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ALCOXIDE CLEAVAGE OF BENZOYL-t-BUTYL-DIIMIDE: CARBANION AND RADICAL MECHANISMS

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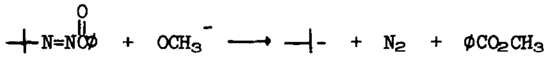
Diimides or their conjugate bases have been proposed to be intermediates in the Wolff-Kishner reaction (1,2), the McFadyen-Stevens rearrangement (3), the hydrolysis of aryl-azoformate esters (4), the acid and base hydrolysis of benzoyl-phenyldiimide (5), the alcoxide cleavage of alkyl-benzoyldiimides (6), and the base cleavage of 1-aryl-2-tosyl-hydrazides (7).

The idea that it might be possible to generate carbanions from diimide anions, 1, is originally due to Cram (2) but so far if carbanions are intermediates in these reactions (1,7),

1 $$R\text{-}N{=}N^- \longrightarrow R^- + N_2$$

they have been generated in protic solvents and captured by protons and it is complicated to distinguish the intermediacy of R-N=N$^-$ from R-N=N-H (8).

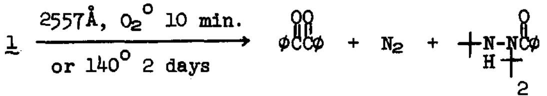
In this communication we show how carbanions can be generated via the diimide route in the absence of proton donors both in heterogeneous and homogeneous systems (9). The reaction studied here involves the proposed alcoxide cleavage of benzoyl-t-butyldiimide, 2.

2 

$$-\!\!\!+\!N{=}N\overset{\overset{O}{\|}}{C}\phi + OCH_3^- \longrightarrow -\!\!|^{-} + N_2 + \phi CO_2CH_3$$

1

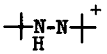
N-Benzoyl-N′-t-butylhydrazine, from t-butyl hydrazine and methyl benzoate (10) was oxidized with yellow mercuric oxide to benzoyl-t-butyldiimide, 1. Compound 1 is a dark red oil, ir 1720 cm^{-1}, b.p. 78°/0.7 mm, τ 2.13-2.81 (multiplet, 5H), 8.68 (singlet 9H). This compound decomposes, 3, rapidly at 0° in light (medium pressure mercury lamp) or slowly at 140°, with evolution of nitrogen to give a mixture of benzil and N, N′-di-t-butyl-N-benzoylhydrazine, m.p. 73-74°, 2. An isomer of 2, m.p. 154-156°, 3, was isolated in later work, see below.

3 

$$1 \xrightarrow[\text{or } 140^{\circ}\text{ 2 days}]{2557\text{Å},\ O_2\ 0^{\circ}\ 10\text{ min.}} \phi\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\phi + N_2 + +\underset{H}{N}-\underset{+}{N}\overset{O}{\overset{\|}{C}}\phi$$

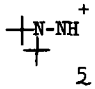
2

Compounds 2 and 3 were distinguished by means of their nmr spectra, 2 gives two equal t-butyl lines whereas 3 gives only one, and the presence of a cation m/e 143 (M^{+}-φCO) in the mass spectrum of 2, absent in that of 3. Mass 143 is more likely to be 4 than 5;, hence, 3 is N, N-di-t-butyl-N′-benzoylhydrazine. These results establish that the t-butyl radical adds to



$+\underset{H}{N}-N+^{+}$

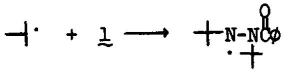
4



$+\underset{+}{N}-NH^{+}$

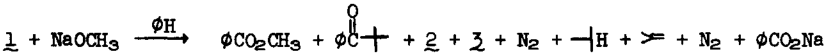
5

the nitrogen adjuacent to carbonyl in 1.

4 

$$\dashv\cdot + 1 \longrightarrow +N-\underset{\cdot +}{N}\overset{O}{\overset{\|}{C}}\phi$$

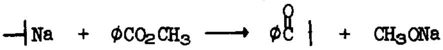
Compound 1 reacts with a variety of bases such as hydroxides, amides, alcoxides, phenoxide and sodium oxide in benzene, toluene, pentane, dioxane, THF and DMF. For instance, the slow addition, at room temperature, over two hours, of 1, 0.1 M in benzene to an equimolar suspension of sodium methoxide in benzene (oxygen and moisture-free system) results in the immediate evolution of nitrogen together with, after work-up, methyl benzoate (11), 2,2-dimethylpropiophenone, 3, isobutane, sodium benzoate isobutylene and 2. No biphenyl was detected among these products.

