to the u,u conformer by adding a π-acid such as tetracyanoethylene, benzoquinone, or dinitrobenzene to the NMR samples. Although an immediate coloration was noticed (particularly in the case of tetracyanoethylene), we did not, unfortunately, detect a significant change of the ratio of the high-field singlets.

Experimental Section

General Procedure. All ^{1}H NMR spectra were recorded on a Varian HA-100 spectrometer. VPC analyses were conducted on a Varian 2800 chromatograph equipped with a flame ionization detector using either a SE-30 or a QF-1 column ($^1/_8$ in. × 8 ft). Preparative runs were conducted on a Varian 90-P instrument. All irradiation was carried out on a "merry-go-round" apparatus[6] with irradiation samples degassed and sealed in the usual manner.[7]

Bis(3,3-dimethylbutyroyl)durene (7). The Friedel–Crafts reaction was conducted in the usual manner. A mixture of 40 g (0.3 mol) of anhydrous $AlCl_3$, 200 mL of CS_2, 28 mL (0.2 mol) of dimethylbutyroyl chloride, and 6.78 g (0.05 mol) of durene after refluxing for 10 h and usual workup yielded 12.5 g of a white crystalline solid (78%), mp 221–222 °C, after recrystallization from benzene. The spectral data are consistent with the expected bis acylated product: ^{1}H NMR ($CDCl_3$) δ 1.24, 2.19, 2.86 (3 s, relative intensity 9:6:2); MS M^+ 330; IR (Nujol) 1680 cm^{-1}.

Bis(1-hydroxy-3,3-dimethyl-1-butyl)durene (8). Diketone 7 (9.9 g, 0.03 mol) was reacted with 8.48 g (0.3 mol) of $LiAlH_4$ at refluxing THF (250 mL) for 2 days giving 6.11 g of the diol: ^{1}H NMR ($CDCl_3$) δ 5.3 (diastereotopic AB signals). Without further purification the crude product was used for the next step.

Bis(3,3-dimethyl-1-butenyl)durene (1). Dehydration of the diol 8 (5.0 g) was accomplished with the aid of a Dean–Stark trap with 250 mL of benzene and catalytic amounts of β-naphthalenesulfonic acid. The hydrocarbon was purified by chromatography on a silica gel column, giving 1.68 g of a white solid (12.5% yield from 8). Spectral data are consistent with the expected product with the t,t geometry: ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 18 H), 2.20 (s, 12 H), 5.58 (d, 2 H, J = 17 Hz), 6.30 (d, 2 H, J = 17 Hz); MS M^+ 298; IR (neat) 968, 1360, 1460 cm^{-1}.

***cis,cis*-1.** A solution of 0.2 g of *t,t*-1, 0.5 g of benzophenone, and 25 mL of hexane was deoxygenated with a stream of N_2 and irradiated with light ≥320 nm. The end mixture contained approximately 85% *c,c*-1 and 15% *c,t*-1. The dicis isomer, a viscous oil, was purified by preparative GLC: ^{1}H NMR ($CDCl_3$, room temperature) δ 0.83, 0.86 (*tert*-butyl, 2:1), 2.18, 2.20 (benzylic CH_3's, 1:2), 5.55 (d), 6.18 (2 d, coupled vinylic H's, J = 12.5 Hz).

Bis(3,3-dimethylbutyroyl)mesitylene (9) was obtained in the same manner as 7: 62% yield; mp 108–109 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 18 H), 2.08 (s, 3 H), 2.16 (s, 6 H), and 2.58 (s, 4 H); MS M^+ 316.

