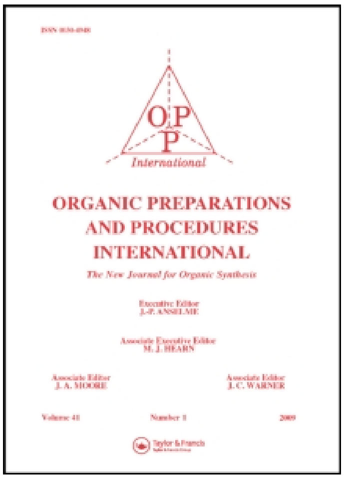

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1-ETHYL-4-CARBOMETHOXYPYRIDINYL (Pyridinyl, 1-ethyl-4-carbomethoxy)

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1-ETHYL-4-CARBOMETHOXYPYRIDINYL
(Pyridinyl, 1-ethyl-4-carbomethoxy)

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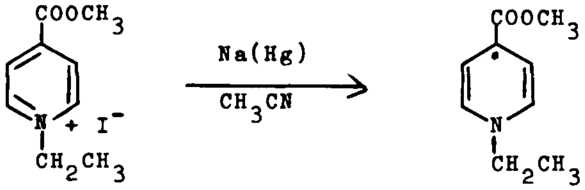
1-Ethyl-4-carbomethoxypyridinyl has been previously prepared by the reduction of the pyridinium iodide either electrochemically[1] or chemically[2] with zinc and acetonitrile or with magnesium in the melt. The present procedure is much more convenient, lends itself to moderate scale operations and provides a purer product.

Pure stable radicals are useful in studies of the physical and chemical properties of radicals.[3] Distillation is probably the most convenient purification procedure for materials with the level of reactivity towards oxygen possessed by pyridinyl radicals.



EXPERIMENTAL

1-Ethyl-4-carbomethoxypyridinium iodide[4] (5.86 g.,2.03 mmoles) is placed in the 50 ml. bulb A of the reaction apparatus illustrated in Fig. 1 along with several large pieces of 3% sodium amalgam[5] (17.2 g.,2.25 mg. at. sodium) and a teflon-coated magnetic bar. After ensuring that the entry

