FORMATION OF PYRYLIUM SALTS IN THE ACYLATION OF STERICALLY HINDERED QUINONES

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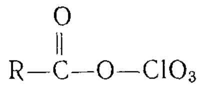
The reaction of 3,5-di-tert-butyl-o-benzoquinone and 2,6-di-tert-butyl-p-benzoquinone with solutions of 70% $HClO_4$ in acetic and propionic anhydrides and with boron trifluoride etherate in acetic anhydride leads to the formation of pyrylium salts in high yields.

The diacylation of olefins with carboxylic acid chlorides and anhydrides in the presence of strong mineral acids or Lewis acids is one of the general methods for the synthesis of pyrylium salts [1-4]. The use of perchloric acid in the reactions gives the highest yields of heterocycles [5, 6]. Acylium cations are assumed to be the acylating agents in such systems; the reaction of the carboxylic acid anhydride with $HClO_4$ is depicted by the equation [7]

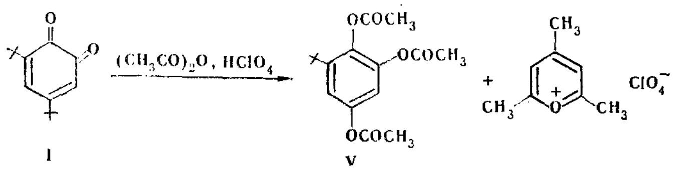
$$(RCO)_2O + HClO_4 \rightleftharpoons RCO^+ClO_4^- + RCOOH$$

The reality of the existence of acylium cations, which follows from data from the NMR and IR spectra [8], was confirmed by x-ray diffraction study of acetylium hexafluoroantimonate $CH_3-C\equiv O^+SbF_6^-$ by the method in [9]. Although acyl perchlorates have been found to be covalently constructed mixed anhydrides  $R-\overset{\overset{O}{\|}}{C}-O-ClO_3$ [10], this does not change the situation essentially, since experiments with nonaqueous solutions of "pure" acyl perchlorates have shown [11-13] that they are extremely active acylating agents. An analogy with hydrogen chloride, which is a covalent but polar molecule that is readily converted to an ionic state, is evidently legitimate here.

The acylation of isobutylene with acetic anhydride in the presence of $HClO_4$, i.e., acetyl perchlorate, leads to the formation of 2,4,6-trimethylpyrylium perchlorate in 78% yield [14].

Perchloric acid has been found [15] to be the most effective catalyst for the Thiele acylation of quinones, which makes it possible to obtain triacetozybenzene and its derivatives in close-to-quantitative yields [16, 17].

It is also known [18] that many reactions of sterically hindered phenols and quinones, particularly with oxidizing agents and electrophilic agents, proceed with splitting out of tert-butyl substituents.



I

V

We have observed that dark-red 3,5-di-tert-butyl-o-benzoquinone reacts virtually instantaneously with a solution of 70% $HClO_4$ in acetic anhydride to give a colorless

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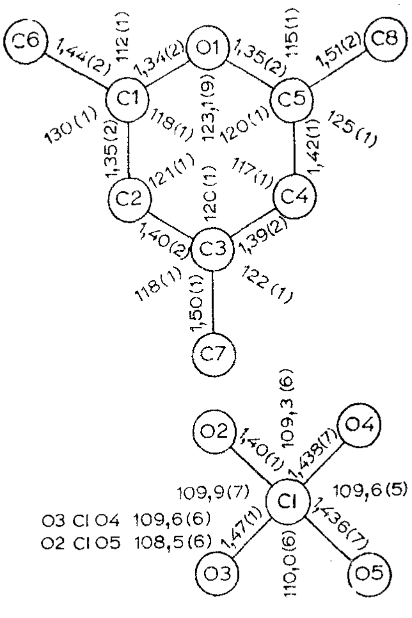


Fig. 1. Molecular diagram of 2,4,6-trimethylpyrylium perchlorate.

