

TERTIARY BUTYLATION OF FIVE MEMBERED HETEROCYCLES. A UPS STUDY

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Abstract - The reaction of 2-chloromercuryfuran and t-butylbromide was studied by UV photoelectron spectroscopy. During the reaction the formation of t-butylfuran, 2,5-di-t-butylfuran, t-butylchloride, isobutylene and furan were found. In accordance with the experimental observations a novel reaction mechanism has been proposed. The first fast and the second slow step of the reaction has been interpreted. The corresponding thiophene derivative gave similar results.

t-Butyl (TB) furan is a much studied compound by theoretical methods both comparing its properties to the corresponding trimethylsilyl compounds or as a model compound for gathering information of sterical effect of the TB group^{1,2}. TB-furanes are useful starting materials for the synthesis of various synthetic intermediates and are singlet oxygen acceptors^{3,4}.

The preparation of 2,5-di-t-butylfuran is the subject of several recent patents⁵. The reaction path that was first described by Brown and Wright created much interest for further investigations as the unexpected disubstituted compound was obtained instead of the monosubstituted product⁶:



2,5-Di-t-butylfuran is also obtained from 3-chloromercuryfuran and TBBr. During the reaction two steps could be distinguished. In the first few seconds a rapid exothermic reaction took place followed by a much slower process that took about 14 days.

The aim of our work was to study the mentioned reaction. To follow the reaction process we used UV photoelectron spectroscopy. During the last years this technique proved to be very effective in the investigations of different gas phase reactions⁷. Studying the vapours of the reaction mixture and monitoring the changing of the vapour phase composition we hoped to get new informations for the mechanism of the reaction.

EXPERIMENTAL

The starting materials used in the reaction were synthesised by usual methods⁸. The photoelectron spectrometer applied has been described previously⁹. The reaction was first carried out in CHCl_3 . Later it was found that the

of 2-chloromercurythiophene and TBBr as shown in Fig. 2. The reaction products were isobutylene, TBCl, thiophene, 2-TB-thiophene and 2,5-di-TB-thiophene in the order of their volatility.

When a different amount of TBBr was used in the reaction the same products were obtained although the quantity of 2-TB-furan changed. As the molar ratio of TBBr increased less 2-TB-furan was formed and some unconsumed TBBr remained in the reaction mixture.

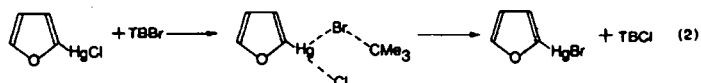
Table 1
Boiling points of the investigated compounds (in °C)

Compound	b.p.	Compound	b.p.
Isobutylene	-9	2-TB-furan	120
Furan	31	2-TB-thiophene	164
TBCl	52	2,5-di-TB-furan	210
TBBr	73	2,5-di-TB-thiophene	226
Thiophene	84		

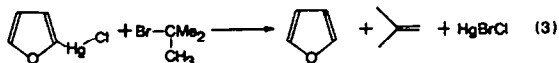
DISCUSSION

The appearance of TBCl in the reaction is a surprising observation. As it can be detected in the first some seconds of the reaction it should be one of the products formed in the first step of the process. In order to investigate the role of TBCl in the reaction TBCl instead of TBBr was added to 2-chloromercuryfuran. In this case no reaction was observed and after immediately analysing the mixture by UPS no other volatile product than TBCl was found. When the analysis was repeated four hours after starting the reaction isobutylene, furan and TB-furanes were found in the spectra. The product peaks were enhanced relative to that of TBCl when larger reaction time (1 day) was applied. Based on this observation it is thought that the second slow period of the reaction is given by the reaction of TBCl and 2-chloromercuryfuran.

