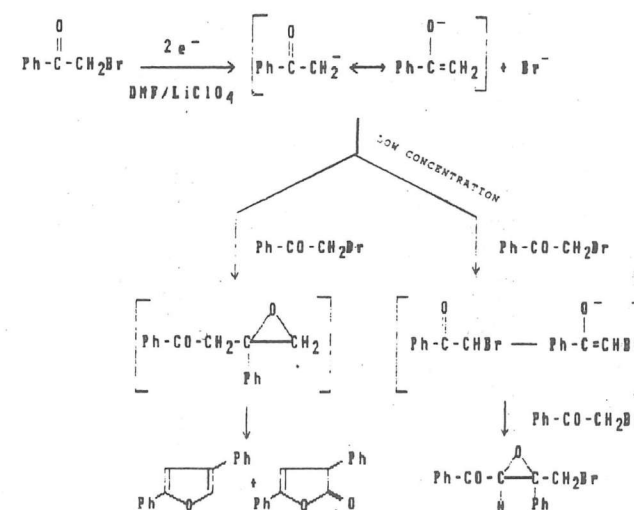


CATHODIC REDUCTION OF α -HALOCARBONILIC COMPOUNDS IN THE PRESENCE OF APARENTLY NON-REACTIVE SUBSTANCES.

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The cathodic reduction of phenacyl bromide gave different products, depending on the reaction conditions (1),(2) as shown in scheme 1.



On this paper, we are going to study the structure of the 2-(3H)-3,5-diphenyl furanone, and the reactivity of the generated intermediate Ph-CO-CHBr^- towards electrophiles as ethyl bromoacetate. We also propose a logical route to explain the formation of the products obtained.

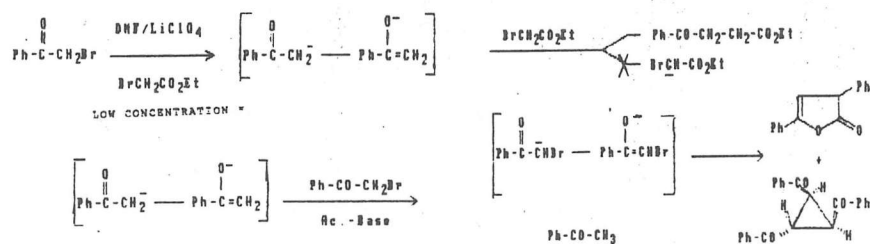
Reactivity towards electrophiles

We will abord first the reaction towards electrophiles: the cathodic cleavage of the C-Br bond leads to the Ph-CO-CH_2^- anion, which is expected to react as a nucleophile with ethyl bromoacetate giving $\text{Ph-CO-CH}_2\text{-CH}_2\text{-COOEt}$. In fact, we have detected it in a very low yield. On the other hand, this anion is expected to react as a base, obtaining the intermediate $\text{Br-CH}^- \text{-COOEt}$, but we reject this possibility because we have not found any product derived from this anion. Therefore, the only

possibility for the intermediate Ph-CO-CH^- , is reacting as a base towards a neutral molecule of phenacyl bromide giving the anion Ph-CO-CHBr and Ph-CO-CH_2 .

This brominated anion is expected to react as a nucleophile with ethyl bromoacetate in a nucleophilic substitution reaction, leading to $\text{Ph-CO-CHBr-CH}_2\text{COOEt}$, but we have found no trace of it.

Instead of all these substances, the products obtained were trans-1,2,3-tribenzoyl-cyclopropane and 2-(3H)-3,5-diphenyl furanone, both in a 50% yield. This furanone is the same as the one obtained in the reduction of phenacyl bromide when no ethyl bromoacetate is present. This is summarize in scheme 2.



Scheme 2.

Structure of the 2-(3H)-3,5-diphenyl furanone

In the literature it is reported two different structures corresponding to this compound: a monomeric and a dimeric one. We support the first one in order of the following reasons:

1)The mass spectrum of the compound gives a molecular ion corresponding to the monomeric pattern.

2)The chemical ionization mass spectrum gives the corresponding $M^+ + 1$, $M^+ + 29$ and $M^+ + 41$ peaks of the monomer (methane was used as carrier gas).

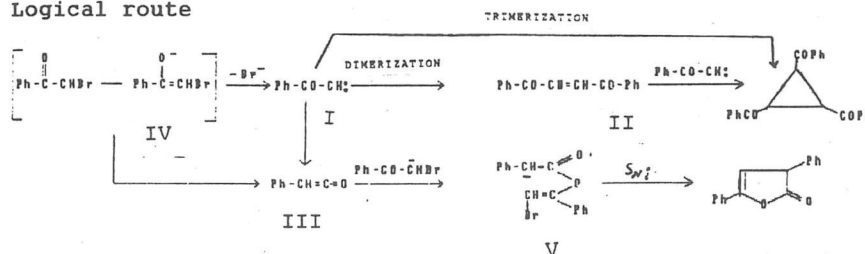
3)The reaction between the furanone and hidrazine gives the N-amino-pirrolone of the monomer.