Bis(3,3-dimethyl-1-butenyl)mesitylene (2) was obtained by $LiAlH_4$ reduction of 9 followed by acid-catalyzed dehydration following the procedure described for 8 and 1. The reduction reaction apparently failed to reach completion because, from the final product mixture, the expected product 2, mp 34.6–36 °C (44%), was isolated along with small amounts (13%) of the ketostyrene 3. The spectral data for 2 are: ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 18 H), 2.21 (3, 9 H), 5.60 (d, 2 H, J = 17 Hz), 6.18 (d, 2 H, J = 17 Hz); MS M^+ 284; IR (Nujol) 955, 1250, 1346, 1445 cm^{-1}. And those for 3 are: ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 18 H), 2.12, 2.18 (6 s, 9 H), 2.58 (s, 2 H), 5.65 (d, 1 H, J = 17 Hz), 6.13 (d, 1 H, J = 17 Hz); IR 960, 1350, 1450, 1695 cm^{-1}.

***cis,cis*-2** was obtained in the same manner as *cis,cis*-1: ^{1}H NMR ($CDCl_3$, room temperature) δ 0.90, 0.94 (s, 1:1.3, *tert*-butyl), 2.16 (br s, benzylic CH_3's), 5.48 (d, J = 12.5 Hz), 5.95, 6.03 (two sets of d, J = 12.5 Hz). See text for high-temperature spectra.

***cis*-3** was obtained by irradiation in the presence of benzophenone. The conversion was complete within 3 h. The product was isolated by column chromatography on silica gel (petroleum ether 30–60 °C): ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 1.15 (s, 9 H), 2.15–2.2 (3 s, 9 H), 2.60 (s, 2 H), 5.62 (d, 1 H, J = 13 Hz), 6.00 (d, 1 H, J = 13 Hz), 6.84 (br s, 1 H).

***cis*-4** was obtained by $LiAlH_4$ reduction of *cis*-3 in a manner similar to that described for 8. The product was isolated by chromatography over silica gel (benzene): ^{1}H NMR ($CDCl_3$) δ 0.89, 0.92 (2 s, 9 H), 1.06 (s, 9 H), 1.36 (d, 1 H), 1.47 (s, 1 H), 2.02 (dd, 1 H), 2.16 (s, 3 H), 2.36 (br s, 6 H), 5.20 (d, 1 H), 5.55, 5.98 (d and d, 1 H, 1 H, J = 13 Hz), 6.66 (s, 1 H). At temperatures above 130 °C the two high-field singlets coalesce into an averaged singlet. At room temperature in the presence of $Eu(fod)_3$ shift reagent, the singlet at δ 1.06 also split into two singlets. IR (neat) 735, 1360, 1470, 3480 cm^{-1}.

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Registry No. *t,t*-1, 71734-33-3; *c,c*-**1**, 71734-34-4; *c,t*-**1**, 71734-35-5; *t,t*-**2**, 71766-68-2; *c,c*-**2**, 71734-36-6; *trans*-**3**, 71734-37-7; *cis*-**3**, 71734-38-8; *cis*-**4**, 71734-39-9; **7**, 71734-40-2; **8**, 71734-41-3; **9**, 71734-42-4; dimethylbutyroyl chloride, 7065-76-5; davene, 95-93-2.

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Conversion of Nitriles to Amides and Esters to Acids by the Action of Sodium Superoxide

Nathan Kornblum* and Saraswathi Singaram

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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To our surprise, we have found that sodium superoxide smoothly converts nitriles to amides at room temperature. The utility of this transformation is apparent from Table I, in which yields refer to pure isolated products.

Our surprise derives from the fact that the cyano group is reported to be stable to superoxides.[1-3] It well may be that our choice of solvent is responsible for the discrepancy; whereas previous workers used benzene,[1] pyridine,[2] and acetonitrile,[2] we employ Me_2SO. Another, probably less significant, difference is that the previous workers used potassium superoxide and 18-crown-6 ether (to enhance the solubility of the superoxide), while we employ the sodium salt without a crown ether.

