Note

Polyethylene glycol mediated reductive
decyanation of diphenylacetonitrile
moderately enhanced by microwave heating

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An efficient and clean procedure for the preparation of
alkyl diphenylmethanes and 4,4-diphenylbutylamines from their
corresponding nitriles by using sodium hydroxide-polyethylene
glycol reagent system in a domestic microwave oven is described.
The products are isolated by simple aqueous work up in excellent
yields.

The utilization of nitrile function, for the stabilization
of carbanion at α-carbon atom, and its use for C-C
bond formation reaction occupies an important
position in organic synthesis. For the preparation of
alkyl diphenylmethanes removal of a nitrile group
from corresponding diphenylacetonitriles by one step
reductive decyanation, could be a better way, than the
hydrolysis followed by decarboxylation. A number of
methods have been reported for decyanation such as
dehydration, oxidative decyanation, and reductive decyanation by metal hydride, transition metal complexes, electrolysis, alkali metal in
various solvents and by potassium hydroxide fusion
method. Some disadvantages of these methods are,
long reaction period, expensive reagent and some
times formation of side products like carboxylic acid
or reduction to primary amine.

In recent years the applications of microwave
irradiation in organic synthesis are increasing very
rapidly, due to advantages like short reaction time,
suppressions of side products, less polluting processes
and at the same time excellent yields. We report here
in the reductive decyanation of alkyl diphenyl-
acetonitriles by using sodium hydroxide-PEGs in
domestic microwave oven.

In the preliminary experiment of reacting
diphenylacetonitrile with sodium hydroxide–PEG-400
reagent system, diphenylacetamide and diphenylacetic
acid were not found in the product, but only
diphenylmethane formed within 2 min. To confirm it,
the evolved gas was trapped in \( \text{NH}_3\text{OH-CuSO}_4 \) indicator. Its decolourization indicated the presence of
HOCN, formed in the process of reductive
decyanation (Scheme I).

In a standardized procedure, the diphenylacet-
onitrile was irradiated under microwave for 2 min. in
the presence of sodium hydroxide and PEG-400. The
formation of diphenylmethane in high yield was
observed even at low concentration of sodium
hydroxide (25mmoles) and the reaction was
marginally faster in potassium hydroxide–PEG
systems.

In decyanation PEG exhibited a crown ether type
role. Alkali disappeared rapidly during irradiation,
**Scheme II**

**Table I**—Reductive decyanation of alkyldiphenyl-acetonitriles under microwave irradiation

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>R^+ / Y^-</th>
<th>Yield (%)</th>
<th>mp/bp °C</th>
<th>(°C/Torr/Lit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>-H</td>
<td>98</td>
<td>260-62</td>
<td>(120/10)</td>
</tr>
<tr>
<td>2.</td>
<td>-CH_2CH_3</td>
<td>93</td>
<td>280-82</td>
<td>(145/18)</td>
</tr>
<tr>
<td>3.</td>
<td>-(CH_2)_2CH_3</td>
<td>90</td>
<td>271-72</td>
<td>(138/15)</td>
</tr>
<tr>
<td>4.</td>
<td>-(CH_2)_3CH_3</td>
<td>92</td>
<td>268-70</td>
<td>(157/30)</td>
</tr>
<tr>
<td>5.</td>
<td>-CH_3Ph</td>
<td>85</td>
<td>53-54</td>
<td>(54)</td>
</tr>
<tr>
<td>6.</td>
<td>-(CH_2)_5CH_3</td>
<td>92</td>
<td>268-70</td>
<td>(157/30)</td>
</tr>
<tr>
<td>7.</td>
<td>-CH_2COOH</td>
<td>89</td>
<td>Viscous liq.</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>-CH_2COOH</td>
<td>89</td>
<td>157-58</td>
<td>(157)</td>
</tr>
<tr>
<td>9.</td>
<td>N-Phenyl</td>
<td>68</td>
<td>290-93</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>N-Methyl</td>
<td>71</td>
<td>287-89</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>Morpholine</td>
<td>81</td>
<td>Viscous liq.</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>Pyrrolidine</td>
<td>65</td>
<td>257-60</td>
<td>(150/15)</td>
</tr>
<tr>
<td>13.</td>
<td>Piperidine</td>
<td>72</td>
<td>278-80</td>
<td>(171HCl)</td>
</tr>
</tbody>
</table>

(a) Yields are of isolated and purified products. All products were characterized by IR, HNMR spectral data and their physical constant data.

* Refer to Scheme II, Table I, entry no. 1 to 8
† Refer to Scheme I, Table I, entry no. 9 to 13

As it complexed with PEG. When aqueous sodium hydroxide–PEG system was used as solvent, instead of decyanated diphenylmethane product, the diphenylacetamide and diphenylacetic acid the hydrolyzed products were formed. The PEGs being water-soluble, in aqueous solution there was no possibility of complex formation with Na+. Decyanation also did not take place in solvents like ethylene glycol, DMSO, DMF and with or without phase transfer catalyst (Aliquat-336). These observations confirmed the importance of PEGs for reductive decyanation reaction.

Using PEGs like PEG-200, PEG-400, PEG-600, PEG-1500 and PEG-4000 yield of decyanated product increased as the molecular weight of PEG increased. Reaction was stopped at 30 sec, 60 sec, and 90 sec however no significant change was observed in the

**Figure 1**—Transformation of diphenylacetonitrile to diphenylmethane by conventional heating and microwave irradiation yields of decyanated product once the reaction was allowed to expose to microwave for 2 min. A number of alkyldiphenylacetonitriles on reacting with sodium hydroxide–PEG-400 reagent system gave quantitative yields of the corresponding alkyldiphenylmethanes (Scheme II, Table I, entry No. 1-8). Using the same methodology a few 4,4-diphenylbutylamines, which are reported to be antilipidperoxidative, neuroleptic and antihypertensive agents were also prepared (Scheme I, Table I, entry No. 9-13).

The reductive decyanation by conventional heating and that by microwave heating (Figure 1) were compared to know whether the reaction rate is truly enhanced by the latter. For the transformation of diphenylacetonitrile to diphenylmethane 1hr was required by conventional heating at 225 °C and isolated yield was 96%, whereas under microwave irradiation 98% yield was obtained in just 2 min (Figure 1).

In conclusion, a simple and efficient method has been developed for the synthesis of alkyldiphenylmethanes by reductive decyanation of corresponding nitriles using less amount of sodium hydroxide. Reductive decyanation reaction could be accelerated by microwave irradiation.

**Experimental Section**

The microwave oven used for the reaction was a Kelvinator T-37 magicook model modified for condenser attachment with a power output of 700 watts (microwave oven operating at 2450 MHz frequency). Infrared spectra were recorded on Jasco FTIR 410 spectrometer. The HNMR spectra in CDCl_3 were recorded on a Varian 360 L spectrometer using TMS as internal standard (chemical shifts in δ,
ppm). unit. Solvents were purified using standard procedure.

**General procedure for the reductive decyanation.** A mixture of alkylated diphenylacetonitrile (5 mmole), PEG-400 (10 mL) and sodium hydroxide (25 mmole) was irradiated in a microwave oven for 2 to 3 minutes. The reaction mixture was allowed to cool to room temperature and then poured into ice-cold water. The organic layer was extracted with heptane or pet. ether (50 mL). The combined organic extracts were washed with water, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo to afford the product. All alkyldiphenylmethanes were purified by passing through a column of silica using toluene-petroleum ether as eluent.

**References**