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THE BENZILIC ESTER REARRANGEMENT.EVIDENCE FOR A SET PATHWAY IN THE BENZILIC ESTER AND/OR ACID REARRANGEMENT

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Summary.Benzil and 9,10-phenanthrenoquinone are transformed to the benzilic acid-type esters by the action of lithium *tert*-butoxide in tetrahydrofuran (THF)-benzene. The semidione of the diketone has been shown by ESR spectroscopy to be an intermediate.

It has been pointed out[1] that the benzilic acid rearrangement "...is something of an oddity, since it is one of the few *base*-catalyzed skeletal rearrangements that are known". Indeed,other base catalyzed rearrangements , e.g. the Wittig rearrangement , have been shown to involve free radical intermediates[2]. It is the purpose of this communication to provide experimental evidence , suggesting that the benzilic acid rearrangement may follow a SET pathway , and to describe the direct transformation of *vic*-diketones to the respective esters of benzilic-type acids by the action of lithium alkoxides, e.g. eq. (1).

$$ArC(=O)-C(=O)Ar + LiOBu^t \longrightarrow Ar_2C(OLi)CO_2Bu^t \qquad (1)$$

Ar = Ph , *tert-butyl benzilate, 96%* ;Ar,Ar = 2,2'-biphenylyl, *tert-butyl 9-hydroxy-fluorene-9-carboxylate, 73% ,m.p. 99-100* ^{0}C *(hexane)* .

The reaction with lithium *tert*-butoxide appears to be very clean, while with other alkoxides is less so, or even fails with certain ones, e.g. LiOEt , under our conditions[3]. Our attempts to rearrange benzil with lithium dialkylamides, $LiNR_2$ (R = Et, *i*-Pr) , were unsuccessful, eq. (2).

$$PhC(=O)-C(=O)Ph + LiNR_2 \not\longrightarrow Ph_2C(OLi)CONR_2 \qquad (2)$$

Intensive coloration develops upon mixing aromatic *vic*-diketones with LiOR in THF solvent. Benzil gives a violet solution , and 9,10-phenanthrenoquinone a brownish-red solution . At this stage the reaction mixture is paramagnetic. For example, a solution of benzil and $LiOBu^t$ in benzene-THF (99:1 v/v %), exhibited the ESR spectrum shown in Fig.1 , which is assigned to the lithium semidione of benzil[4]. On the basis of this evidence the following SET mechanism is suggested for benzilic ester and/or acid rearrangement, Scheme 1 .

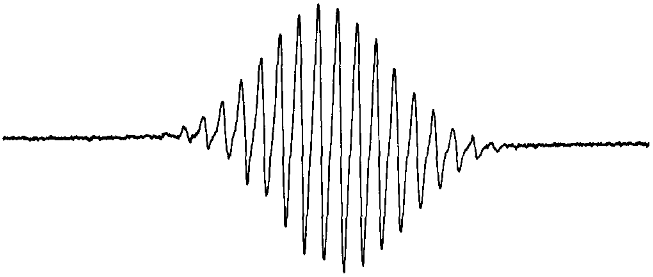
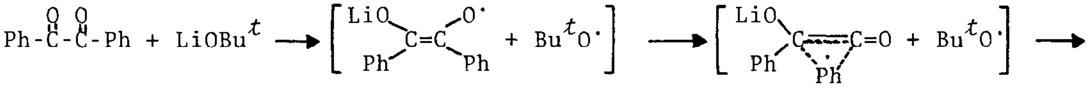


Fig.1 (See the text)

SCHEME 1



$Ph_2C(OLi)CO_2Bu^t$

Namely, we suggest that benzilic ester and/or acid rearrangement is of the "neophyl" type, but here the migrating Ph radical is π-bonded to a ketenic system, rather than to a simple olefinic double bond[5]. The geminate radical RO˙ must play some important role in the transformation. This is suggested by the fact that, although LiOEt converts benzil to the relevant semidione ,it fails however to cause rearrangement.

In conclusion, benzilic acid and/or ester rearrangement appears to occur through a SET pathway, as do other base catalyzed reactions, i.e.the Meerwein-Ponndorf-Verley reductions[6] and the Cannizzaro reaction[7].

REFERENCES

1. A.L.Ternay, "Contemporary Organic Chemistry",W.B.Saunders Co.Philadelphia,1976 ,p.493
2. U.Schlosser, Angew.Chem.Internat.Edit.9,763(1970)
3. Solvent:THF-C_6H_6 (70:30 v/v %),48 h at room temp. under argon, followed by a 3.5 h reflux, careful hydrolysis with iced water.
4. See e.g. N.L.Bauld,J.Am.Chem.Soc.,87,4788 (1965)
5. J.W.Wilt,in "Free Radicals" Vol.1, J.K.Kochi, ed. Wiley, N.Y.1973,chapter 8
6. C.G.Screttas and C.T.Cazianis, Tetrahedron,34,933(1978);E.C.Ashby, A.B.Goel and J.N. Argyropoulos,Tetrahedron Lett. 23,2273(1982)
7. E.C.Ashby,D.T.Coleman III and M.P.Gamasa, *ibid.* 24,851(1983); Sung-Kee Chung, J.C.S. Chem.Commun. 480(1982)

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