Our understanding of the mechanism of this conversion of a nitrile to an amide by sodium superoxide is meager. The fact that benzonitrile on treatment with potassium superoxide in dry benzene containing 18-crown-6 ether fails to react after 2 days at ambient temperature[1] and that cinnamonitrile is stable to superoxide in pyridine[2] does not rule out the possibility that superoxide in Me_2SO is capable of directly attacking a cyano group. But it certainly encourages one to consider alternate mechanisms.

Thus, although we employed dry reagents and reasonable precautions, we made no effort rigorously to exclude moisture. Adventitious water would react with superoxide as shown in eq 1,[4] and this would likely be followed by a

$$H_2O + 2O_2^{-}\cdot \rightarrow HO^- + HOO^- + O_2 \tag{1}$$

$$HOO^- + Me_2SO \rightarrow HO^- + Me_2SO_2 \tag{2}$$

second reaction–that of eq 2.[5] The sodium hydroxide so

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[1] J. San Filippo, Jr., L. J. Romano, C. Chern, and J. S. Valentine, *J. Org. Chem.*, **41**, 586 (1976).

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Table I. Conversion of Nitriles to Amides[a]

nitrile	reaction time, h	amide	yield, %
n-undecyl cyanide	8	*n*-undecylamide	70
cyclohexyl cyanide	7	cyclohexylcarboxamide	85
benzonitrile	6	benzamide	78
isophthalonitrile	2	isophthalamide	85
o-chlorobenzonitrile	16[c]	*o*-chlorobenzamide	80
m-methoxybenzonitrile	3	*m*-methoxybenzamide	80
p-methoxybenzonitrile	21[c]	*p*-methoxybenzamide	88
p-cyano-α-nitrocumene	5	*p*-carboxamido-α-nitrocumene	68
2,6-dichlorobenzonitrile	31[c]	2,6-dichlorobenzamide	81
mesitonitrile	7	mesitamide	73
ethyl *p*-cyanobenzoate	5[d]	*p*-carboxamidobenzoic acid	96

[a] All reactions were carried out in Me_2SO at 25 °C, using 3 mmol of NaO_2 for each mmol of nitrile. Many of these reactions were carried out with exposure to two 20-W fluorescent lights; subsequently it has been found that such illumination is not necessary. [b] Pure, isolated product. [c] These reaction times are substantially reduced by nitrobenzene; see Discussion and Experimental Sections. [d] In minutes.

Table II. The Influence of Nitrobenzene[a]

nitrile	reaction time, h	mol % of nitrobenzene	nitrile recovered, %[b]	amide yield, %[b]
o-chlorobenzonitrile	2	0	58	15
	2	20	44	35
	2	50	22	60
	2	100	13	75
p-methoxybenzonitrile	2	0	64	15
	2	50	42	32
	2	100	6	77
	2	300	5	82
2,6-dichlorobenzonitrile	4	0	66	18
	4	20	50	27
	4	50	27	48
	4	100	7	74

[a] All reactions were carried out in Me_2SO at 25 °C, using 3 mmol of NaO_2 for each mmol of nitrile. [b] Pure, isolated material.

produced would be far more reactive than aqueous sodium hydroxide, and indeed, it is known that in the hydrolysis of nitriles sodium hydroxide in Me_2SO is ca. 10^4 times more effective than aqueous sodium hydroxide.[6,7] And, of course, any HOO^- which is not reduced by Me_2SO[8] would also convert the nitrile to an amide.[9]

The view that HO^- and/or HOO^- are responsible for the conversion of nitriles to amides has a fundamental deficiency–it does not provide a basis for explaining the fact that nitrobenzene catalyzes this reaction. As is shown in Table I, three of the nitriles studied, *o*-chlorobenzonitrile, *p*-methoxybenzonitrile, and 2,6-dichlorobenzonitrile, react relatively slowly with NaO_2. However, as can be seen from Table II, the addition of nitrobenzene produces an unambiguous increase in the rate of conversion of these nitriles to the corresponding amides.

