

Table I<sup>12</sup>

ArSO <sub>2</sub> CHYZ $\xrightarrow{RX}$ ArSO <sub>2</sub> (R)YZ						
Ar	Y	Z	RX	Yield, %	Mp, °C <sub>1</sub>	
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	Br	C <sub>2</sub> H <sub>5</sub> Br	67	98–100	
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	Br	C <sub>4</sub> H <sub>9</sub> Br	68	41–42 <sup>a</sup>	
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	60	79–81 <sup>b</sup>	
C <sub>6</sub> H <sub>5</sub>	Cl	Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	84	145–147	
C <sub>6</sub> H <sub>5</sub>	Cl	Cl	C <sub>2</sub> H <sub>5</sub> Br	72	74–76	
C <sub>6</sub> H <sub>5</sub>	Br	Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	75	168–170	
1- <i>p</i> -Tolylsulfonyl-1-bromocyclopropane				73	138–140	
1,6-Di- <i>p</i> -tolylsulfonyl-1,1,6,6-tetrachlorohexane <sup>d</sup>				87	214.5–216	

<sup>a</sup> Bp 146–149° (0.1 mm). <sup>b</sup> Lit.<sup>13</sup> mp 79–82°. <sup>c</sup> Alkylation with ethylene dibromide. <sup>d</sup> Molar ratio of dichloro sulfone to dibromobutane 2:1.

Table II<sup>12</sup>

Mp, °C				
R <sup>1</sup>	R <sup>2</sup>	Yield, %	Obtained	Lit. <sup>3</sup>
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	90	105–107	106–107
CH <sub>3</sub>	CH <sub>3</sub>	91	94–95	93.5–94
C <sub>6</sub> H <sub>5</sub>	H	60	153–154	157–159 dec
(CH <sub>3</sub> ) <sub>2</sub> CH	H	65	82–84	
(CH <sub>2</sub> ) <sub>5</sub>		90	54–55	54–55

tolyl sulfone (3.06 g, 15 mmol), 50% aqueous sodium hydroxide (10 ml), acetonitrile (2 ml), TEBA (0.05 g), and acetone (1.04 g, 18 mmol) were stirred at 30–35° (mild exothermic effect) for 45 min. The product was isolated and purified by crystallization (carbon tetrachloride–hexane) (Table II, second entry).

4.  $\alpha,\alpha$ -Dichloropropyl Phenyl Sulfone. Dichloromethyl phenyl sulfone (2.25 g, 10 mmol), ethyl bromide (1.3 g, 12 mmol), 50% aqueous sodium hydroxide (10 ml), and TEBA (0.05 g) were vigorously stirred at 35–40° for 1 hr (exothermic effect). The mixture was diluted with water and the product was isolated and crystallized from methanol (Table I, fifth entry).

## References and Notes

- Paper LXI in the series Reactions of Organic Anions. Part LX: A. Jończyk and M. Mąkosza, *Rocz. Chem.*, in press.
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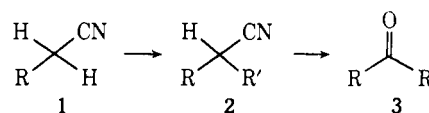
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The Oxidative Decyanation of Secondary Nitriles via  $\alpha$ -Hydroperoxynitriles

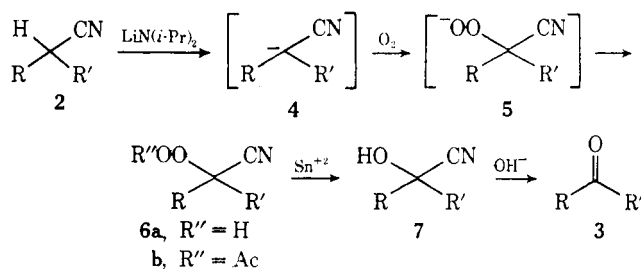
**Summary:** The oxidative decyanation of secondary nitriles to ketones was effected by trapping nitrile anions with molecular oxygen, reducing the resulting  $\alpha$ -hydroperoxynitriles to cyanohydrins with stannous chloride, and converting the cyanohydrins to ketones with sodium hydroxide.

**Sir:** To demonstrate the functional equivalence of primary nitriles 1 as acyl carbanion equivalents<sup>1</sup> required methodology for effecting the monoalkylation<sup>2</sup> of 1 and the oxidative decyanation of secondary nitriles 2 to ketones 3. Proce-



dures which accomplish the latter transformation (2  $\rightarrow$  3) effect the oxidation of nitriles to cyanohydrins via intermediate  $\alpha$ -chloro,<sup>3</sup>  $\alpha$ -iodo,<sup>4</sup> and  $\alpha$ -thiophenoxynitriles<sup>5</sup> and subsequent conversion of the cyanohydrins to ketones. Few procedures, however, allow for the direct introduction of an oxygen substituent  $\alpha$  to a nitrile.<sup>6</sup> We now wish to report a general oxidative decyanation procedure which realizes this objective.

