Reaction of Pyrazine-2,3-dicarbonitrile and 1,3-Dimethyllumazine with Alkyl Radicals

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Pyrazine-2,3-dicarbonitrile (**1**) reacts with alkyl radicals to give mono- **3** and di-alkylated pyrazine-2,3-dicarbonitriles **4**. Similarly 1,3-dimethyllumazine (**2**) reacts with alkyl radicals to give 7-alkyl-1,3-dimethyllumazines **8** as the major product. The reactivity of alkyl radicals decreases in the order tertiary, secondary, and primary, and **1** is more reactive than **2** in those radical substitution reactions.

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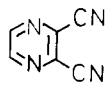
Pyrazine-2,3-dicarbonitrile is a typical π-deficient nitrogen heterocycle and undergoes substitution reactions with nucleophiles such as amines and alcohols [1]. Alkyl radicals have nucleophilic character and have been reported to react with protonated pyridine or quinoline derivatives [2] and also with an unprotonated 5-arylpyrazine-2,3-dicarbonitrile [3].

Pyrazine-2,3-dicarbonitrile (**1**) can be transformed into pteridines by first substitution of one of the nitrile groups with amino group [4]. Thus alkylated pyrazine-2,3-dicarbonitriles are expected to be transformed into alkylated pteridines. It has been reported that lumazine, pteridine-2,4-dione, reacts with acyl radicals to give an acyllumazine [5]. In structure-reactivity relationships, the carbonitrile group on the pyrazine ring and the uracil moiety fused to the pyrazine ring must affect the reactivity to alkyl radicals in different ways. Those prospects prompted us to carry out the radical alkylation of pyrazine-2,3-dicarbonitrile (**1**) and 1,3-dimethyllumazine (**2**) and the results are reported here.



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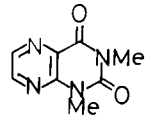

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Alkyl radicals were generated by silver(II)-mediated oxidation of carboxylic acids by peroxodisulfate (equation 1) as reported by Minisci *et al* [6].

$$R\text{-}COOH \xrightarrow{AgNO_3\text{-}NH_4S_2O_8} R\cdot + CO_2 + H^+$$

Equation 1

A mixture of pyrazine-2,3-dicarbonitrile (**1**), carboxylic acid, ammonium peroxodisulfate, and silver nitrate in ethanenitrile-water (4:1) was heated under nitrogen. The reaction of **1** with 2,2-dimethylpropanoic acid gave a single product, 5-(*t*-butyl)pyrazine-2,3-dicarbonitrile (**3a**), but the reaction with 2-methylpropanoic acid gave diisopropylpyrazine-2,3-dicarbonitrile (**4b**) in addition to a monoisopropyl product **3b**. Similarly 2-ethylbutanoic acid gave a mono-, **3c**, and a dialkylated product **4c**. Propanoic acid also gives both mono-, **3d**, and diethyl substituted products **4d**. Similarly 3-phenylpropanoic acid gave a mono-, **3e**, and a dialkylated product **4e**. The structures of **3** and **4** were easily deduced by the replacement of one or two H-nmr signal due to the hydrogen on the pyrazine ring with the signal due to the alkyl group.

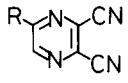
The product yields are shown in Table 1. The yield can be optimized under improved reaction conditions, but the values under the standard reaction conditions are listed to compare relative reactivities. When the reaction was carried out with one oxidation equivalent of peroxodisulfate (run 2), the product yield of **3a** decreased to about half with the recovery of **1**. This fact suggests that the reaction

Table 1

Radical Alkylation of Pyrazine-2,3-dicarbonitrile (**1**)

Run	Radical (R·)	Product Yield (%) **3**	**4**	Recovered **1** (%)
1 [a]	$-C(CH_3)_3$	94	—	—
2 [b]	$-C(CH_3)_3$	41	—	56
3 [a]	$-CH(CH_3)_2$	25	35	—
4 [a]	$-CH(CH_2CH_3)_2$	58	5	25
5 [a]	$-CH_2CH_3$	32	29	11
6 [c]	$-CH_2CH_3$	45	41	11
7 [a]	$-CH_2CH_2C_6H_5$	40	9	35
8 [a]	$-CH(OH)CH_3$	33	—	61
9 [c]	$-COCH_3$	21	[d]	43

