chlorozincate).

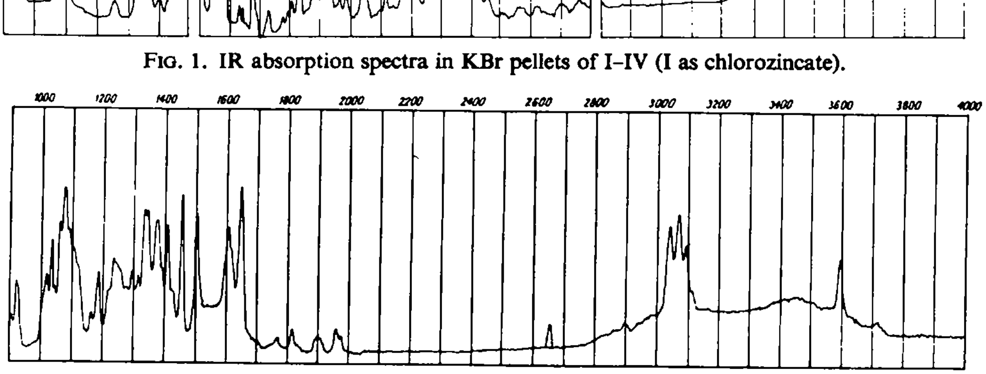

FIG. 2. IR absorption spectra in CCl_4 solution of III (0·1 mm cell) and partially deuterated III (cell of 5 mm thickness) ---------------

for the species in solution formulas IIIa, IIIc, IIId and IIIe having no OH group must be eliminated. Two alternatives are left: either the dihydropyridol structure IIIf, or the iminoenol formula IIIb.

Although colourless in solid state, III becomes yellow at ca. 107° before decomposing, and gives in EtOH, CCl_4 C_6H_6 or Et_2O, yellow solutions. While IV has in ethanol bands at 253 (lgϵ 4·70), 268 sh (4·56) and 311 mμ (3·93), III presents in ethanol a poorly defined maximum at 255 mμ (4·14), with two shoulders at ca. 280 (4·15) and 235 mμ (4·16), and a well-defined low-extinction band at 449 mμ (lgϵ 2·3). Extinction coefficients cannot be determined precisely because of the conversion into IV. This may be followed by UV spectrophotometry in ethanol by the increase of the 253 mμ pyridine band ($T_{1/2}$ of the first order reaction at ca. 22° is 175 min). The low-extinction band varies markedly with the nature of the solvent: EtOH, 449 mμ; tBuOH, 446; Me_2SO, 416 (and a shoulder at 464 mμ, which both are replaced in time by a band at 447 mμ); CH_2Cl_2, 416; CH_3CN, 418; C_6H_6, 422; CH_3NO_2, 408; CCl_4, 415 mμ. These large effects are probably due to the prevalence of different tautomers in different solvents.

The disappearance of the 1643 cm^{-1} band (better than the decrease of the 3586 cm^{-1} band or of the increase of the 1600 and 1556 cm^{-1} bands) gives the following $T_{1/2}$ values by IR spectrophotometry at ca. 27°: 8 min in benzene, 25 min in diethyl ether, 28 min in carbon tetrachloride, 54 min in dichloromethane and 110 min. in acetonitrile. These half lives are roughly proportional to the polarity of the solvent, expressed by Brownsteins's S-values,[22a] or by Dimroth and Reichardt's E_T values.[22b] Non-polar solvents give deviations; $T_{1/2}$ values are very sensitive to traces of acids in these solvents.

In deuterochloroform III presents above τ3 two peaks at τ3·25 and 6·95.

All attempts to prepare an acyl derivative of III, to perform its reaction with 2,4-dinitrophenylhydrazine, diazomethane or nitrous acid or to cause a *cis* → *trans* isomerization failed because of the easy conversion into IV. Treatment of III with concentrated HCl or $HClO_4$ did not regenerate 2,4,6-triphenylpyrylium (I), but gave instead salts of 2,4,6-triphenylpyridine (IV).

While the easy conversion into IV would find a ready explanation by formula IIIf which can also be accomodated with the infrared spectrum, the UV spectrum shows that in solution a more extended chromophoric system is present. Formula IIIb seems to account for most of the properties of this species including the long-wavelength absorption due to the presence of a conjugated hydroxy-imino system, giving also the band at 1643 cm^{-1}. The preference in solution of the iminoenolic IIIb over the amino-ketonic form IIIe, evidenced by the presence of the enolic band and by the insensitivity of the 1643 cm^{-1} band to the medium is interesting because it is contrary to the situation in amides: compound III is a "double vinylogue" of an amide.

In solid state, the colourless product could have structure IIIc and IIId giving saturated CH stretching vibrations; however, the UV and IR data do not allow an unambiguous choice; an equilibrium of several tautomeric forms may exist. The absence of NH stretching bands in the IR spectra of III is intriguing.

