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BORON TRIFLUORIDE COMPLEXES OF AROMATIC ALDEHYDES.[1]

O- vs. N-COMPLEXATION OF PARA-DIALKYLAMINOBENZALDEHYDES

Mordecai Rabinovitz and Amiram Grinvald

Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel.

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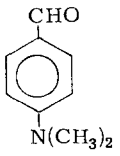
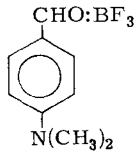
We have recently shown that aromatic aldehydes form stable 1 : 1 complexes with boron trifluoride in which the BF_3 acceptor is linked to the carbonyl oxygen donor.[2] It is known that aromatic compounds carrying a substituent such as a methoxy or a dialkylamino group form BF_3 complexes.[3] Aromatic aldehydes bearing another basic substituent should be able, in principle, to form three different types of BF_3 complexes: two 1 : 1 complexes and one 1 : 2 complex. Anisaldehyde forms only one 1 : 1 BF_3 complex; in this case the Lewis acid is linked to the carbonyl oxygen and not to the methoxy group.[2] We now report the formation of three different types of BF_3 complexes of para-dimethylaminobenzaldehyde (I) and its diethylamino analog.

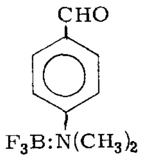
The 1 : 1 stable complex in which the BF_3 is linked to the carbonyl oxygen II, is prepared by the addition of BF_3 gas to a CCl_4 or CH_2Cl_2 solution of the free aldehyde.[4] When a solution of this complex is maintained for several days and the solvent is then evaporated, a second 1 : 1 aldehyde-BF_3 complex III is isolated.[4,5] In analogy to previous observations a marked red shift[2] in the uv spectrum (relative to the free aldehyde) is observed in the case of II, while III shows an opposite effect. The blue shift observed in the case of III indicates the breaking of a p-π



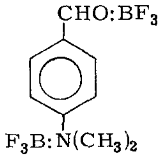
I



II



III



IV

TABLE: Some Spectral Data of para-Dimethylaminobenzaldehyde (I),[1] its BF_3 Complexes and Related Compounds

Compound	UV, λ_{max}, nm (ϵ)[2]	IR, ν, cm^{-1},[3]	NMR, δ, ppm[4]
para-Dimethylaminobenzaldehyde (I)	338.5 (32,800)	1664	9.760
1 : 1 O-complex II	401	1588	8.697
1 : 1 N-complex III	238.2 (17,000)	1713	10.108
1 : 2 complex IV	267.5	—	—
para-Nitrobenzaldehyde	265 (15,500)	1712	10.178
para-Nitrobenzaldehyde BF_3 complex	278.4 (21,600)	1642	9.999

[1] para-Diethylaminobenzaldehyde and its complexes showed similar properties.

[2] Strongest band (Unicam SP-800). [3] Carbonyl frequency (Perkin Elmer 621).

[4] Formyl proton at 100 MHz (TMS as internal reference, Varian HA-100 D).

conjugation (as in the case of the anisole-BF_3 complex[3]) which in turn means that the BF_3 is linked to the nitrogen of the dialkylamino group (Table). The two 1 : 1 complexes differ also in the formyl proton nmr shifts (δ = 9.760, 8.697, 10.108 ppm[6] for I, II and III respectively). The high field shift of the formyl proton in the case of II (relative to the free aldehydes) is typical of all O-BF_3 complexes. Conversely, the low field shift of the formyl proton in the case of III is typical of aromatic aldehydes bearing a strong electron withdrawing group (Table). The ir spectra (Table) also support these assignments; the carbonyl frequency of II shows the "normal" trend (ca. 80 cm^{-1}) to lower wave numbers[2] (relative to the free aldehydes) due to an enhanced polarity of the complexed carbonyl group, while the carbonyl absorption of III resembles the carbonyl absorption of para-nitrobenzaldehyde. The transformation of II to III may be monitored both by the uv spectra and by the formyl proton nmr shifts.[5,6]

On addition of an excess of BF_3 gas to a solution of the free aldehyde a 1 : 2 aldehyde-BF_3 complex IV is obtained in solution. Its composition was deduced from the uv spectral data (Table) which resemble the absorption of the BF_3 complex of para-nitrobenzaldehyde (as well as of the free aldehyde), i. e., an aromatic nucleus bearing two strong electron withdrawing groups (vide supra). On addition of dilute ethanol, the 267.5 nm maximum of IV disappears and the