[a] A mixture of **1** (1.0 mmole), carboxylic acid (1.2 mmoles), ammonium peroxodisulfate (1.4 mmoles), and silver nitrate (0.5 mmole) in 100 ml of ethanenitrile-water (4:1) was refluxed for 6 hours under nitrogen. [b] Compound **1** (1.0 mmole) carboxylic acid (1.2 mmoles), ammonium peroxodisulfate (0.5 mmole), silver nitrate (0.5 mmole), refluxed for 6 hours. [c] Compound **1** (1.0 mmole), carboxylic acid (3.0 mmoles), ammonium peroxodisulfate (4.0 mmoles), silver nitrate (0.5 mmole), reflux 7 hours. [d] The nmr spectrum of the crude product indicated the formation of diacetylated product but it is extremely unstable and darkens fast on tlc plate.



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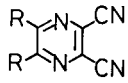

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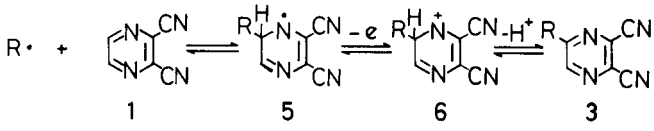
3a: R = $-C(CH_3)_3$ 3b,4b: R = $-CH(CH_3)_2$ 3c,4c: R = $-CH(CH_2CH_3)_2$

3d,4d: R = $-CH_2CH_3$ 3e,4e: R = $-CH_2CH_2C_6H_5$ 3f: R = $-CH(OH)CH_3$

3g: R = $-COCH_3$



1 5 6 3

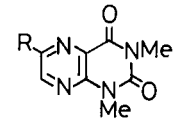
Equation 2

takes place in two steps; the oxidation of the carboxylic acid (equation 1) and a radical intermediate **5** (equation 2). The reactivity of alkyl radicals decreases in the order of tertiary, secondary, and primary. The ethyl radical gives lower amounts of the dialkylated product than the isopropyl radical. It is noteworthy that the **t**-butyl radical is the most reactive but it does not give the di-*t*-butylated product. That feature can be understood by the reaction scheme depicted in equation 2. The second alkylation proceeds *via* a radical intermediate corresponding to **5** and a cation intermediate corresponding to **6**. In those states the rupture of the *t*-butyl radical or *t*-butyl cation takes place in preference to the rupture of a hydrogen atom or a proton due to both stability of the *t*-butyl radical or cation and steric hindrance in the di-*t*-butylated product in which two bulky groups locate at *ortho*-positions. With the same reason, 5-arylpyrazine-2,3-dicarbonitrile does not give the *t*-butylated pyrazine on reaction with a *t*-butyl radical under oxidative conditions [3] though it reacts with an isopropyl radical under the same reaction conditions.

The 1-hydroxyethyl radical generated from 2-hydroxypropanoic acid gave a mono-alkylated product **3f** in moderate yield. Product **3f** is unstable and is transformed into an acetyl derivative by air oxidation on tlc plates and the oxidation product is identical to 4-acetylpyrazine-2,3-dicarbonitrile (**3g**) obtained by the reaction of 2-oxopropanoic acid under the same reaction conditions. 4-Acetylpyrazine-2,3-dicarbonitrile is also unstable and darkens, but the spectroscopic data support structure **3g**.

Alkylation of 1,3-dimethyllumazine (**2**) was carried out under the similar conditions to the case of pyrazine-2,3-dicarbonitrile and the results are shown in Table 2.

The *t*-butyl radical does not give a di-*t*-butylated product, but gives two mono-*t*-butylated products **7a** and **8a**. Product **7a** and **8a** were discriminated by ^{13}C-nmr spectroscopy (see Table 3). The ^{13}C-nmr signals due to the carbons other than C-6 and C-7 remain essentially in the same field but the signals due to C-6 and C-7 change dramatically in intensities and chemical shifts in the expected manner. The chemical shifts of C-6 and C-7 were assigned by considering the *para*-substituent to those carbons; amide carbonyl to C-7 and amide nitrogen to C-6. Alkyl substitution at C-6 or C-7 moves the chemical shift to lower field and weakens the intensity of the signals due to those carbons.