We succeeded in preparing a solid derivative of the unstable iminoenol IIIb by

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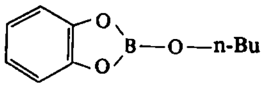
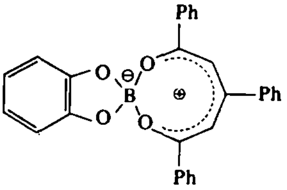
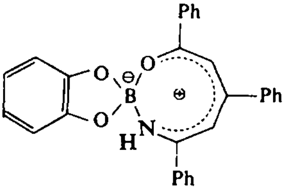
[22] [a] S. Brownstein, *Canad. J. Chem.* **38**, 1590 (1960); [b] C. Reichardt, *Angew. Chem.* **77**, 30 (1965).



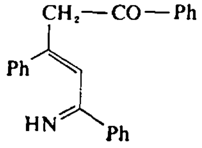
V



VI



VII



VIII

reaction with 2-*n*-butoxy-1,2,3-benzodioxaborole V. This reagent affords with the pseudobase of 2,4,6-triphenylpyrylium (IIc) in benzene, *on heating*, a red crystalline compound VI (a brown intermolecularly coordinated form was also isolated).[23] Combination of benzenic solutions of V and III at room temperature affords an orange-coloured crystalline product which gives an elementary analysis corresponding to formula VII, or to an intermolecularly-coordinated structure. On heating in benzene, it undergoes decomposition: addition of petroleum ether precipitates triphenylpyridine (IV). Its infrared spectrum is similar to that of VI, presenting strong or very strong bands at 1632, 1494, 1240, 1101, 1061, 920, 763, 745 and 698 cm^{-1}.

An orange-coloured oily by-product formed in very small yield from I and NH_3 could be isolated from the ethereal layer. It is much more soluble in ether and ethanol than III or IV, and could not be obtained free from triphenylpyridine IV. Its infrared spectrum presents a strong band at 1693 cm^{-1} and weak bands at 2830 and 1215 cm^{-1}, along with bands common to IV. It affords a 2,4-dinitrophenylhydrazone and has probably a *trans* structure, e.g. VIII, which prevents its cyclization to IV.

The formation of a transient yellow coloration, in the conversion of alkyl-substituted pyrylium salts into pyridines under the action of ammonia, indicates that similar intermediates are involved. Although we could not isolate them, we provide conclusive IR and UV spectral evidence for their formation.

The reaction of 2,6-di-t-butyl-4-methylpyrylium perchlorate (IX, R = tBu) with ammonia in t-butanol is accompanied by the coloration of the solution in yellow due to a low-extinction band at 374 mμ which disappears rapidly. The IR spectrum of a CCl_4 solution prepared by adding rapidly the perchlorate into a separatory funnel with cold CCl_4 and aqueous ammonia, shaking, decanting the CCl_4 layer in a test-tube with anhydrous Na_2SO_4, and introducing the dried solution into the IR cell, presents strong bands at 3598 and 1672 cm^{-1} which decrease rapidly and disappear in 5–10 min, with the appearance of bands due to 2,6-di-t-butyl-4-picoline (1576 cm^{-1}) and to water (1688 and 3450 cm^{-1}, broad). A very strong band at 1603 cm^{-1}, common both to the

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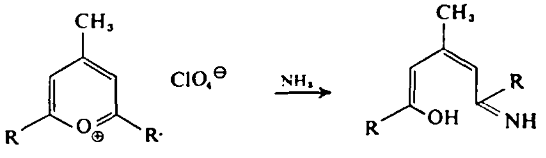
[23] A. T. Balaban, C. N. Rentea and M. Mocanu, *Tetrahedron Letters* 2049 (1964); A. T. Balaban, C. N. Rentea and M. Băcescu-Roman, *Rev. Roumaine Chim.* **10**, 863 (1965).

intermediate X (R = tBu) and to the resulting 2,6-t-butyl-4-picoline, remains constant. The strong bands appearing at 1400 and 1081 cm^{-1} in X, R = tBu and at 1375 and 1105 cm^{-1} in III are tentatively assigned to the bending vibrations of the hydroxy group.

Similar phenomena are observed in the reaction of 2,4,6-trimethylpyrylium perchlorate (IX, R = Me) with ammonia, but the corresponding intermediate (X, R = Me) dehydrates much more rapidly because of the absence of steric or conjugative stabilizing factors. The IR bands of this intermediate appear at 3601 and 1675 cm^{-1}. The gradual decrease of the νO—H and νC=O (or C=NH) frequencies in the sequence X, R = Me, tBu and III: 2,4,6-trimethyl (3601, 1675 cm^{-1}), 2,6-di-t-butyl-4-methyl (3598, 1672 cm^{-1}) and 2,4,6-triphenyl (3586, 1643 cm^{-1}) is paralleled by the increase in stability.



IX X

EXPERIMENTAL

In the present and the two succeeding papers the IR spectra were recorded with a Jena UR-10 apparatus, the UV spectra with an Optica (Milano) CF$_4$ apparatus, and the NMR spectra with a Jeol JNM-3H-60 apparatus.

