CHEMISTRY LETTERS, pp. 1329-1330, 1980. © The Chemical Society of Japan 1980

FORMATION OF ARYL RADICALS FROM NITROSOARENES BY THE REACTION WITH DIPHENYLMETHYLENEAMINO RADICALS

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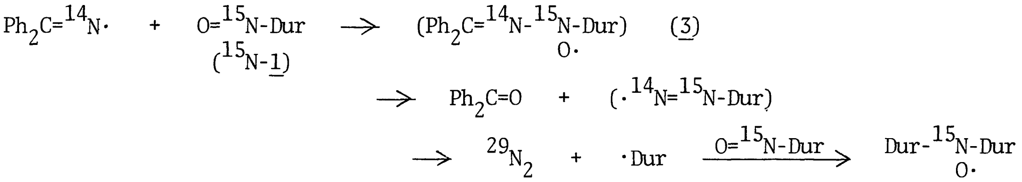
By the reaction between nitrosoarenes and diphenylmethyleneamino radicals at 60 - 70 °C aryl radicals are generated together with nitrogen and benzophenone.

Nitrosoarenes yielded aryl radicals together with nitrogen and ketones when they came to react with iminyl radicals and these transformations induced often confusions in the studies of radical reactions by spin trapping techniques. In the spin trapping reaction using 2,3,5,6-tetramethylnitrosobenzene (1) (nitrosodurene) and bis(diphenylmethylenecarbamoyl) peroxide (2) in benzene in an Ar atmosphere at 60 - 70 °C, we observed an ESR signal of diduryl nitroxide.1) To elucidate the course of the formation of diduryl nitroxide, we studied the products formed in the spin trapping reaction using glpc and mass spectrometry and deduced a possible mechanism of formation of diduryl nitroxide as follows:



$$\mathrm{Ph_2C{=}^{14}N\cdot} \quad + \quad \underset{(^{15}\mathrm{N}\text{-}1)}{\mathrm{O{=}^{15}N\text{-}Dur}} \longrightarrow (\mathrm{Ph_2C{=}^{14}N\text{-}}\underset{\mathrm{O\cdot}}{^{15}\mathrm{N}}\mathrm{\text{-}Dur}) \quad (3)$$

$$\longrightarrow \mathrm{Ph_2C{=}O} \quad + \quad (\cdot{}^{14}\mathrm{N}{=}^{15}\mathrm{N\text{-}Dur})$$

$$\longrightarrow {}^{29}\mathrm{N_2} \quad + \quad \cdot\mathrm{Dur} \xrightarrow{\mathrm{O{=}^{15}N\text{-}Dur}} \mathrm{Dur\text{-}}\underset{\mathrm{O\cdot}}{^{15}\mathrm{N}}\mathrm{\text{-}Dur}$$

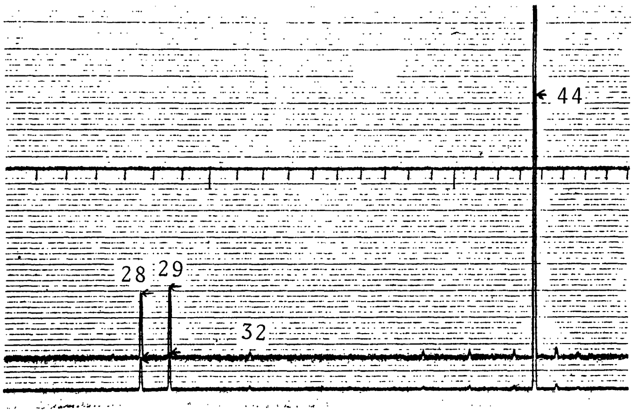
(Dur stands for duryl group.)

We heated a toluene solution of 1 and 2 at 60 °C for 65 min, 10 times as long as the half life of the decay of 2, and determined the products by glpc. The results are listed in the Table. In the presence of 1 in 2 moles or more against 1 mole of 2, the free iminyl radicals were completely captured by 1 except those consumed in the cage reaction (ca. 2% of 2). Benzophenone was produced when 1 was present in the reaction mixtures. The formation of benzophenone from diphenylmethyleneamine by hydrolysis or by oxidation was excluded by blanc experiments.

We then isolated the gas formed in the spin trapping reaction in toluene using ^{15}N-1 and ^{14}N-2 in a mole ratio 2:1 , and analyzed the gas by mass spectrometry (electron: 70 eV). The ion peaks measured between M^+/e 20 and 50 are shown in the Figure. The peroxide 2 evolved $^{44}CO_2$, and $^{44}CO_2$ gave ^{28}CO by a fragmentation reaction. Very small amounts of $^{32}O_2$ and $^{28}N_2$ of air were detected. The formation of $^{29}N_2$ indicates clearly the bond making between diphenylmethyleneamino

Table. PRODUCTS FORMED IN THE THERMOLYSIS OF 2 IN TOLUENE IN THE PRESENCE AND ABSENCE OF 1 (60 °C)

Mole ratio	Yield (mole% per mole 2)			
1/2	$Ph_2C=O$	$Ph_2C=NH$	$Ph_2C=N-N=CPh_2$	$Ph_2C=N-CH_2Ph$
0.0	trace	112	24.5	37.3
0.9	—	—	3.9	trace
1.1	54	111	—	—
1.8	—	—	2.7	trace
2.0	65	119	—	—
2.8	—	—	1.8	trace
2.6	84	123	—	—



Figure

nitrogen and nitrosodurene nitrogen, producing a nitroxide 3. The nitroxide 3 was however not identified by the ESR method.

The formations of diaryl nitroxides were also observed in the spin trapping reactions using 2 and nitrosoarenes such as 2,4,6-trimethylnitrosobenzene, 2,6-dimethylnitrosobenzene, and 2,6-dimethyl-4-t-butylnitrosobenzene.[1)]

The generation of duryl radical, benzophenone, and nitrogen in the spin trapping reaction using 1 and 2 can be explained supposing the formation of a transient nitroxide 3, and a fragmentation of 3 according to the manner similar to the oxidation of benzophenone phenylhydrazone with manganese dioxide where phenyl radical, nitrogen and benzophenone are produced.[2)]

We are very grateful to Dr. Hiroshi Hirota of the University of Tokyo who analyzed the gases by mass spectrometry.

References

1) T. Suehiro, S. Masuda, N. Motoyama, M. Kamimori, M. Yoshida, and K. Tokumaru, Chem. Lett., 1980, 985.

2) Ila Bhatnagar and M. V. George, J. Org. Chem., 32, 2252 (1967).

(Received July 14, 1980)