Secondary nitrile anions 4 generated using lithium diisopropylamide trapped molecular oxygen at  $-78^\circ$  to afford lithium  $\alpha$ -cyanohydroperoxides 5. Quenching 5 with aqueous acid or acetyl chloride provided the isolable  $\alpha$ -hydroperoxynitrile<sup>7</sup> 6a or the acetate derivative 6b, respectively. The reduction of 5 with an acidic stannous chloride solution<sup>8</sup> furnished the cyanohydrin 7. Subsequent exposure of 7 to aqueous sodium hydroxide afforded the ketone 3 in good overall yield from the nitrile 2 (Table I).<sup>9</sup> For example, 2 (R = CH<sub>2</sub>Ph; R' = CH<sub>3</sub>) was sequentially converted to 6a, 7, and 3 in isolated yields of 92, 89, and 98%, respectively. In contrast to reported oxidative decyanation procedures,<sup>4,5</sup> this methodology was applicable to the synthesis of dialkyl ketones as well as alkyl aryl and diaryl ketones from 2. Primary nitriles 1 afforded only low yields of al-



**Table I**  
The Oxidative Decyanation of  
Secondary Nitriles 2 to Ketones 3

R	R'	Isolated yield of ketone 3, %
CH <sub>3</sub>	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	67
CH <sub>3</sub>	c-C <sub>6</sub> H <sub>11</sub>	78
CH <sub>3</sub>	CH <sub>2</sub> Ph	82
CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	90
CH <sub>2</sub> Ph	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	83
CH <sub>2</sub> Ph	c-C <sub>6</sub> H <sub>9</sub>	70
	-(CH <sub>2</sub> ) <sub>5</sub> -	64 <sup>a</sup>
Ph	CH <sub>3</sub>	86
Ph	CH <sub>2</sub> CH <sub>3</sub>	69
Ph	CH(CH <sub>3</sub> ) <sub>2</sub>	81
Ph	c-C <sub>6</sub> H <sub>11</sub>	74
<i>p</i> -FPh	CH <sub>3</sub>	92
<i>p</i> -ClPh	CH <sub>3</sub>	79
$\alpha$ -Np	CH <sub>3</sub>	80
<i>p</i> -PhPh	CH <sub>3</sub>	82
Ph	Ph	92

<sup>a</sup> Isolated as the 2,4-dinitrophenylhydrazone derivative.

dehydes<sup>10</sup> 3 (R' = H). However, secondary carboxylic esters underwent  $\alpha$ -hydroxylation in good yield.<sup>11</sup>

The following is a typical experimental procedure. To a solution of 1.1 mmol of lithium diisopropylamide in 3.0 ml of THF at  $-78^\circ$  under a nitrogen atmosphere was added 145 mg (1.0 mmol) of 2 (R = CH<sub>2</sub>Ph; R' = CH<sub>3</sub>) in 1.0 ml of THF. Dry oxygen gas was bubbled (250 ml/min) into the lithionitrile solution for 30 min at  $-78^\circ$ . The reaction was quenched with 2 ml of 1 M stannous chloride in 2 M hydrochloric acid and allowed to stir for 30 min at 0°. Following an ether-water work-up procedure which involved washing with 1 M sodium hydroxide, the product was chromatographed on Merck silica gel F254 to afford 110 mg (82%) of phenylpropanone which was identical with an authentic sample.<sup>12</sup>