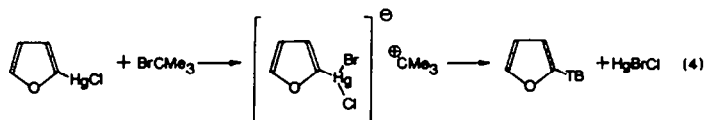
A possible route for TBCl formation is given in Eq. (2)



Isobutylene can be formed from TBBr (and TBCl) by mercury catalyzed HBr (HCl) elimination. As neither HBr nor HCl appears in the spectra although these compounds have very sharp and intense bands, an other possible reaction is preferred:



With the help of this reaction the simultaneous formation of furan and isobutylene can be easily explained. 2-Chloromercuryfuran and TBBr can give 2-TB-furan via carbenium ion as it can be seen in Eq. 4.



However, as Brown and Wright reported the formation of 2,5-di-TB-furan from 3-chloromercuryfuran and TBBr, an alternative route is preferred in which a neighbouring molecule is alkylated according to Eq. 5.

result was similar if the reaction was carried out without using solvent to avoid contaminating photoelectron peaks due to chloroform. As a typical procedure 0.3 g (1 mmole) 2-chloromercuryfuran and 0.2 ml (2 mmole) TBBr were measured into a small reaction flask and attached to the spectrometer through a needle valve. After a few second induction period a vigorous reaction started, indicated by the increasing pressure and temperature of the reaction mixture. The reaction was completed within 8-10 seconds. The products were slowly introduced into the UPS instrument. During the measurement the spectra were continuously scanned and the count of electrons detected at each energy were accumulated digitally using a multichannel analyser. The obtained spectra were continuously monitored. When new bands appeared suggesting a change in the vapour phase composition the accumulated spectra were plotted and the spectrum accumulation was restarted. One scan took 50 seconds while each plot represents 4-8 accumulated scans. The whole measurement took about 25 minutes.

Identical methods were used to obtain photoelectron spectra of the corresponding thiophene derivative. Similar reaction conditions were used and similar results were found but the reaction seemed to be less vigorous.

RESULTS

The spectra in Fig. 1 were obtained from a typical reaction of 2-chloromercuryfuran and TBBr. Fig. 1a shows the photoelectron spectrum of pure TBBr. As it can be seen in Fig. 1b soon after the beginning of the reaction the starting material disappears and new bands emerge. The band-system which has a vertical ionization potential of 9.45 eV can be assigned to the first band of isobutylene¹⁰. The lowest energy band at 8.89 eV can be ordered to the $a_2(\pi)$ orbital of the unsubstituted furan¹¹. (The 10.32 eV band of furan is overlapped by the n_{Br} bands of TBBr.) The fourth characteristic band in the spectrum at 10.72 eV can be unambiguously assigned to the n_{Cl} band of TBCl¹⁰. The spectrum in Fig. 1c is dominated by TBCl as might be accepted if the volatility of the compounds is taken into consideration (see Table 1). In Fig. 1d some new bands can be seen at the low energy side of the spectrum. In the course of time the intensity of the TBCl peaks diminished and the spectrum of 2-TB-furan appeared (Fig. 1e)¹. At last the least volatile 2,5-di-TB-furan made an appearance (Fig. 1f)¹. Similar results were obtained for the reaction

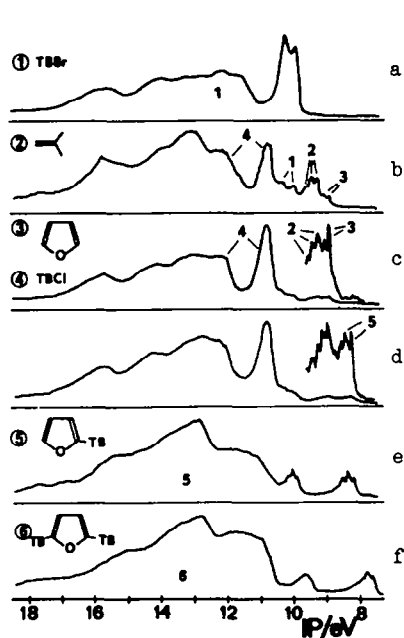


Fig.1. Photoelectron spectra in the reaction of 2-chloromercuryfuran and TBBr.