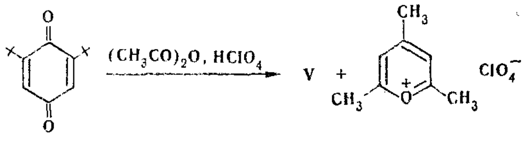
substance that crystallizes when ether is added. An x-ray diffraction study showed that this substance is 2,4,6-trimethylpyrylium perchlorate (Fig. 1). 2,3,5-Triacetoxy-tert-butylbenzene was also isolated from the reaction mixture in ∿90% yield. The yield of the pyrylium salt based on one cleaved tert-butyl group was 80%.

The chemical shifts of the protons in the PMR spectrum were as follows: 6.98 and 6.93 (aromatic ring protons, two s, 2H); 2.20, 2.15, and 2.10 (acetoxy protons, three s, 9H); 1.60 ppm (tert-butyl protons, s, 9H).

Replacement of perchloric acid by boron trifluoride etherate leads to the formation of 2,4,6-trimethylpyrylium tetrafluoroborate.

2,6-Diethyl-4-methylpyrylium cations are formed in propionic anhydride.

The same compounds as those from quinone I were also obtained from 2,6-di-tert-butyl-p-benzoquinone; however, in this case the reaction proceeds slowly, and contact of the reagents for many hours is necessary for its conclusion:



VI

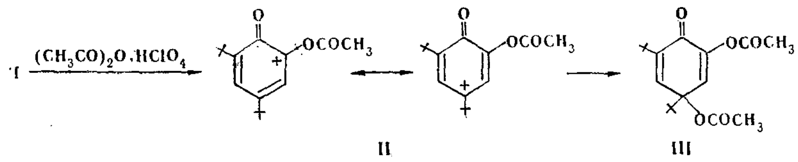
Pyrylium salts are not formed in reactions with 2,5-di-tert-butyl-o-benzoquinone. On the basis of the results of elementary analysis and data from the IR and PMR spectra the isolated substance was identified as 2,3,5-triacetoxy-1,4-di-tert-butylbenzene (XV).

The chemical shifts of the protons in the PMR spectrum of XV were as follows: 6.80 (aromatic ring proton, s, 1H); 2.23, 2.20, and 2.15 (acetoxy protons, three s, 9H); 1.32 and 1.28 ppm (tert-butyl protons, two s, 18H).

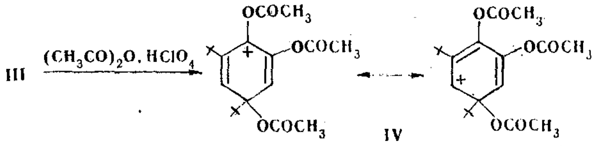
The data obtained make it possible to draw several conclusions regarding the possible mechanism of these reactions.

The conversion of 3,5-di-tert-butyl-o-benzoquinone can be represented by the following steps:

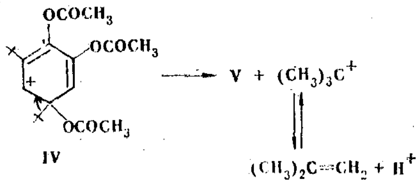
1) acylation of the carbonyl group to give quinolide compound III with a tert-butyl group attached to the terminal (sp^3-hybrid) carbon atom of the quinolide system:



2) acylation of the second carbonyl group, which leads to the development of positive charge on the carbon atom adjacent to the sp^3-hybrid atom bearing the acetoxy and tert-butyl groups:

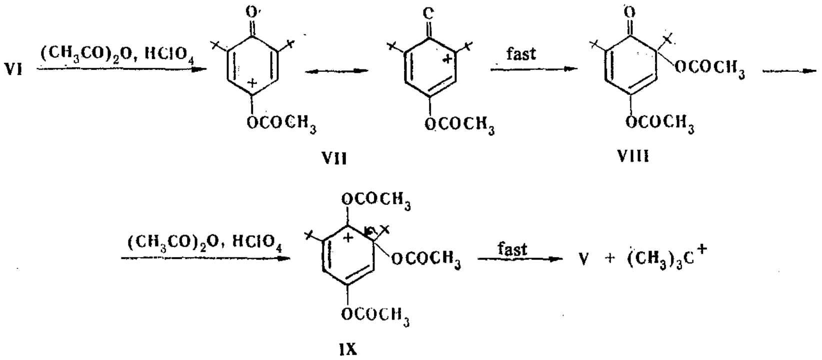


3) intramolecular oxidation by the resulting carbonium ion of the adjacent C—C bond between the two tertiary carbon atoms, which leads to aromatization of the ring and splitting out of a tert-butyl cation:

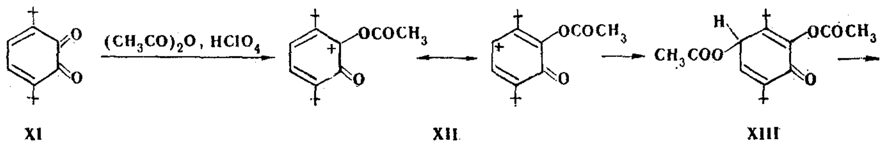


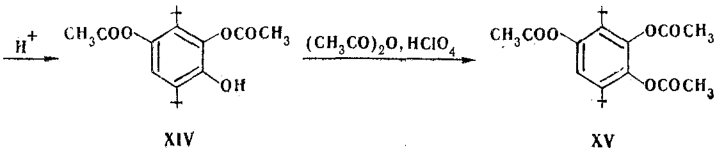
Trimethylpyrylium perchlorate is formed as a result of diacylation of the isobutylene that exists in equilibrium with the tert-butyl cation.

Similar structures are also produced in the acylation of 2,6-di-tert-butyl-p-benzoquinone. The slower character of the process can evidently be explained by steric hindrance in the acylation of the second carbonyl grouping:



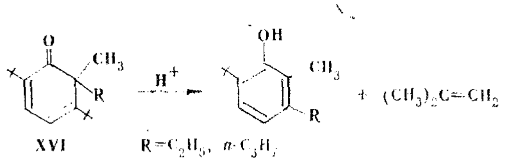
In the case of 2,5-di-tert-butyl-o-benzoquinone, however, the sp^3-hybrid carbon atom of intermediate quinolide compound XIII is bounded to a hydrogen atom rather than to a tert-butyl group. Thus a proton rather than a carbonium ion



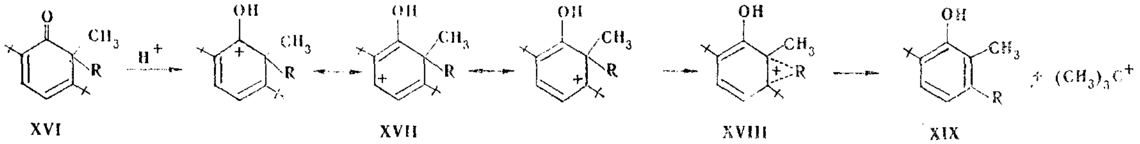


is split out in the next step (the pronounced tendency of such compounds to undergo prototropic isomerization, particularly acidic media, is well known [18]).

Common to all of these transformations is the formation of a quinolide compound with the cleaved grouping or the atom attached to the sp^3-hybrid carbon atom and the development of positive charge on the adjacent carbon atom during subsequent electrophilic attack of the oxygen of the carbonyl group. The reaction (presented in [19])



shows that the transition state that precedes splitting out of the alkyl grouping may have the character of a cyclic carbonium ion with a three-center two-electron bond (XVIII):



EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Tesla BS-487C spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of mineral oil suspensions were recorded with a Specord 71-IR spectrometer.