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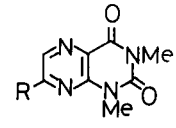

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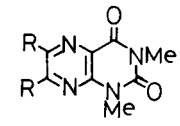

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7a,8a: R = $-C(CH_3)_3$ 8b,9b: R = $-CH(CH_3)_2$ 8c: R = $-CH(CH_2CH_3)_2$

8d,9d: R = $-CH_2CH_3$ 8e: R = $-CH_2CH(CH_3)_2$ 8f: R = $-COCH_3$

Table 2

Radical Alkylation of 1,3-Dimethyllumazine (**2**) [a]

Run	Radical (R·)	Product Yield (%) **7**	**8**	**9**	Recovered **2** (%)
1	$-C(CH_3)_3$	9	39	—	36
2	$-CH(CH_3)_2$	—	62	4	13
3	$-CH(CH_2CH_3)_2$	—	25	—	35
4	$-CH_2CH_3$	—	34	2	46
5	$-CH_2CH(CH_3)_2$	—	11	—	56
6	$-CH(OH)CH_3$ [b]	—	9	—	not isolated

[a] A mixture of **2** (1.0 mmole), carboxylic acid (1.5 mmoles), ammonium peroxodisulfate (1.5 mmoles), and silver nitrate (0.1 mmole) in 50 ml of ethanenitrile-water (4:1) was refluxed for 5 hours under nitrogen. [b] The product was **8f** formed by the secondary oxidation of the 1-hydroxyethyl group to the acetyl group.

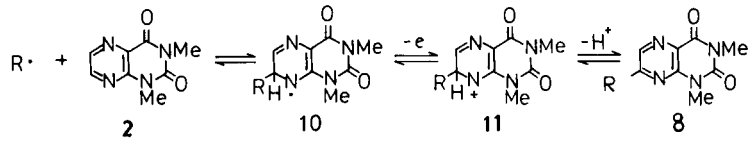
Table 3

^{13}C-NMR Chemical Shifts of Alkylated Lumazines [a]

Compound	C-2	C-4	C-4a	C-8a	C-6	C-7	N-Me	R
2	159.7	150.4	127.9	148.2	140.1	147.3	28.0, 29.3	
7a	160.0	150.6	126.0	146.0	160.2	144.4	28.8, 29.5	29.2, 36.6
8a	160.0	150.8	125.1	146.8	137.4	168.7	28.9, 29.5	29.0, 37.6
8b	160.0	150.7	125.5	147.5	138.9	166.6	28.8, 29.0	21.8, 34.4
8d	160.0	150.7	125.3	147.2	139.6	163.0	29.0, 29.2	12.6, 28.8

[a] Ppm from tetramethylsilane in deuteriochloroform. Peak assignment was done by off-resonance measurement.

On the reaction with **2**, an isopropyl radical gave a higher yield of products than a *t*-butyl radical, and it is in sharp contrast to the reaction of **1**. Steric situations of the reaction sites of **1** and **2** are essentially the same, and the difference in reactivity must derive from an electronic origin. The formations of radical adducts **5** and **10** are considered to be reversible and the equilibrium may be more unfavorable for **10** than for **5** due to the loss of a larger delocalization energy. Other features in the reac-



Equation 3

tion of **2**, however, are similar in those of **1**, and the *t*-butyl radical gives only mono-subtitution products whereas isopropyl and ethyl radicals gave disubstitution products **9**. In the reaction of **2**, those two radicals are less nucleophilic [7] and more regiospecific to attack the electron deficient C-7 position. On the other hand, *t*-butyl radical is more nucleophilic and attacks also the C-6 position in minor extent.

1,3-Dimethyllumazine (**2**) is less reactive than pyrazine-2,3-dicarbonitrile (**1**) to the present radical substitution. The competitive reaction with a *t*-butyl radical gave the products **3a** and **8a** in the ratio of 27:1. Similarly the competitive reaction with an isopropyl radical gave **3b** and **8b** in the ratio of 8.7:1 (see the Experimental for the conditions). Thus two carbonitrile groups in **1** withdraw π-electrons from the pyrazine ring more efficiently than the fused uracil moiety in **2** and hence the nucleophilic radical attacks **1** with greater ease.