This ability of nitrobenzene to catalyze the nitrile to amide transformation may be related to the fact that nitrobenzene reacts rapidly and reversibly with superoxide according to eq 3.[13,14] The resulting nitrobenzene radical anion is

$$O_2^{-}\cdot + C_6H_5NO_2 \rightleftarrows C_6H_5NO_2^{-}\cdot + O_2 \qquad (3)$$

an excellent electron transfer agent; if the reasonable assumption is made that its sodium salt is more soluble in Me_2SO than sodium superoxide,[14] then the overall result ought to be that nitrobenzene facilitates electron transport from the relatively insoluble superoxide to the nitrile. However, any mechanism which invokes one-electron transfer to the cyano group is suspect because of the relatively high voltage needed for the one-electron reduction of the cyano group.[16]

Thus, as stated at the outset, our understanding of the matter of mechanism is, indeed, meager. But, clearly, any attempt to provide a rationale for the nitrile to amide trans formation will have to cope with the fact of nitrobenzene catalysis.

In 1976 it was reported that esters are cleaved at ambient temperature by potassium superoxide in benzene containing 18-crown-6 ether.[1,15] It transpires that esters are cleaved much more rapidly by sodium superoxide in Me_2SO. Thus, in addition to the last entry of Table I, we have found that dimethyl terephthalate is converted to terephthalic acid in 15 min (97% yield), methyl laurate gives a 91% yield of lauric acid after 3 h, and methyl myristate gives an 85% yield of myristic acid in 8 h.

Experimental Section

Most of the products are known compounds. They were purified, usually by recrystallization, and characterized by melting point, by their infrared and NMR spectra, and in several instances by elemental analysis. The following is typical of the procedure employed.

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(5) M. J. Gibian and T. Ungermann [*J. Org. Chem.*, 41, 2500 (1976)] have shown that Me_3COO^- and Me_2SO react very rapidly at room temperature to give Me_3CO^- and Me_2SO_2. It is, therefore, likely that HOO^- would quickly be reduced to HO^- by Me_2SO under our conditions; see ref 8, however, for a contrary view.

(6) W. Roberts and M. C. Whiting, *J. Chem. Soc.*, 1290 (1965).

(7) Indeed, formation of the highly reactive sodium hydroxide in Me_2SO may conceivably occur via the alternate route of eq a–c.[2,9,10,11,12,5]

$$O_2^{-}\cdot + Me_2SO \rightarrow HOO\cdot + {}^{-}CH_2SOCH_3 \qquad (a)$$

$$HOO\cdot + O_2^{-}\cdot \rightarrow HOO^- + O_2 \qquad (b)$$

$$HOO^- + Me_2SO \rightarrow HO^- + Me_2SO_2 \qquad (c)$$

(8) C. Chern, R. DiCosimo, R. DeJesus, and J. San Filippo, Jr., *J. Am. Chem. Soc.*, **100**, 7324 (1978).

(9) M. J. Gibian and T. Ungermann, *J. Am. Chem. Soc.*, 101, 1291 (1979).

(10) D. T. Sawyer, M. J. Gibian, M. M. Morrison, and E. T. Seo, *J. Am. Chem. Soc.*, **100**, 627 (1978).

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(13) R. Poupko and I. Rosenthal, *J. Phys. Chem.*, **77**, 1722 (1973).

(14) G. A. Russell and A. G. Bemis, *Inorg. Chem.*, **6**, 403 (1967).

(15) The cleavage of esters by electrochemically generated $O_2^{-}\cdot$ in DMF, and in pyridine, is also known [F. Magno and G. Bontempelli, *J. Electroanal. Chem.*, **68**, 337 (1976)]; for a discussion of the mechanism of this reaction see ref 2.

(16) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, 1970, p 335.