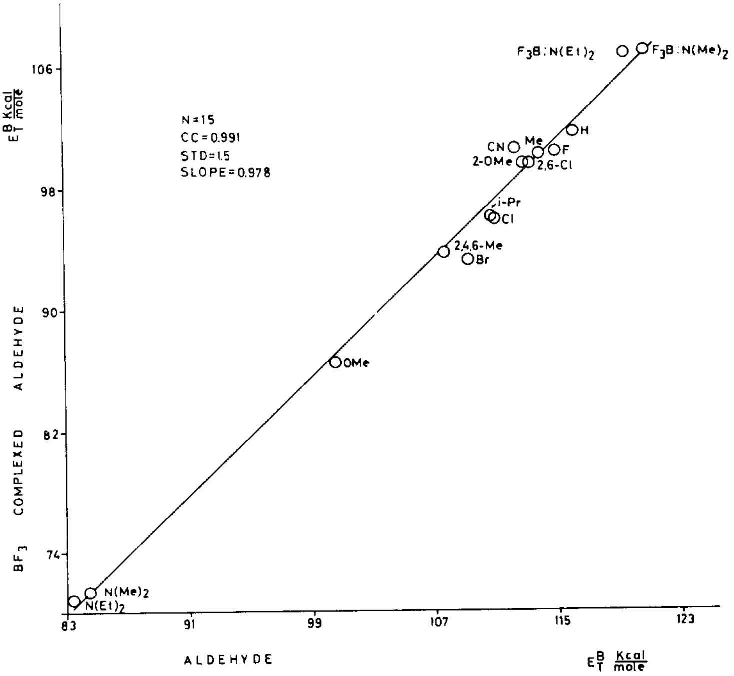


FIGURE 1: The correlation[7] of the uv strong band transition energy (E_T^B) of the free aldehydes vs. the BF_3-complexed aldehydes for 17 aldehydes and complexes including **III** and IV and their para-diethylamino-analogs. The unnumbered substituents refer to para positions.

238.2 nm, typical of III is observed. We conclude that the 1 : 1 carbonyl oxygen-BF_3 complex II must be the kinetically controlled product. It is formed first, and is then converted into the 1 : 1 nitrogen-BF_3 complex III which should be the thermodynamically controlled product. Lewis bases catalize the conversion of II to III.[5]

The 1 : 1 σ complexes of aromatic aldehydes manifest a displaced benzenoid uv spectrum.[2] The correlation equation (1)[7] correlates the transition energy (E_T) of the strong uv band of the free and BF_3-complexed aldehydes. Substituting the value of III (viewed upon as a "para-substituted benzaldehyde") gives an E_T value for the corresponding "carbonyl complexed" aldehyde IV which fits the observed value excellently. Figure 1 shows the computer best-fit

$$E_T \text{ (complex)} = 0.98\ E_T \text{ (aldehyde)} - 11.9\ \frac{\text{Kcal}}{\text{mole}} \qquad (1)$$

$$(N = 15;\ CC = 0.995;\ STD = 1.09\ \frac{\text{Kcal}}{\text{mole}};\ \text{Slope} = 0.98)$$

line[7] including both III and IV. The results reported herein suggest that the $F_3B: NR_2$ group should be considered a pseudosubstituent of the aromatic nucleus.

References

1. Boron Trifluoride Complexes of Aromatic Aldehydes IV; part III submitted for publication.
2. M. Rabinovitz and A. Grinvald, Tetrahedron Letters, 641 (1971).
3. A. A. Palko, R. M. Healy and L. London, J. Chem. Phys., 28, 214 (1958).
4. The composition of the complexes II and III was obtained by microanalysis of C, H, F. The complexes were found to be 1 : 1 complexes (within experimental error). The m.p. of II and III are 125°C and 170°C respectively. The nmr spectrum of II and III at −60°C showed a very weak formyl band of the free aldehyde I.
5. The uv spectrum of II shows weak bands of III even in a freshly prepared sample of II. The bands of III enhance at the expense of the bands of II. On the addition of dilute ethanol the process II $\longrightarrow$ III is very fast and the bands of III only are observed after a few minutes. In the nmr the formyl band of III enhances at the expense of the band of II but this process is slow. The accelerated process observed in the uv recording conditions (dilute solutions) is probably due to minute concentrations of water in the solvent (CH_2Cl_2). The solvent was distilled over H_2SO_4 and kept over $MgClO_4$.
6. Below exchange temperature.[4]
7. H. H. Jaffè, Chem. Rev., 53, 191 (1953), programmed with our Fortran IV program "Data matrix correlation program."