Acylation of 3,5-Di-tert-butyl-o-benzoquinone (I). A) A previously prepared and cooled (with ice) solution of 0.5 ml of 70% $HClO_4$ in 10 ml of acetic anhydride was added dropwise with stirring and ice cooling to a suspension of 1 g (4.6 mmole) of 3,5-di-tert-butyl-o-benzoquinone (I) in 10 ml of acetic anhydride, during which the solid material dissolved, and the initially dark-brown solution was converted to a light-orange solution. The cooling bath was removed, and, after 2 h, the reaction mixture was treated with ether to precipitate 0.4 g (80%) of 2,4,6-trimethylpyrylium perchlorate with mp 242°C (mp 244°C [6]). No melting-point depression was observed for a mixture of this product with a genuine sample.

Water was added to the filtrate after separation of the trimethylpyrylium perchlorate, the ether layer was separated, and the aqueous layer was extracted with ether. The ether extracts were combined, the ether was evaporated, and hot water was added to the residue. The oil that was liberated upon cooling with ice and trituration gradually began to crystallize. The colorless or slightly yellowish precipitate was removed by filtration, washed several times with water, and dried to give 0.64 g (91%) of colorless crystals of 2,3,5-triacetoxy-tert-butylbenzene (V) with mp 96-99°C (from hexane). IR spectrum: very strong band at 1760 cm^{-1} (CO) with shoulders at 1725, 1755, and 1775 cm^{-1}. Found: C 62.0; H 6.4%. $C_{16}H_{20}O_6$. Calculated: C 62.3; H 6.5%.

The yield of the pyrylium salt decreased to 60% if the reaction mixture was not allowed to stand for 2 h but rather was treated with ether immediately after the addition of the $HClO_4$ solution to a solution of 3,5-di-tert-butyl-o-benzoquinone in acetic anhydride.

B) A 0.2-ml sample of boron trifluoride etherate was added dropwise with stirring to 0.2 g (0.9 mmole) of quinone I in 2 ml of acetic anhydride. Treatment of the mixture with ether gave a white precipitate, which was removed by filtration, washed with ether, and dried. The yield of 2,4,6-trimethylpyrylium tetrafluoroborate with mp 211-218°C, was 0.1 g (53%). The product was identified by comparison of its IR spectrum with the IR spectrum of a genuine sample and from the fact that no melting-point depression was observed for a mixture with a genuine sample. IR spectrum: 1645 (vs) (pyrylium ring vibrations); 1100, 1070, 1050, 1040 cm^{-1} (vs) (BF_4^-).

C) A 0.5-ml sample of 70% $HClO_4$ solution was added dropwise with stirring to 0.5 g (2.3 mmole) of quinone I in 7.6 ml of propionic anhydride. After 10 min, treatment of the reaction mixture with ether gave a white precipitate, which was removed by filtration, washed with ether, and reprecipitated from solution in ether by the addition of ether. The yield of 2,6-diethyl-4-methylpyrylium perchlorate, with mp 183-186°C (mp 189°C [2]), was 0.32 g (56%). IR spectrum: 1645 (vs) (pyrylium ring vibrations) and 1100 cm^{-1} (vs) (ClO_4^-). Found: C 48.3; H 5.8; Cl 14.3%. $C_{10}H_5ClO_5$. Calculated: C 47.8; H 6.0; Cl 14.3%.

Treatment of the filtrate as described in method A led to the formation of an oil, from which we were unable to isolate crystalline 2,3,5-tripropoxy-tert-butylbenzene.