Conversion of Cyclohexyl Cyanide to Cyclohexylcarboxamide. A three-neck flask fitted with two addition tubes,[17] a two-way stopcock, and a magnetic stirrer was employed. The system was swept with dry air while being assembled, and a positive pressure of dry air was maintained throughout the reaction. One addition tube contained 1.78 g (ca. 32 mmol) of 90+% sodium superoxide (Alfa Inorganics), which had been powdered in a mortar and pestle under dry nitrogen in a glove bag and then transfered to the tared tube in the glove bag. The other addition tube held 1.0 g (9.2 mmol) of cyclohexyl cyanide. Finally, 15 mL of Me_2SO[18] (dried by standing over type 4A molecular sieves) was placed in the flask. Stirring was instituted, the nitrile was added to the Me_2SO without opening the flask,[17] and after it had dissolved the NaO_2 was introduced. The resulting mixture was stirred for 7 h at room temperature, after which it was poured into ice-water and extracted with ethyl acetate. The ethyl acetate solution was washed with water and dried (anhydrous Na_2SO_4), and the solvent was removed by vacuum evaporation at room temperature; this gave 0.980 g of white crystals, mp 178–182 °C. Recrystallization from water gave 0.93 g (85% yield) of pure cyclohexylcarboxamide: mp 186–187 °C (lit.[19] mp 185–186 °C); IR (KBr) 3340, 3180, 1630 cm^{-1}.

Conversion of Mesitonitrile to Mesitamide. This was carried out as in the cyclohexyl cyanide case using 10 mL of Me_2SO, 1.0 g (7 mmol) of mesitonitrile, and 1.3 g (ca. 23 mmol) of the 90+% NaO_2. The resulting mixture was stirred for 7 h and then poured into ice-water. Dry ice was added to reduce the alkalinity, and when the solid CO_2 was gone the mixture was extracted with chloroform. The chloroform extracts were washed with water and dried, and the solvent was removed by vacuum evaporation. The resulting pale yellow solid (1.0 g) melted from 100 to 177 °C. It was dissolved in acetone and treated with Norite at the boiling point for several minutes, the mixture was filtered, and the solvent was evaporated. The resulting white solid (mp 103–180 °C; 0.95 g) was leached several times with cold water, and the aqueous extracts were vacuum evaporated at ca. 35 °C. This gave 0.1 g of white crystalline dimethyl sulfone, mp 105–108 °C (lit.[20] mp 107–108 °C). This material exhibits IR and NMR spectra identical with those reported for dimethyl sulfone.[21] This was the only case in which chloroform was used for extraction and the only time that Me_2SO_2 was isolated.

The water-insoluble material was dried and recrystallized from benzene and 0.8 g (73% yield) of mesitamide (mp 186–188 °C) was obtained: lit.[22] mp 187–188 °C; IR (KBr) 3400, 3260, 3180, 1640 cm^{-1}.

Conversion of *p*-Cyano-α-nitrocumene to *p*-Carboxamido-α-nitrocumene. The procedure was that of the cyclohexyl cyanide case except that this was one of the first systems studied, thus dry oxygen was employed instead of dry air and the reaction vessel was exposed to two 20-W fluorescent lights. Ten milliliters of Me_2SO, 0.5 g (2 mmol) of the nitrile, and 0.65 g (ca. 11 mmol) of NaO_2 were allowed to react at room temperature for 5 h. Workup gave 0.4 g of a white solid, mp 150–155 °C, which was recrystallized from benzene: 0.37 g (68% yield); mp 155–156 °C; NMR (Me_2SO-d_6) δ 1.95 (s, 6 H), 3.3 (s, 2 H), 7.35–7.95 (m, 4 H); IR (KBr) 3300, 3200, 1660, 1610, 1520, 1340, 850, 790 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.68; H, 5.80; N, 13.45. Found: C, 57.65; H, 5.56; N, 13.30.

