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Derek H. R. Barton, Joseph Cs. Jaszberenyi, and
Emmanouil A. Theodorakis

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Derek H. R. Barton,* Joseph Cs. Jaszberenyi, and Emmanouil A. Theodorakis

Department of Chemistry, Texas A&M University
College Station, Texas 77843

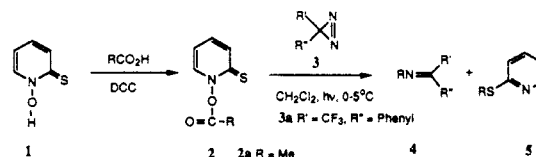
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Functional group transformation by radical methods is becoming an important tool in synthetic organic chemistry.¹ This is especially true in the case of natural products containing structural elements not compatible with the more drastic conditions of traditional ionic processes. An important group of radical reactions that has found widespread synthetic use is based on the radical chain deoxygenation of alcohols (the Barton-McCombie reaction).² Carbon radicals formed in these reactions have also been used for carbon-carbon and carbon-heteroatom bond formation and hence introduction of new functional groups into organic molecules.³

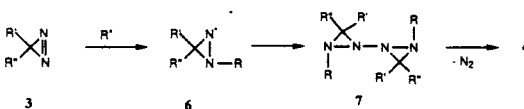
In earlier work we also developed an efficient radical deamination reaction for changing NH₂ into H.⁴ However, at present there is no radical amination reaction for replacing the hydroxyl group by an amino function.⁵ We wish now to report a new reaction for this purpose. A modification of the method using carboxylic acid derivatives as the source of radicals permits the conversion RCO₂H → RNH₂.

Diazirines have not yet been employed as traps in radical chemistry.⁶ We conceived that carbon radicals could add to the N=N bond. It is well documented that the thiohydroxamic acid *N*-hydroxy-2-thiopyridone (1) gives *O*-acyl derivatives 2 that can be photolyzed with visible (tungsten) light to the corresponding acyloxy radicals (Scheme I).⁷ In most cases, easy spontaneous

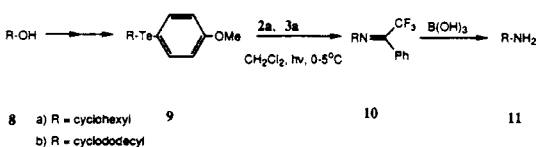
Scheme I



Suggested reaction pathway:



Scheme II



Scheme III

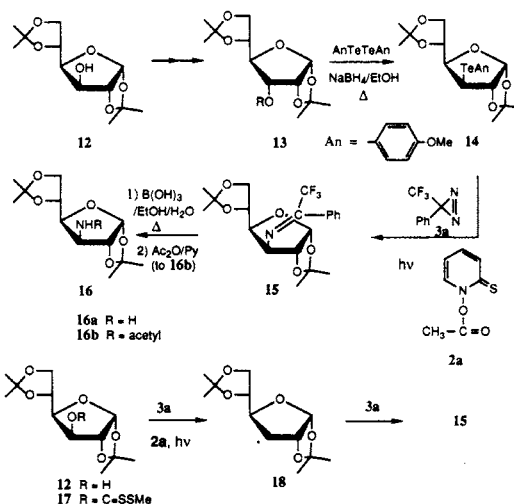


Table I. Yields of the Transformation Products of Thiopyridone Derivatives 2b-f

starting compd	R	yields (%)		
		4 ^a	5 ^a	11 ^b from 4
2b		73	27	91
2c		>89	<11	87
2d		80	20	96
2e		70	30	54 ^c
2f		72	28	43 ^c

^a These yields, based on NMR measurements, are normalized to 100% for 4 + 5. ^b Isolated yield based on the amount of 4 as determined by NMR. ^c In both cases the corresponding 4 and 11 were purified by column chromatography.

decarboxylation occurs to form a carbon radical.⁸ We found that 3-phenyl-3-(trifluoromethyl)diazirine⁹ (3a) (R' = Ph, R'' = CF₃)

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acts as a trap for carbon radicals and furnishes the imines **4** with some byproduct **5**.

We suggest that this reaction involves the adduct radical **6** that is long-lived and does not react with the radical source **2**.¹⁰ This type of dimerization of related hydrazyl radicals is known.¹¹ In our case **6** dimerizes to the tetraazane derivative **7**. This compound then undergoes a rearrangement with the loss of N₂ and formation of 2 mol of imine **4**.

With this reaction we have solved the problem of the transfer of a primary amino group to a carbon radical. The general usefulness of this new reaction has been demonstrated with primary, secondary, and tertiary radicals (Table I). Because of the

radicophilic nature of the thiopyridone thiocarbonyl group in **2**, the formation of some of the 2-pyridyl thioether **5** is seen.

Two newer methods of carbon radical formation depend on radical exchange.¹² Thus an alcohol, converted into the corresponding aryltelluride by ionic chemistry, is radically exchanged with a methyl radical (from photolysis of **2a**). In the second method, the alcohol is converted into xanthate (or another thiocarbonyl derivative), which then gives the desired secondary radical by reaction of the thiocarbonyl group with methyl radicals generated in the same way.¹³

The first method is illustrated in Scheme II where alcohols **8a** and **8b** were converted into the corresponding tellurides **9** and thence into **10a** (100% from the telluride **9a**) and **10b** (>95% from the telluride **9b**). We found that these imines were readily and quantitatively hydrolyzed by reflux in ethanol containing boric acid. Without the boric acid no reaction occurred.

3-Amino-3-deoxy-D-glucose is an important amino deoxy sugar found, for example, in kanamycin A. We report two new syntheses of this sugar (Scheme III). First, the glucose derivative **12** was converted to the epimer **13a** (R = H, 61%).¹⁴ After tosylation to **13b** (R = Tos) and displacement with anisyltelluride to give **14** (35–41% **14** + the rest was recovered as **13a**), the methyl radical exchange process and reaction with **3a** gave the imine **15** (95%),¹⁴ from which the amine **16a** (87%) was obtained.^{15–17} The hydrolysis of the imine was carried out with boric acid in aqueous ethyl alcohol. Acetylation gave the known **16b** (90%).¹⁶

Alternately, the glucose derivative **12** was transformed to the known xanthate² **17** and reacted with the methyl radicals generated from **2a**. The carbon radical **18** can react with diazine **3a** to furnish imine **15** (60%). The stereochemistry of **15** is exclusively 3 β showing, once again,¹⁸ how configuration can be determined in radical reactions simply by steric bulk, in this case that of the 1,2-acetonide group on the α -face of the five-membered ring.

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Supplementary Material Available: Experimental details and spectral data for the synthesis of compounds **14**, **15**, and **16a,b** (4 pages). Ordering information is given on any current masthead page.

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(14) Typical procedure: Telluride **14** (150 mg, 0.31 mmol) and **3a** (20 equiv, 1.15 g, 6.2 mmol) were dissolved in dry dichloromethane (3 mL) at 0–5 °C under argon. To this mixture was added **2a** (0.2 equiv of **14**, 10 mg, 0.06 mmol) at 20-min intervals (180 mg total weight of **2a**) while the solution was photolyzed with two tungsten lamps (150 W each, GE). The progress of the reaction was monitored by TLC. Then the solvent was removed under vacuum, followed by Kugelrohr partial distillation to recover the excess **3a**, and the 2-(methylthio)pyridine formed. The imine **15** (122 mg, 95%) was isolated from the distillation residue by column chromatography on silica gel (hexanes:ether = 8:2).

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