The experimental findings described in this paper provide the synthetic methods of (C-7)-mono- and (C-6,7)-dialkylated lumazine. Naturally occuring pterines having a biological function, however, have a substituent at the (C-6)-position and efficient processes for the transformation of mono alkylpyrazine-2,3-dicarbonitrile (**3**) into a (C-6)-alkylated lumazine must be sought for the pterine syntheses from dimethylmaleonitrile.

EXPERIMENTAL

Reaction of Pyrazine-2,3-dicarbonitrile (**1**) with Alkyl Radicals.

An alkyl radical generated *in situ* was reacted with **1** under the reaction conditions recorded in Table 1. The reaction mixture was filtered to remove precipitates formed, and the volume was reduced under reduced pressure to *ca.* 1/5 volume, and extracted with chloroform (2 x 100 ml). The extract was washed with aqueous sodium hydrogen carbonate to remove unreacted carboxylic acid, and condensed under reduced pressure. The condensate was placed on tlc plates (25 g of silica gel on 20 x 20 cm glass plate) and eluted with chloroform. Extraction with ethyl acetate gave monoalkylated **3**, dialkylated pyrazinedicarbonitrile (**4**) in addition to the starting material **1** in the yields listed in Table 1.

Crystalline products were recrystallized from hexane or methanol-water. Oily products were distilled by a short-path distillation apparatus with a cold-finger type condenser. The ir spectra were measured in chloroform solutions. The ^{1}H-nmr spectra were measured in deuteriochloroform with TMS as the internal standard and coupling constants are recorded in Hz.

Compound **3a** melted at 63-64°; ir: 2975, 2260 cm^{-1}; ^{1}H-nmr: δ 1.45 (s, 9H), 8.81 (s, 1H).

Anal. Calcd. for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.70; H, 5.34; N, 30.19.

Compound **3b** (oil) had bp 117°/0.5 mm Hg; ir: 2980, 2255 cm^{-1}; ^{1}H-nmr: δ 1.25 (d, J = 6.5, 6H), 3.33 (septet, J = 6.5, 1H), 8.83 (s, 1H).

Anal. Calcd. for $C_9H_8N_4$: C, 62.78; H, 4.68; N, 32.54. Found: C, 62.65; H, 4.57; N, 32.71.

Compound **4b** melted at 117-119°; ir: 2980, 2260 cm^{-1}; ^{1}H-nmr: δ 1.33 (d, J = 6.5, 12H), 3.43 (septet, J = 6.5, 2H).

Anal. Calcd. for $C_{12}H_{14}N_4$: C, 67.27; H, 6.59; N, 26.15. Found: C, 67.40; H, 6.45; N, 26.43.

Compound **3c** has bp 98°/0.3 mm Hg; ir: 2975, 2255 cm^{-1}; ^{1}H-nmr: δ 0.84 (t, J = 7, 6H), 1.82 (double q, J = 7 and 6.5, 4H), 2.84 (quintet, J = 6.5, 1H), 8.71 (s, 1H).

Anal. Calcd. for $C_{11}H_{12}N_4$: C, 65.98; H, 6.04; N, 27.98. Found: C, 66.00; H, 6.19; N, 27.73.

Compound **4c** melted at 55° (bp 145°/10.3 mm Hg); ir: 2960, 2255 cm^{-1}; ^{1}H-nmr: δ 0.80 (t, J = 7, 12H), 1.76 (double q, J = 7 and 6.5, 8H), 2.88 (quintet, J = 6.5, 2H).

Anal. Calcd. for $C_{16}H_{22}N_4$: C, 71.08; H, 8.20; N, 20.72. Found: C, 71.04; H, 8.53; N, 20.47.

Compound **3d** boiled at 103°/0.4 mm Hg; ir: 2983, 2249 cm^{-1}; ^{1}H-nmr: δ 1.44 (t, J = 7, 3H), 3.01 (q, J = 7, 2H), 8.71 (s, 1H); ms: Calcd. for $C_8H_6N_4$: m/z = 158.0582. Found: m/z = 158.0609.

