



In principle, such oxidations of 2,4,6-trisubstituted phenols should also be possible in those cases where the substituent on C-4 is capable of departing with its bonding electron pair. The reactions take place at room temperature and require 6–10 hours. Representative conversions are given in the following Table:

Table. Examples of the oxidation of phenols (1) to *p*-quinones (5) by thallium(III) trifluoroacetate.

| R | R ¹ | R ² | R ³ | R ⁴ | Yield (%) |
|-----------------------------------|-----------------------------------|-----------------|----------------|-----------------------------------|-----------|
| (CH ₃) ₃ C | (CH ₃) ₃ C | H | H | (CH ₃) ₃ C | 73 |
| (CH ₃) ₃ C | Br | H | H | Br | 57 |
| (CH ₃) ₃ C | Br | H | H | CH ₃ | 89 |
| (CH ₃) ₃ C | Br | CH ₃ | H | (CH ₃) ₃ C | 70 |
| (CH ₃) ₃ C | CH ₃ | H | H | CH ₃ | 88 |
| (CH ₃) ₃ C | (CH ₃) ₃ C | H | H | C ₆ H ₅ | 62 |
| Br | Br | H | H | Br | 77 |
| Br | Br | H | H | (CH ₃) ₃ C | 81 |
| Cl | Cl | H | H | CH ₃ | 82 |
| I | I | H | H | I | 62 |
| CH ₃ COO | (CH ₃) ₃ C | H | H | (CH ₃) ₃ C | 97 |
| OH | (CH ₃) ₃ C | H | H | H | 91 |
| OH | CH ₃ | H | H | H | 77 |
| OH | CH ₃ | CH ₃ | H | CH ₃ | 82 |
| OH | Cl | Cl | Cl | Cl | 73 |

Hydroquinones can also be oxidized to *p*-quinones by this method (see Table); in this instance reaction is complete within a few minutes at room temperature.

Received: November 7, 1969 [Z 119 IE]
German version: Angew. Chem. 82, 84 (1970)

[*] Dr. A. McKillop and B. P. Swann
School of Chemical Sciences, University of East Anglia,
Norwich (England)
Dr. M. J. Zelesko
McNeil Laboratories,
Fort Washington, Pa. 19034 (USA)
Prof. E. C. Taylor
Department of Chemistry, Princeton University,
Princeton, N. J. 08540 (USA)

[1] Thallium in Organic Synthesis, Part 13. — Part 12: E. C. Taylor, F. Kienzle, and A. McKillop, J. org. Chemistry, in press.

[2] E. Müller, A. Rieker, and A. Schick, Liebigs Ann. Chem. 673, 40 (1964) and preceding papers in this series; H.-D. Becker, J. org. Chemistry 29, 3068 (1964).

[3] T. Matsuura and H. J. Cahnmann, J. Amer. chem. Soc. 82, 2055 (1960); A. Rieker and G. Henes, Tetrahedron Letters 1968, 3775; A. Rieker and N. Zeller, *ibid.* 1968, 4969.

[4] A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor, and G. McGillivray, Tetrahedron Letters 1969, 2423.

[5] R. Criegee, Angew. Chem. 70, 173 (1958); C. J. R. Adderley and F. R. Hewgill, J. chem. Soc. (London) C 1968, 2770.

[6] E. Hecker and R. Lattrell, Liebigs Ann. Chem. 662, 48 (1963).

The Preparation of Solutions of Anhydrous Perchloric Acid in Methylene Chloride: A Cautionary Note

By H. Musso and B. Bock[*]

During an attempt to prepare a solution of anhydrous perchloric acid in methylene chloride according to a published procedure^[1] a violent explosion occurred which completely destroyed a fume hood. A mixture of 25% oleum and 70% perchloric acid was prepared exactly according to the instructions given, allowed to stand overnight, and then extracted with dry methylene chloride. After the extraction apparatus had been working for about one hour and the methylene chloride was boiling gently the mixture in the non-heated part of the apparatus at the methylene chloride interface suddenly began to boil vigorously and immediately exploded. The methylene chloride had been freshly-distilled over P₂O₁₀ and did not contain any impurities that could be detected by gas chromatography.

It is strongly recommended that this procedure be carried out with extreme care and that only small amounts of reagents be used; furthermore, the extraction flask should be kept adequately cooled.

Received: November 20, 1969 [Z 120 IE]
German version: Angew. Chem. 82, 46 (1970)

[*] Prof. Dr. H. Musso and B. Bock
Institut für Organische Chemie der Universität
75 Karlsruhe 1, Richard-Willstätter-Allee (Germany)

[1] F. Klages and P. Hegenberg, Angew. Chem. 74, 902 (1962); Angew. Chem. internat. Edit. 1, 659 (1962).

A New Method for Structure Determination of Hydroxy Steroids**

By E. Breitmaier, W. Voelter, G. Jung, and E. Bayer[*]

Determination of the position and conformation of the OH group in steroids by common chemical and molecular-spectroscopic techniques often runs into considerable difficulties. Since ¹⁹F-NMR spectroscopy of *O*-trifluoroacetylated steroids only detects the OH group, the ¹⁹F-NMR spectra of these compounds are readily interpretable singlet systems; moreover, the amount of sample required for recording the 56.4-MHz ¹⁹F-NMR spectra is reduced to about 10 μmoles, which is much smaller than that required for ¹H-NMR spectra and is a realistic amount for a natural product. Recent measurements on a 94.1-MHz instrument have shown that the amounts required can be reduced by a further factor of ten, and even by several orders of magnitude if the CAT technique and Fourier transformation are applied^[1].

Comparison of the CF₃ signals of the *O*-trifluoroacetyl group (abbreviation: *O*-TFA) attached to C-17 in 5α- and 5β-dihydrotestosterone (see Table) shows that the linkage of rings A and B, which are relatively far removed from C-17, gives rise to a distinct signal shift in the ¹⁹F-NMR spectrum. The ¹⁹F-NMR spectra of 17β-estradiol and 17α-methyl- and 17α-ethynylestradiol, on the other hand, reflect the effect of the substituents attached to C-17 in ring D on the position of the CF₃ signal of the *O*-TFA group on C-3 in ring A.