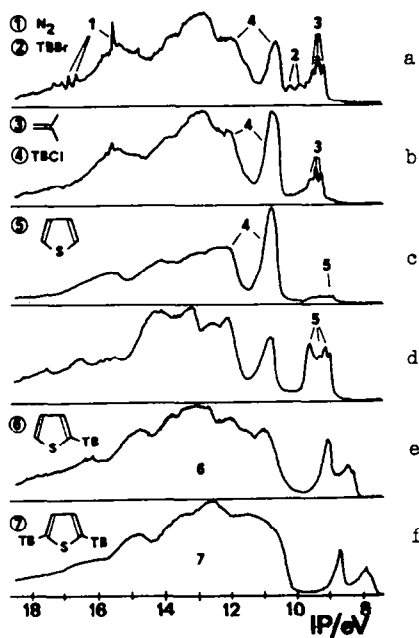
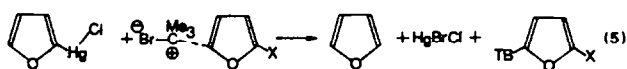
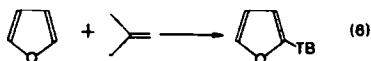


Fig.2. photoelectron spectra in the reaction of 2-chloromercurythiophene and TBBr.



R may be H (2-TB-furan formation) or TB (2,5-di-TB-furan formation). Although R=HgCl or HgBr has not been observed in our experiment (because of the low volatility) its presence cannot be excluded.

An alternative formation of 2-TB-furan may be considered in the addition of furan and isobutylene:



Since the relative intensity of TBCl, furan and isobutylene did not change noticeably after 4 hour staying the latter reaction seems to be unimportant. The whole scheme is summarised in Fig. 3.

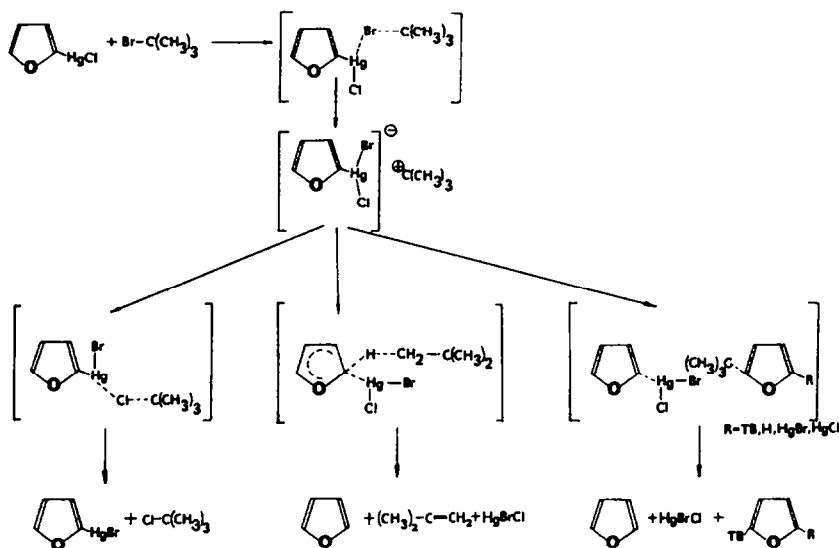


Fig. 3. Proposed mechanism of the reaction.

It can be imagined that the initial step of the reaction is a formation of chloromercurylfuran radical cation and TBBR^{\ominus} radical anion. The stabilization of the radical anion with Br^{\ominus} leaving group is much faster than that of TBCl^{\ominus} therefore the large difference in the rate of the reaction of chloromercurylfuran with TBBR or TBCL can be easily explained.

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