Anal. Calcd. for $C_8H_6N_4$: C, 60.75; H, 3.82; N, 35.42. Found: C, 60.17; H, 3.82; N, 35.34.

Compound **4d** melted at 69.5-70°; ir: 2992, 2250 cm^{-1}; ^{1}H-nmr: δ 1.40 (t, J = 7.5, 6H), 2.97 (q, J = 7.5, 4H).

Anal. Calcd. for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.31; H, 5.55; N, 29.86.

Compound **3e** melted at 114.5°; ir: 3030, 2942, 2252, 1603, 1501 cm^{-1}; ^{1}H-nmr: δ 3.14-3.27 (m, 4H), 6.97-7.45 (m, 5H), 8.52 (s, 1H).

Anal. Calcd. for $C_{14}H_{19}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.79; H, 4.18; N, 24.22.

Compound **4e** melted at 144.5-145°; ir: 3005, 2945, 2251, 1602, 1500 cm^{-1}; ^{1}H-nmr: δ *ca.* 3.1 (diffused m, 8H), 6.85 (m, 10H).

Anal. Calcd. for $C_{22}H_{18}N_4$: C, 78.08; H, 5.36; N, 16.56. Found: C, 78.28; H, 5.31; N, 16.45.

Compound **3f** (oil) had ir: 3300-3500, 2965, 2250 cm^{-1}; ^{1}H-nmr: δ 1.64 (d, J = 7, 3H), *ca.* 3.6 (broad, 1H), 5.19 (q, J = 7, 1H), 9.16 (s, 1H); ms: Calcd. for $C_8H_6N_4O$: m/z = 174.0542. Found m/z = 174.0575. Compound **3f** transformed partly into **3g** on the tlc plate.

Compound **3g** (oil) had ir: 2260, 1716 cm^{-1}; ^{1}H-nmr: δ 2.77 (s, 3H), 9.41 (s, 1H); ms: Calcd. for $C_8H_4N_4O$: m/z = 172.0390. Found: m/z = 172.0385.

Reaction of 1,3-Dimethyllumazine (**2**) with Alkyl Radicals.

An alkyl radical generated *in situ* was reacted with **2** under the reaction conditions recorded in Table 2. A similar work up as in the case of pyrazine-2,3-dicarbonitrile (**1**) but using chloroform-ethyl acetate (8:1 and 4:1) as eluent for tlc gave monoalkylated **7** and **8** and dialkylated lumazine **9** in addition to starting material **2** in the yield listed in Table 2.

The products were purified by recrystallization from methanol-water or sublimation at 100-110°/0.04-0.1 mm Hg. The ir and nmr spectra were measured as described in the former section.

Compound **7a** melted at 142-143°; ir: 2960, 1720, 1676 cm^{-1}; ^{1}H-nmr: δ 1.48 (s, 9H), 3.52 (s, 3H), 3.70 (s, 3H), 8.69 (s, 1H).

Anal. Calcd. for $C_{12}H_{16}N_4O_2$: C, 58.08; H, 6.50; N, 22.57. Found: C, 58.17; H, 6.54; N, 22.84.

Compound **8a** melted at 134-135°; ir: 2960, 1716, 1666 cm^{-1}; ^1H-nmr: δ 1.48 (s, 9H), 3.51 (s, 3H), 3.73 (s, 3H), 8.61 (s, 1H).

Anal. Calcd. for $C_{12}H_{16}N_4O_2$: C, 58.08; H, 6.50; N, 22.57. Found: C, 57.99; H, 6.42; N, 22.30.

Compound **8b** melted at 126°; ir: 2970, 1719, 1664 cm^{-1}; ^1H-nmr: δ 1.40 (d, J = 6.5, 6H), 3.25 (septet, J = 6.5, 1H), 3.55 (s, 3H), 3.74 (s, 3H), 8.49 (s, 1H).

Anal. Calcd. for $C_{11}H_{14}N_4O_2$: C, 56.40; H, 6.02; N, 23.92. Found: C, 56.28; H, 5.87; N, 24.18.