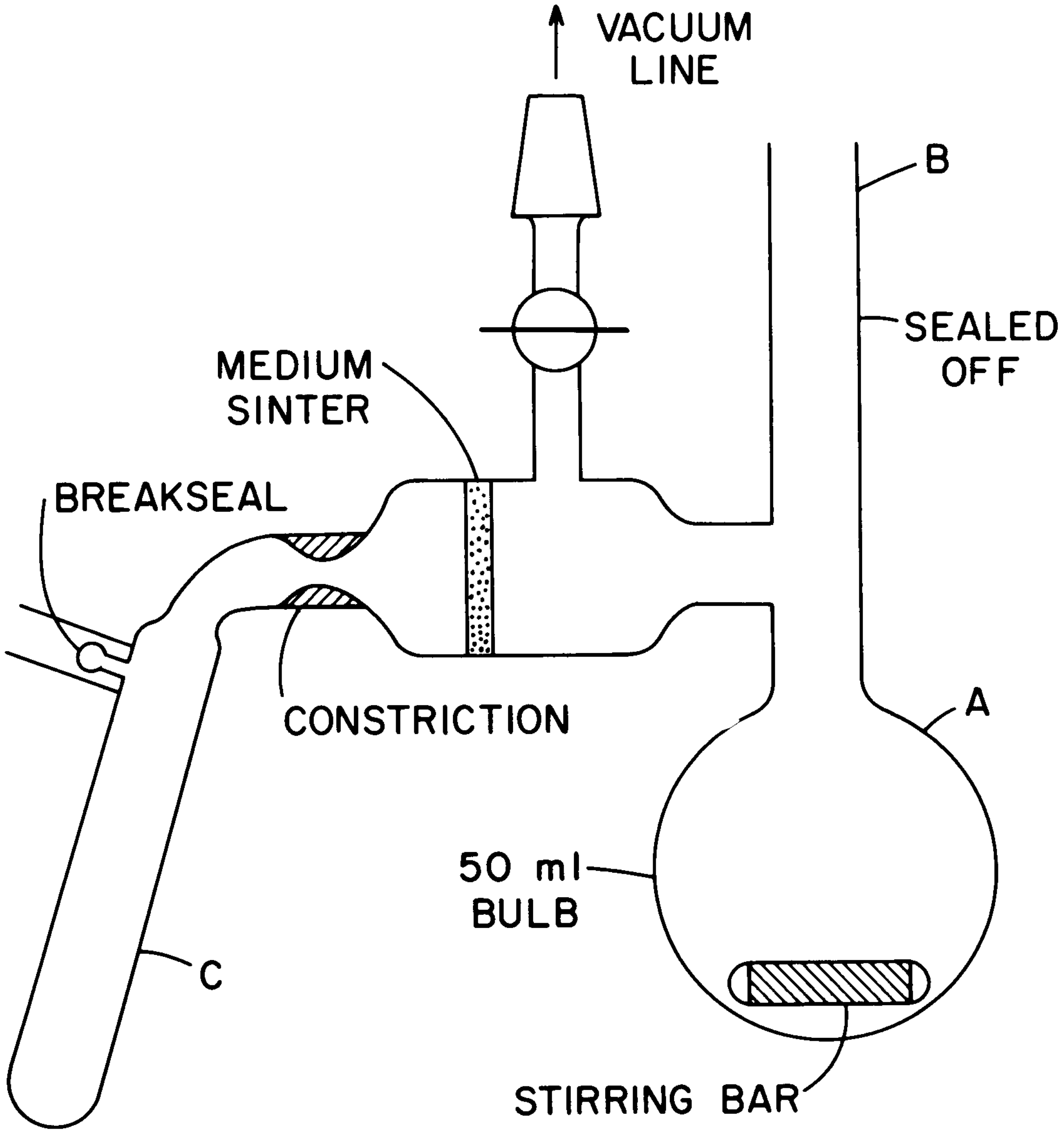

VACUUM LINE
B
SEALED OFF
MEDIUM SINTER
BREAKSEAL
CONSTRICTION
A
50 ml BULB
C
STIRRING BAR

Fig. 1

tube B is completely clean, it is sealed off. The apparatus is connected to the vacuum line and evacuated.[6]

After 30 minutes pumping to ensure dryness, degassed acetonitrile (25 cc.)[7] is distilled in with the aid of liquid nitrogen. The solvent is melted with a bath[8] and the mixture stirred at or below 0° for 30 minutes. The resulting deep blue suspension is filtered, the reaction vessel rinsed with acetonitrile distilled from the filtrate and the rinse solvent filtered into the ampoule containing the filtrate. The ampoule (C) and bulb (A) are frozen by plunging into liquid nitrogen and the ampoule (C) sealed off at the constriction.

The ampoule (C) is sealed through a breakseal connection to a vacuum line distillation apparatus (Fig. 2), the filtrate introduced, the apparatus sealed off at the constriction and the solvent carefully evaporated with stirring to a receiver on the line. The cold finger of the condenser is filled with liquid nitrogen and the emerald-green pyridinyl radical is distilled (hot-air "gun") onto the cold finger, condensing as a sapphire-blue solid. Fresh degassed acetonitrile is distilled onto the condenser, the liquid nitrogen removed and the pyridinyl radical solution allowed to flow into the collection ampoule (D), which is then sealed off. The distillation procedure is repeated in another apparatus (Fig. 2) to remove small amounts of high-boiling material and solid.

The solution of pyridinyl radical in acetonitrile is divided among 4 - 8 ampoules bearing breakseals with the apparatus shown in Fig. 3. After freezing the solutions simultaneously with liquid nitrogen, the ampoules are sealed off, the solution melted[8] and the ampoules stored in the freezer.