5 

$$1 + NaOCH_3 \xrightarrow{\phi H} \phi CO_2CH_3 + \phi\overset{O}{\overset{\|}{C}}+ + 2 + 3 + N_2 + \dashv H + \succ\!= + N_2 + \phi CO_2Na$$

20% 19% 1% 1% 65% 20% 10% 70% 30%

Clearly, the first five of these products come from the carbanion route, 2, followed by the well-known types of addition and abstraction reactions, 6 to 8. On the other hand, the

6 

$$\dashv Na + \phi CO_2CH_3 \longrightarrow \phi\overset{O}{\overset{\|}{C}}\dashv + CH_3ONa$$

7(12) 

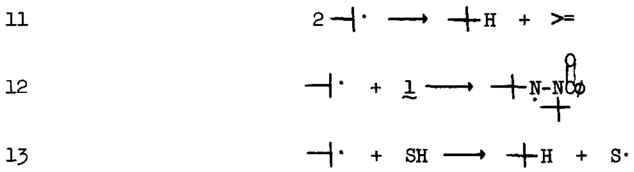
$$\dashv Na + 1 \longrightarrow \times\!\underset{\times}{N}-\bar{N}\overset{O}{\overset{\|}{C}}\phi Na^{+}$$

8 $\dashv Na + SH \longrightarrow \dashv H + SNa$

remaining products must come from radicals, steps 11 to 13. Note that

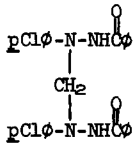
9 $1 + NaOCH_3 \longrightarrow \dashv\cdot + N_2 + \phi CO_2\dot{C}H_3^{-}Na^{+}$

10 $Na^{+}\phi CO_2\dot{C}H_3^{-} \longrightarrow \phi CO_2Na + (CH_3\cdot)$



$\underset{\sim}{2}$ is already known to come from the t-butyl radical and $\underset{\sim}{1}$.

To account for the above results and for the formation of sodium benzoate it is necessary to also postulate an alcoxide induced initiation of radicals, which is faster than the thermal decomposition of $\underset{\sim}{1}$. Steps 9 and 10 are most closely in accord with the data. This sequence involves C-O cleavage (13).



$$\begin{array}{c} p\text{Cl}\phi\text{-N-NH}\overset{O}{\overset{\|}{C}}\phi \\ | \\ \text{CH}_2 \\ | \\ p\text{Cl}\phi\text{-N-NH}\overset{O}{\overset{\|}{C}}\phi \end{array}$$

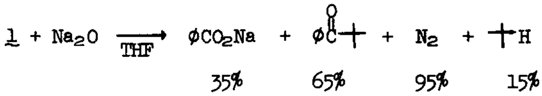
$\underset{\sim}{6}$

When $\underset{\sim}{1}$ is reacted with sodium methoxide in benzene in the presence of bromine, the only products are t-butylbromide and methyl benzoate. There is no sodium benzoate formed. This means, any $\phi\text{CO}_2\dot{\text{C}}\text{H}_3^-$ formed via 9 is oxidized back to the ester by bromine (14).

$$\begin{array}{lllllll} 14 \quad \underset{\sim}{1} + \text{NaOCH}_3 + \text{Br}_2 \longrightarrow & \dashv\text{Br} & + & \text{N}_2 & + & \phi\text{CO}_2\text{CH}_3 \\ & 75\% & & 80\% & & 80\% \end{array}$$

Finally, radical formation is avoided entirely in the sodium oxide fragmentation of $\underset{\sim}{1}$ in THF, 15. This supports the suggestion that radical formation requires the C-O bond originally in alcoxide to cleave.

15



$$\begin{array}{lllllllll} \underset{\sim}{1} + \text{Na}_2\text{O} \xrightarrow[\text{THF}]{} & \phi\text{CO}_2\text{Na} & + & \phi\overset{O}{\overset{\|}{C}}\text{-}t\text{Bu} & + & \text{N}_2 & + & t\text{BuH} \\ & 35\% & & 65\% & & 95\% & & 15\% \end{array}$$

In summary, we find here that carbanion compounds can be generated via the diimide route. In the present example, it appears that the alcoxide fragmentation of $\underset{\sim}{1}$ proceeds by both an anion and a radical path (15). It is interesting that the reaction of $\underset{\sim}{1}$ with t-butyl anion, 7, and radical, 4, is selective.

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(11) Sodium benzoate was detected in the product mixture before work-up.

(12) The 1, 4 addition of organometallics to acylazo compounds is well-known, see R. Stolle and W. Reichart, J. Prakt. Chem., 122, 2, 344 (1929).

(13) The fate of ($CH_3\cdot$) could not be determined; neither methane, ethane, hydrogen nor dimethyl ether were detected among the reaction products. Running the reaction in the presence of cyclohexane gave no norcarane. It is most likely that this fragment is ultimately incorporated in dimeric compounds from 1, that is, the unaccounted part of the mass balance. Such a dimer has been isolated by Hoffmann (6), 6, from methoxide fragmentations of p-chlorophenylbenzoyldiimide.

(14) Since bromine could capture t-butyl radical or anion, we need not be concerned with the details of t-butylbromide formation, just that sodium benzoate formation is suppressed.

(15) In the presence of oxidizing agents such reactions give radical products, Ref. 5.