Acylation of 2,6-Di-tert-butyl-p-benzoquinone (VI). A 1-ml sample of 70% $HClO_4$ was added dropwise with stirring and ice cooling to 1 g (4.6 mmole) of 2,6-di-tert-butyl-p-benzoquinone (VI) in 10 ml of acetic anhydride, during which the solution took on a violet coloration. After 2 days, treatment of the solution with ether precipitated 0.7 g (70%) of 2,4,6-trimethylpyrylium perchlorate with mp 244°C. Water was added to the filtrate, the ether layer was separated, and the aqueous layer was extracted with ether. The other extracts were combined, the ether was evaporated, and hot water was added to the residue. The resulting oil began to crystallize upon cooling. The brown-colored (by impurities) crystalline precipitate was removed by filtration, washed with water, and dried. The IR spectrum virtually coincided with the IR spectrum of pure 2,3,5-triacetoxy-tert-butylbenzene. Recrystallization from hexane gave colorless crystals with mp 96-99°C. The identical character of this product and the product obtained from o-quinone was also confirmed by the results of elementary analysis and the PMR spectrum. The yield of crude product was 1.33 g (95%).

Acylation of 2,5-Di-tert-butyl-o-benzoquinone (XI). Five drops of 70% $HClO_4$ were added with stirring to 0.1 g (0.46 mmole) of 2,5-di-tert-butyl-o-benzoquinone (XI) in 2.5 ml of acetic anhydride. After 1 h, an oil, which began to crystallize on standing, was liberated by the addition of water. The colorless precipitate was removed by filtration, washed with water, and dried at 70°C to give 0.08 g (48%) of 2,3,5-triacetoxy-1,4-di-tert-butylbenzene (XV) with mp 156-160°C (from hexane—chloroform). IR spectrum: 1735 (vs) with shoulders at 1720 and 1745 cm^{-1} (CO). Found: C 65.7; H 7.4%. $C_{20}H_{28}O_6$. Calculated: C 65.9; H 7.7%.

LITERATURE CITED

1. A. T. Balaban and C. D. Nenitzescu, Ann. Chem., 625, 66 (1959).
2. A. T. Balaban and C. D. Benitzescu, Ann. Chem., 625, 74 (1959).
3. P. F. G. Praill, Chem. Ind., No. 36, 1123 (1959).
4. P. F. G. Praill and A. L. Whitear, Proc. Chem. Soc., No. 10, 312 (1959).
5. A. T. Balaban and C. D. Nenitzescu, Tetrahedron Lett., No. 2, 7 (1960).
6. A. T. Balaban and C. D. Nenitzescu, J. Chem. Soc., No. 9, 3553 (1961).
7. H. Burton and P. F. G. Praill, J. Chem. Soc., No. 4, 1203 (1950).
8. G. A. Olah, S. I. Kuhn, W. S. Tolgyesi, and E. B. Barker, J. Am. Chem. Soc., 84, 2733 (1962).
9. F. P. Boer, J. Am. Chem. Soc., 88, 1572 (1966).
10. K. Baum and C. D. Beard, J. Org. Chem., 40, 81 (1975).
11. H. Burton and P. F. G. Praill, J. Chem. Soc., No. 8, 2034 (1950).
12. H. Burton and P. F. G. Praill, J. Chem. Soc., No. 2, 529 (1957).
13. H. Burton and P. F. G. Praill, J. Chem. Soc., No. 3, 827 (1953).
14. G. N. Dorofeenko, Yu. A. Zhdanov, V. I. Dulenko, and S. V. Krivun, Perchloric Acid and Its Compounds in Organic Synthesis [in Russian], Izd. Rostovsk. Univ. (1965).
15. H. A. E. Mackenzie and E. R. S. Winter, Trans. Faraday Soc., 44, 159, 171, 243 (1948).
16. H. Burton and P. F. G. Praill, J. Chem. Soc., No. 3, 755 (1952).
17. H. Burton and P. F. G. Praill, Chem. Ind., No. 1, 92 (1950).
18. V. V. Ershov, G. A. Nikiforov, and A. A. Volod'kin, Sterically Hindered Phenols [in Russian], Khimiya, Moscow (1972).
19. B. Miller and H. Margulies, J. Am. Chem. Soc., 89, 1678 (1967).