A new method for dehydrogenation of symmetric hydrazo compound

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A new synthetic route with N-bromosuccinimide (NBS) and pyridine as oxidation system to dehydrogenate symmetric hydrazo compounds for preparing azo compounds is reported for the first time. Eight azo compounds are prepared in good yields under mild conditions and possible mechanism has been suggested.

Azo compounds have been widely utilized as dyes and analytic reagents. Recently, many noteworthy studies show that azo benzene derivatives possess very good optic memory and photoelectric properties. Optical-switching and image storage can be made by azobenzene liquid crystal film. Research on the preparation of azo compounds has attracted new interest since conventional methods for preparing azo compounds have certain limitations.

In our laboratory, we have successfully dehydrogenated aryl substituted semicarbazides to N-2-diaryl diazenecarboxamides and aryl substituted carbazides to bisaryl carbodiazones using NBS and pyridine as oxidizing agent. In this note we report the dehydrogenation of hydrazo compounds using NBS as oxidant (Scheme I). Compared with the oxidants already exploited for dehydrogenation of hydrazo compounds to prepare azo compounds, such as EtONa, NaOX, KFer(CN)₆ in alkali solution and NO₃⁻, NBS as an oxidant has been found to be a superior one, since dehydrogenation with NBS requires simple instruments and the reaction can be carried out at room temperature and in a short time.

ArNHNHAr + CH₂COOHBr, C₂H₄N → ArN=NAr

Scheme I

Experimental Section

General. Melting points were determined with Kofler micro melting point apparatus and are uncorrected. IR spectra in KBr were recorded on a SP3-300 spectrophotometer; UV spectra on a Perkin-Elmer Lamabda-17 UV/VIS spectrophotometer (USA); 'H NMR spectra in CDCl₃ on a JEOL-Fx-90Q spectrometer using TMS as internal standard; and MS spectra on a KRATOS-AEI-MS50 (UK) spectrometer. Elemental analyses were performed on a Carlo-Erba 1102 elemental analyzer. M⁺ values and C, H, N analyses were within the experimental error.

Symmetric hydrazo compounds are prepared according to literature method.

Dehydrogenation of hydrazo compounds. To a solution of hydrazo compound 1 (1 mmole) in 10 mL dichloromethane was added pyridine (1 mmole). While shaking the solution continuously NBS (1.02 mmole) was added portionwise during 5-6 min. The solution was thus turned into orange-red or deep-red and was allowed to stand at room temperature for another 5 min. The solution was washed with water (2x15 mL), 10% sodium hydroxide (1x10 mL), and water again (2x15 mL). The resulting solution was dried for 2 hr over anhydrous magnesium sulfate. After removing the solvent under reduced pressure, orange, yellow, orange-red or red crystals were obtained. The crystals were chromatographed on a column of silica (60-100 mesh) and eluted with petroleum ether (60-90°C) for purification (Table I).

Results and Discussion

Each of the symmetric hydrazo compounds gives a sharp absorption peak while the products do not show any absorption peak at 3300-3500 cm⁻¹ in the IR spectra, indicating that hydrogen atoms on the hydrazo compounds have been dehydrogenated. Other physical constants further confirmed the formation of -N=N- bond (Table I).

Hydrazo compounds are sensitive since they undergo rearrangement or semi-rearrangement easily in acid environment. Thus they are usually dehydrogenated in strong alkali circumstances as mentioned above. But in the present note a milder method using pyridine (a weak base) and NBS has been reported for the dehydrogenation of hydrazo compounds.
Table I—Characterization data of compound 2

<table>
<thead>
<tr>
<th>Compd 2</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>UV (λmax, nm)</th>
<th>'H NMR (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6H5</td>
<td>80.4</td>
<td>65-67 (67-68)</td>
<td>320</td>
<td>7.35-7.80(m, 10H, ArH)</td>
</tr>
<tr>
<td>p-CH3C6H4</td>
<td>99.5</td>
<td>143-45 (144)</td>
<td>366</td>
<td>2.42 (s, 6H, 2CH3), 7.30-7.85(dd, 8H, ArH)</td>
</tr>
<tr>
<td>p-CIC6H4</td>
<td>93.6</td>
<td>186-88 (188)</td>
<td>331</td>
<td>7.45-8.10(dd, 8H, ArH)</td>
</tr>
<tr>
<td>o-CH3C6H4</td>
<td>92.2</td>
<td>54-55 (55)</td>
<td>330</td>
<td>2.40(s,6H, 2CH3), 7.30-7.85(dd, 8H, ArH)</td>
</tr>
<tr>
<td>o-CIC6H4</td>
<td>90.4</td>
<td>135-36 (137)</td>
<td>320</td>
<td>7.45-8.10(m, 8H, ArH)</td>
</tr>
<tr>
<td>o-BrC6H4</td>
<td>87.6</td>
<td>185-86 (187)</td>
<td>326</td>
<td>7.42-8.00(m, 8H, Ar)</td>
</tr>
<tr>
<td>o-CH3OC6H4</td>
<td>84.8</td>
<td>151-53 (153)</td>
<td>354</td>
<td>3.90(s, 6H, 2CH3), 7.00-8.00(m, 8H, ArH)</td>
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<tr>
<td>1-naphthyl</td>
<td>90.6</td>
<td>188-89 (190)</td>
<td>345</td>
<td>7.20-8.10(m, 12H, ArH)</td>
</tr>
</tbody>
</table>

Scheme II

Mechanism
Bromination with NBS usually proceeds through a free radical mechanism. NBS was reported to undergo homolytic fission into succinimidy radical and bromine atom by irradiation with light. In this experiment, one mole of NBS can dehydrogenate two moles of hydrogen atoms in daylight and we deduce the reaction probably proceeds through a free radical mechanism as shown in Scheme II wherein succinimide is almost recovered quantitatively from the washings of water and sodium hydroxide solution.

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References