### References and Notes

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- (5) S. J. Selikson and D. S. Watt, *Tetrahedron Lett.*, 3029 (1974).
- (6) Previous reports on the oxidation of nitriles were limited to aryl substituted acetonitriles, failed to isolate the intermediate  $\alpha$ -hydroperoxynitriles, and noted the formation of dimeric products: (a) M. S. Kharasch and G. Sosnovsky, *Tetrahedron*, **3**, 97 (1958); (b) H. G. Aurich, *Tetrahedron Lett.*, 657 (1964); (c) S. S. Kulp, *Org. Prep. Proced.*, **2**, 137 (1970). In our hands, these procedures failed to convert dialkylacetonitriles to ketones.
- (7)  $\alpha$ -Hydroperoxynitriles 6a have also been prepared from azobisnitriles R<sub>2</sub>C(CN)N=NC(CN)R<sub>2</sub>: (a) M. Talat-Erben and N. Onol, *Can. J. Chem.*, **38**, 1154 (1960); (b) L. Dulog and W. Vogt, *Tetrahedron Lett.*, 5169 (1966).
- (8) Other reducing agents [H<sub>2</sub>, NaBH<sub>4</sub>, P(OCH<sub>3</sub>)<sub>3</sub>, Zn-HOAc] were effective but less convenient than stannous chloride which was reported to effect the quantitative reduction of alkyl hydroperoxides to alcohols: D. Barnard and K. R. Hargraves, *Anal. Chim. Acta*, **5**, 476 (1951).
- (9) All compounds had ir, nmr, and mass spectral data in accord with assigned structures. The acetate derivatives 6b, isolated in a majority of instances, gave satisfactory elemental analyses.
- (10) For example, phenylacetonitrile and 3-phenylpropionitrile afforded benzaldehyde and phenylacetaldehyde in 43% and 8% yield, respectively. The formation of carboxylic acids in the oxidation step of the sequence accounted for the low yields of aldehydes.
- (11) For example, methyl cyclohexanecarboxylate afforded the  $\alpha$ -hydroxy derivative in 69% yield. Similar  $\alpha$ -hydroxylations of carboxylic esters have recently been reported: (a) E. Vedejs, *J. Amer. Chem. Soc.*, **96**,

- 5944 (1974); (b) P. E. Pfeffer and L. S. Silbert, U.S. Patent 3,652,612 (March 28, 1972) [*Chem. Abstr.*, **76**, 139938z (1972)].  
(12) We would like to thank the Research Corporation for their financial support and the University of Colorado for a Summer Research Initiation Faculty Fellowship.

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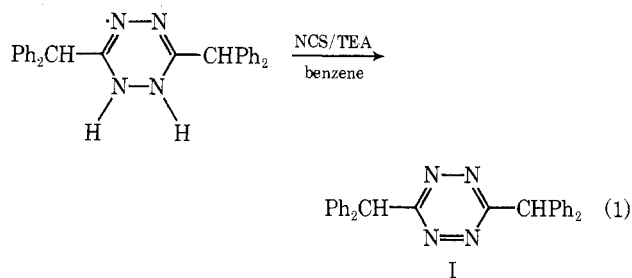
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### A Mild and Efficient Oxidizing Agent for Dihydroxybenzenes

**Summary:** A mild, efficient oxidizing reagent, *N*-chlorosuccinimide-triethylamine complex, is reported for the conversion of *o*-quinones from catechols and diphenyldiazomethane from benzophenone hydrazone and oxidative coupling of anthrone to bianthrone.

**Sir:** In the course of the preparation of the tetrazine I (e.g., reaction 1), we discovered a marked activation effect of triethylamine (TEA) on the oxidation reactions of *N*-chlorosuccinimide (NCS).



Preliminary experiments indicate that the TEA-NCS reagent is a mild oxidizing agent for the conversion of catechols to *o*-quinones, hydroquinones to *p*-quinones, benzophenone hydrazone to diphenyldiazomethane, and *p*-toluenesulfonylhydrazide to *p*-toluenesulfonyl chloride and the coupling of anthrone to bianthrone. While the scope and limitations of this reagent are still under investigation, we report here on the oxidation of some dihydroxybenzenes.

There exists a number of methods for the oxidation of hydroquinones and catechols to quinones. Chromic and nitric acids,<sup>1-3</sup> ferric chloride,<sup>4,5</sup> silver oxide,<sup>6</sup> silver carbonate/Celite,<sup>7</sup> manganese dioxide,<sup>8</sup> sodium dichromate,<sup>9</sup> sodium chlorate/vanadium pentoxide,<sup>10</sup> thallium triacetate,<sup>11</sup> iodic acid,<sup>12</sup> ceric ammonium nitrate,<sup>13</sup> and *o*-chloranil<sup>14</sup> have been used for this transformation. Pfitzner-Moffatt<sup>15</sup> type oxidations have also been employed recently by Martin, *et al.*,<sup>16</sup> to convert hydroquinone to quinone.

Scheme I is indicative of the efficacy of the TEA-NCS reagent.

The reaction is rapid (~10 min), quantitative (*via* nmr and ir), and takes place under mild conditions ( $-25$  to  $0^\circ$ ). In the case of catechol oxidations, only the red form of the *o*-quinone was observed.

The following control experiments are indicative of the specific effect of TEA: (1) the hydroxy benzenes did not react with NCS in the absence of TEA, and (2) contrary to recent reports on other aliphatic hydroxyl oxidations,<sup>16,17</sup> the hydroxy benzenes *did not* react with NCS in the presence of dimethyl sulfide (DMS) and the absence of TEA.

To our knowledge, TEA-NCS has not been used in the past as an oxidizing reagent. However, pyridine was used in the moderate yield NCS oxidation of alcohols to ketones.<sup>18</sup>