2,4,6-*Triphenylpyrylium perchlorate* (I) was prepared[24] from 2 moles chalcone[25] and 1 mole acetophenone by heating on the steam bath at 100° with 1·5 moles 70% HClO$_4$ with stirring for 2 hr, then refluxing with 0·5 l. EtOH and precipitating after cooling all the perchlorate with ether. After filtration, the perchlorate was washed with ether, recrystallized from acetic acid, and dried, m.p. 290°.

2,4,6-*Triphenylpyrylium chlorozincate*, was prepared by hydride abstraction from 1,3,5-triphenylpentane-1,5-dione[26] (66 g) which was heated with stirring in 400 g acetic anhydride with 50 g anhydrous ZnCl$_2$ at 70° for 4 hr. Water was then added with cooling for hydrolysis of the anhydride, and the crystals of chlorozincate were filtered off after cooling and washed with ether, yield 38 g. For purification it can be recrystallized from EtOH, acetic acid, or dil HClaq; yellow crystals m.p. 289°. (Found: C, 57·67; H, 3·78; Cl, 21·4. $C_{23}H_{17}Cl_3OZn$ requires: C, 57·42; H, 3·78; Cl, 22·11%.)

Preparation of III. Triphenylpyrylium perchlorate (10 g) was shaken in a separation funnel with 80 ml ether and 40 ml 28% NH$_4$OH at room temp for 3 min. The ethereal layer was concentrated rapidly in a stream of air to 1/4 of its volume and the liquid decanted from the deposited pale yellow crystals. These were washed with 3 portions of 5 ml ether which was decanted. Colourless crystals were obtained by dissolving this product in ether, and concentrating it rapidly in a stream of air; m.p. 115–116° (dec) with resolidification after dehydration. (Found: C, 84·67; H, 6·12; N, 4·31. $C_{23}H_{19}NO$ requires: C, 84·89; H, 5·89; N, 4·30%.) IR bands (in KBr pellet) of III which are absent in the spectrum of IV: 2960 w, 2905 w, 1643 vs, 1569 vs, 1425 m, 1375 vs, 1340 s, 1290 w, 1105 vs, 1015 ms, 940 m, 920 m.

Preparation of VII. A conc. solution of III in anhydrous benzene prepared just before use and decanted from non-dissolved III was treated with V.[27] The solution became brown and on scratching deposited crystals of VII which were filtered off and washed with benzene, yielding stable orange crystals m.p. 99–101° with dec and foaming. (Found: C, 76·97; H, 5·45; N, 3·52; B, 2·35. $C_{29}H_{22}BNO_3$ requires: C, 78·58; H, 5·00; N, 3·16; B, 2·44%.)

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[24] A. T. Balaban, *C. R. Acad. Sci., Paris* **256**, 4239 (1963).

[25] E. P. Kohler and H. M. Chadwell, *Organic Syntheses* (2nd Edition) Coll. Vol. I, 78 (1941).

[26] St. v. Kostanecki and G. Rossbach, *Ber. Dtsch. Chem. Ges.* **29**, 1488 (1896).

[27] A. T. Balaban, G. Mihai, R. Antonescu and P. T. Frangopol, *Tetrahedron* **16**, 68 (1961).

Compound with presumed formula VIII. Evaporation to dryness of the etheral layer in a stream of air left at the bottom of the beaker a mixture of III and IV, and on the walls of the beaker a ring of an oily orange-coloured product VIII. This was separated and purified from triphenylpyridine (IV) by taking advantage of its higher solubility in ether and alcohol. The alcoholic layer afforded an orange 2,4-dinitrophenylhydrazone m.p. 165–167° from EtOH. (Found: N, 13·99. $C_{29}H_{23}N_5O_4$ requires: N, 13·85%.) The IR spectrum of VIII was determined in CCl_4 and indicated a high content of IV; a better purity could be obtained by extracting a solution of the product in conc. HCl with a small amount of CCl_4, drying this extract over $MgSO_4$ and recording its IR spectrum.

Reaction of 2,6-*di-t-butyl-4-methylpyrylium perchlorate with ammonia.* In a separatory funnel containing 5 ml CCl_4 and 15 ml cold conc. NH_4OH, 2,6-di-t-butyl-4-methylpyrylium perchlorate[8] (1 g) was added, the lower layer was separated after shaking and dried quickly over Na_2SO_4. This yellow solution afforded an oily red-orange precipitate with 2-n-butoxy-1,3,2-benzodioxaborole (V). IR bands (in CCl_4) of X(R = tBu) which are absent in the spectrum of 2,6-di-t-butyl-4-picoline: 1675 s, 1450 ms, 1400 s, 1390 w, 1320 m, 1278, 1235 s, 1188 m, 1125 s, 1081, vs, 1065 m, 1012 m, 1005 m, 985 w, 935 w, 912 s, 878 s.

Acknowledgements—Thanks are expressed to Miss E. Sliam for elementary analyses, to Mr M. Elian and Mrs. R. Romas for infra-red spectra, to Mrs. M. Paraschiv for ultraviolet spectra, to Mrs. Dr. C. Măntescu for preparing di-t-butyl-4-picoline, to Dr. H. Mantsch for discussions, and to Professor C. D. Nenitzescu for his support.