4)In the literature (3) the heating of the furanone in pyridine leads to a very intense fluorescence under UV irradiation, which is attributed to the rupture of the dimer, being the produced radical responsible of the fluorescence. We can also explain it, considering that enolization of the

furanone by heating effect leads to an hidroxy-furan and it is well-known that furans give fluorescence.

5)The principal reason we aduce to support the monomeric form is the impossibility to find nor in literature nor ourselves a logical route to explain the dimer formation, while we do propose the formation route of the monomer.

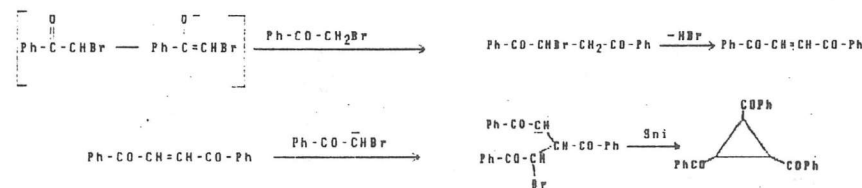
Logical route



From the brominated anion Ph-CO-CHBr^- we can explain the formation of the cyclopropane by elimination of Br^- and formation of the carbene I which by trimerization or dimerization (we have detected the unsaturated diketone II), leads to the cyclopropane.

The furanone can be explained by the formation of the ketene III either by a Wolff transposition from I or by a pseudo-Favorskii transposition from the brominated anion IV. Therefore III can undergo addition by a molecule of IV to give the intermediate V which undergoes intramolecular nucleophilic substitution to lead to the furanone.

Japanese authors (4) have reported recently an ionic-type mechanism for the formation of the cyclopropane as shown in the scheme 3.



Scheme 3

We uphold the via carbene instead of the ionic way because

we have synthesised the cyclopropane by a chemical way, using NaNH_2 in ether from the phenacyl bromide, either in conditions of low concentration or in normal conditions. In the first case just the cyclopropane was obtained. In the second case, where we are reproducing the conditions of the proposed ionic mechanism: high concentration of neutral molecules of phenacyl bromide in the presence of the brominated anion, 2-Br-1,3-diphenyl-3-epoxy-butanone was obtained as exclusive product.

To finish this report, we discuss the experimental results in the formation of the furanones synthesised from several substituted phenacyl bromides, using the following substituents in 4-position: H, Cl, Br, CH_3 , OCH_3 , C_6H_5 , NO_2 .

No trace of the corresponding furanones were obtained when the 4-substituents were OCH_3 , C_6H_5 and NO_2 .

We explain that result considering that the donor substituents OCH_3 and C_6H_5 increase the anion Ph-CO-CH_2^- nucleophilicity. Consequently, the furan formation by nucleophilic addition is favoured instead of the behaviour as a base towards a neutral molecule of phenacyl bromide.

On the other hand, the transpositions to obtain the ketene are unfavored with withdrawing substituents, as NO_2 .

References:

- (1)-F. Barba, M.D. Velasco y A. Guirado; *Synthesis* 625 (1981)
- (2)-F. Barba, M. D. Velasco, M. I. López, A. Zapata, A. Aldaz; *J. Chem. Res. (s)* 44 (1988)
- (3)-R. Pummerer, E. Buchta; *Ber.* 69B,1005 (1936).
- (4)-T. Fuchigami, K. Suzuki, T. Nonaka; *Electrochimica Acta* 35,239 (1990)

COMPLEXATION OF ELECTROCHEMICALLY REDUCED CROWN ETHERS INCORPORATING ANTHRAQUINONE NUCLEI WITH ALKALI METAL IONS.

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Selective molecular recognition of organic molecules by metal ions is a very interesting and important subject, because it is the basis of many biochemical processes and has wide application in many areas of chemistry, from the theoretical as well as from the practical point of view. Among the synthetic receptor molecules, ionophores such as macrocyclic crown ethers, have successfully been used for complexation. As well as showing ability to bind metal ions, they can also present characteristics of cationic selectivity owing to their selective complexation properties towards specific cations ^(1,2). If the crown ether is appended to electroactive groups which can be reversibly reduced and if they are in a favourable position to interact with the cation, this association behaviour and binding power to the metal ion can suffer a significant change ^(3,4). In this way, it is possible to extend this sensitive principle to enhance cation sensitivity and possibly discriminate among metal ions.

The host ligands presented in this study were prepared incorporating an anthraquinone subunit within a macrocyclic crown ether with six or seven oxygen atoms in the macroring (Scheme I). Li^+ , Na^+ and K^+ were the alkali cations studied.