Compound **9b** melted at 157-158°; ir: 2965, 1718, 1660 cm^{-1}; ^1H-nmr: δ 1.36 (d, J = 6.5, 6H), 1.39 (d, J = 6.5, 6H), *ca.* 3.2-3.8 (m, 2H), 3.54 (s, 3H), 3.74 (s, 3H), 8.49 (s, 1H).

Anal. Calcd. for $C_{14}H_{20}N_4O_2$: C, 60.85; H, 7.29; N, 20.27. Found: C, 60.81; H, 7.31; N, 20.39.

Compound **8c** melted at 49-51°; ir: 2960, 1719, 1671 cm^{-1}; ^1H-nmr: δ 0.87 (t, J = 7, 6H), 1.85 (quintet, J = 7, 4H), 2.81 (quintet, J = 7, 1H), 3.47 (s, 3H), 3.71 (s, 3H), 8.39 (s, 1H).

Anal. Calcd. for $C_{12}H_{18}N_4O_2$: C, 59.53; H, 6.92; N, 21.36. Found: C, 59.19; H, 7.00; N, 20.97.

Compound **8d** melted at 149°; ir: 2965, 1721, 1665 cm^{-1}; ^1H-nmr: δ 1.41 (t, J = 7, 3H), 2.99 (q, J = 7, 2H), 3.52 (s, 3H), 3.71 (s, 3H), 8.44 (s, 1H).

Anal. Calcd. for $C_{10}H_{12}N_4O_2$: C, 54.54; H, 5.49; N, 25.44. Found: C, 54.34; H, 5.49; N, 25.54.

Compound **9d** melted at 112-113°; ir: 2965, 1713, 1666 cm^{-1}; ^1H-nmr: δ 1.36 (t, J = 7, 3H), 1.39 (t, J = 7, 3H), 2.99 (q, J = 7, 4H), 3.54 (s, 3H), 3.73 (s, 3H).

Anal. Calcd. for $C_{12}H_{16}N_4O_2$: C, 58.05; H, 6.50; N, 22.57. Found: C, 57.80; H, 6.41; N, 22.38.

Compound **8e** melted at 107-108°; ir: 2960, 1702, 1672 cm^{-1}; ^1H-nmr: δ 1.00 (d, J = 6.5, 6H), 2.26 (nona, J = 6.5, 1H), 2.81 (d, J = 6.5, 2H), 3.49 (s, 3H), 3.68 (s, 3H), 8.36 (s, 1H).

Anal. Calcd. for $C_{12}H_{16}N_4O_2$: C, 58.08; H, 6.50; N, 22.57. Found: C, 58.05; H, 6.57; N, 22.32.

Compound **8f** [5] melted at 192-194°; ir: 1728, 1710, 1687 cm^{-1}; ^1H-nmr: δ 2.78 (s, 3H), 3.56 (s, 3H), 3.78 (s, 3H), 9.08 (s, 1H).

Competitive Reaction of Alkyl Radicals Between Pyrazine-2,3-dicarbonitrile (**1**) and 1,3-Dimethyllumazine (**2**).

i) *t*-Butyl Radical.

A mixture of **1** (1.0 mmole), **2** (1.0 mmole), 2,2-dimethylpropanoic acid (1.2 mmoles), ammonium peroxodisulfate (1.4 mmoles), and silver nitrate (0.5 mmole) in 100 ml of ethanenitrile-water (4:1) was refluxed for 6 hours under argon. The mixture was filtered, evaporated under reduced pressure to *ca.* ¼ volume, and extracted with chloroform (5 x 20 ml). The extract was washed with aqueous sodium hydrogen carbonate and condensed under reduced pressure. The condensate was separated into four components by silica gel plates (25 g silica gel on 20 x 20 cm glass plates); **1** (0.16 mole, 16%), **3a** (0.80 mmole, 80%), **2** (0.93 mmole, 93%), and **8a** (0.03 mmole, 3%).

ii) Isopropyl Radical.

Reaction conditions and separation procedure were essentially the same as in the case of the *t*-butyl radical described above but using 2-methylpropanoic acid instead of 2,2-dimethylpropanoic acid. The recovered starting materials and products were **1** (22%), **3b** (61%), **4b** (5%), **2** (87%), **8b** (7%), and **9b** (0.1%).

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