Conversion of Methyl Laurate to Lauric Acid. Here again, an oxygen atmosphere and two 20-W fluorescent lights were employed; it is highly probable that they are not needed. Otherwise the procedure was the same as that used for cyclohexyl cyanide. A mixture consisting of 2 g (9 mmol) of methyl laurate, 1.4 g (ca. 27 mmol) of NaO_2, and 30 mL of Me_2SO was stirred at room temperature for 3 h. The product was poured into ice-water and then sodium laurate was isolated by filtration. It was suspended in water, and the mixture was acidified with 25% hydrochloric acid; the lauric acid was isolated by filtration, washed with water, and dried: 1.65 g (91% yield), mp and mmp 44–45 °C (lit.[23] mp 44 °C).

The Influence of Nitrobenzene. The reaction of *p*-methoxycyanobenzene in the presence of 50 mol % of nitrobenzene is typical of the experiments summarized in Table II. The procedure used for cyclohexyl cyanide was followed except that 0.54 mL (50 mol %) of nitrobenzene was introduced after the NaO_2. The initially yellow suspension gradually became brown. After 2 h at room temperature, the reaction mixture was worked up in the usual way. The pale yellow solid (1.67 g) so obtained melts from 48–152 °C. It was washed with pentane and recrystallized from benzene. This gave 0.5 g of pale yellow crystals, mp 165–167 °C, which after being dissolved in acetone and treated with Norite gave white crystals of *p*-methoxybenzamide (0.49 g; 32% yield), mp 167–168 °C. The benzene mother liquor on evaporation yielded 0.79 g of material which was dissolved in acetone and treated with Norite. The 0.63 g of yellow solid so obtained had mp 55–59 °C. It was dissolved in benzene and chromatographed on silica gel. In this way 0.59 g (42% recovery) of white, crystalline *p*-methoxybenzonitrile, mp 57–59 °C, was obtained.

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Registry No. *n*-Undecyl cyanide, 2244-07-7; cyclohexyl cyanide, 766-05-2; benzonitrile, 100-47-0; isophthalonitrile, 626-17-5; *o*-chlorobenzonitrile, 873-32-5; *m*-methoxybenzonitrile, 1527-89-5; *p*-methoxybenzonitrile, 874-90-8; *p*-cyano-α-nitrocumene, 58324-82-6; 2,6-dichlorobenzonitrile, 1194-65-6; mesitonitrile, 2571-52-0; ethyl *p*-cyanobenzoate, 7153-22-2; *n*-undecylamide, 2244-06-6; cyclohexylcarboxamide, 1122-56-1; benzamide, 55-21-0; isophthalamide, 1740-57-4; *o*-chlorobenzamide, 609-66-5; *m*-methoxybenzamide, 5813-86-5; *p*-methoxybenzamide, 3424-93-9; *p*-carboxamido-α-nitrocumene, 71648-09-4; 2,6-dichlorobenzamide, 2008-58-4; mesitamide, 4380-68-1; *p*-carboxamidobenzoic acid, 6051-43-0; terephthalic acid, 100-21-0; dimethyl terephthalate, 120-61-6; methyl laurate, 111-82-0; lauric acid, 143-07-7; methyl myristate, 124-10-7; myristic acid, 544-63-8; dimethyl sulfone, 67-71-0; sodium superoxide, 12034-12-7.

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Tetracyclopropylethylene Glycol

Jack W. Timberlake* and Young M. Jun

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122

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As part of our interest in cyclopropyl chemistry, we have prepared tetracyclopropylethylene glycol.[1-3] While the diol has been reported,[4] no synthetic procedure is available, although it was probably prepared from tetracyclopropylethylene. The latter has been reported from at least three routes, each of which is either long and tedious[5,6] (six steps from dicyclopropyl ketone), produces a mixture of products[7] (the pyrolysis of the tosylhydrazone salt of dicyclopropyl ketone gives five products), or gives low yields (6% overall,[5,6] 11%,[7,8] 7%[9]).

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