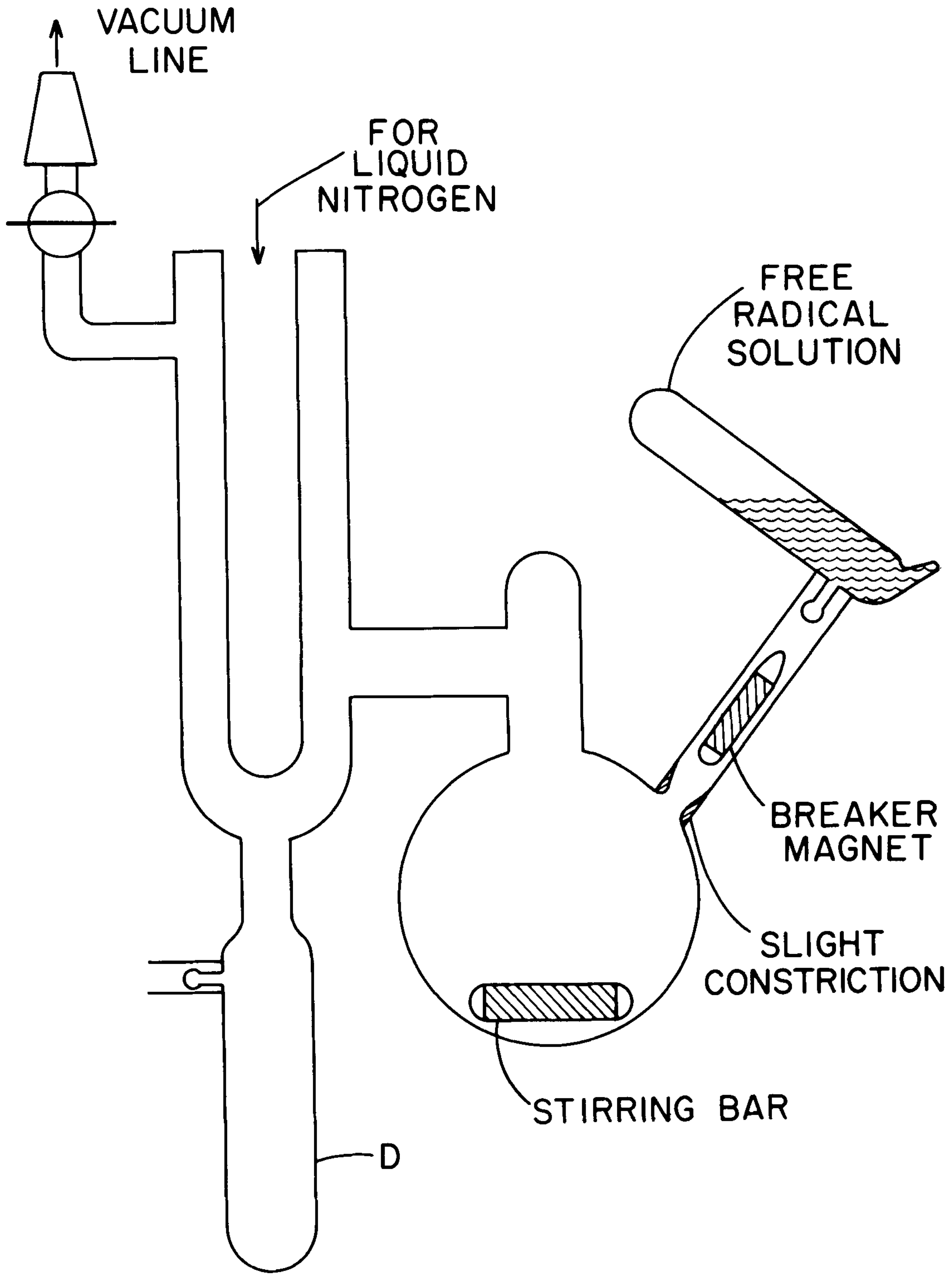

VACUUM LINE
FOR LIQUID NITROGEN
FREE RADICAL SOLUTION
BREAKER MAGNET
SLIGHT CONSTRICTION
STIRRING BAR
D

Fig. 2

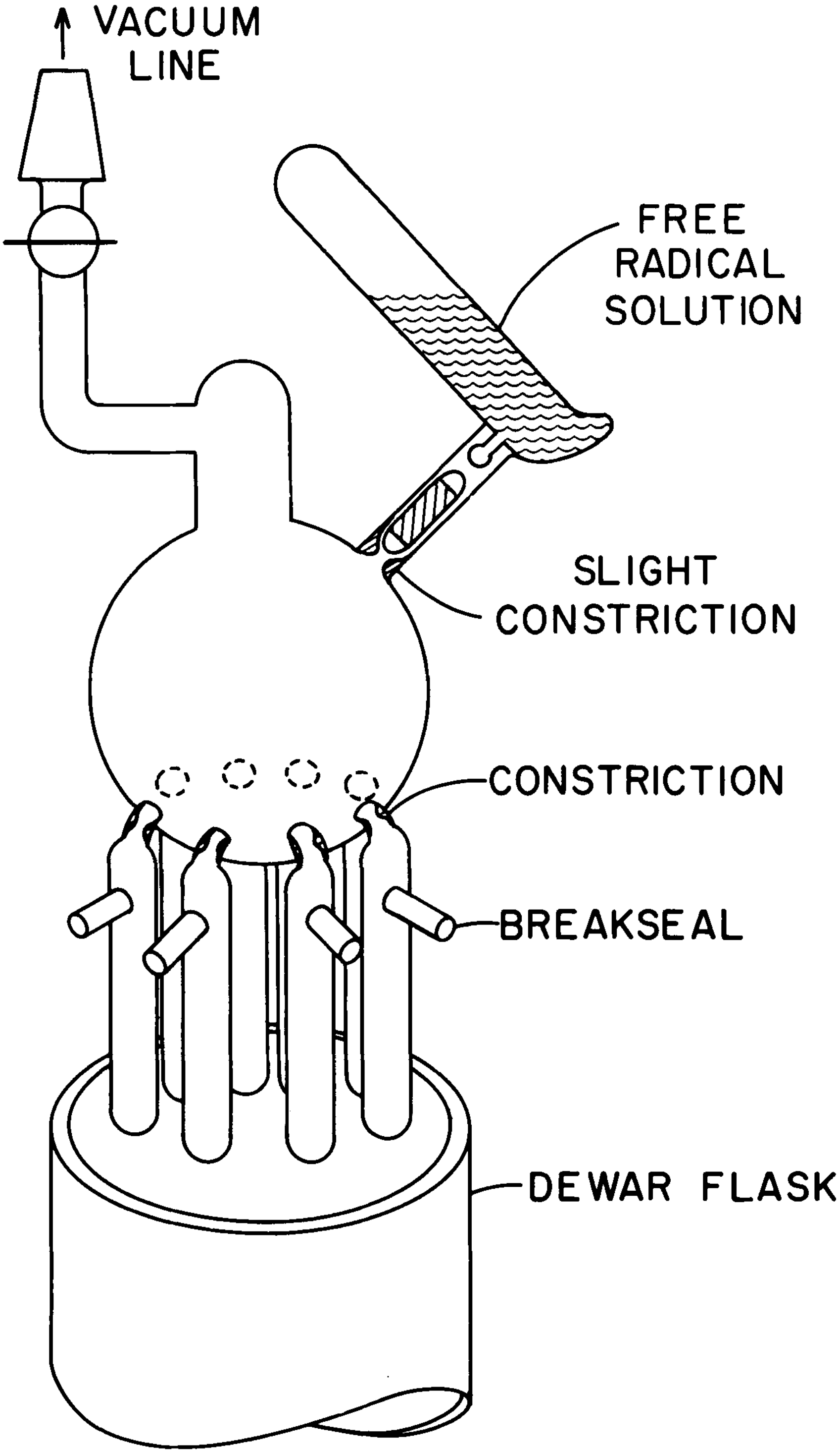

VACUUM LINE
FREE RADICAL SOLUTION
SLIGHT CONSTRICTION
CONSTRICTION
BREAKSEAL
DEWAR FLASK

Fig. 3

The concentration is measured spectrophotometrically.[9] The yield of the radical varies from 10 - 30%.[10]

The 1-methyl and 1-isopropyl radicals can be prepared by the same procedure. However, the methyl derivative is less stable than the 1-ethyl- and 1-isopropyl radicals. The 1-isopropyl radical forms long violet crystals on the walls during the distillation.

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4. Methyl isonicotinate (Reilly Tar & Chemical Corp., Indianapolis, Indiana) and ethyl iodide in ethanol or acetone at reflux for 5-8 hours yield the required quaternary salt. Recrystallization from acetone produces *orange* crystals, m.p. 110 - 112°. The color of the salt is due to light absorption in the charge-transfer band, *not* impurities.
5. Sodium amalgam is prepared according to the directions given in L. F. Fieser, Reagents for Organic Synthesis, John Wiley and Sons, Inc., 1967, p. 1030.
6. The vacuum line equipped with a mercury diffusion pump,

a forepump and traps is operated at a pressure of 1 x 10^{-5} mm. Long pumping times ensure removal of adsorbed oxygen.

7. Acetonitrile (Spectroquality) from Matheson Coleman and Bell or J. T. Baker, is satisfactory for this preparation.
8. The relatively high (-40°C.) melting point of acetonitrile can lead to difficulty (even cracking of apparatus) if care is not exercised in the melting operation. A beaker of acetone at room temperature is ideal for this step.
9. Data are: λ_{max} (ϵ_{max}) 6325(83), 3940(4925), 3100(11,000). The visible maximum does not obey Beer's Law above ∽0.03 M due to reversible dimerization.
10. Acetonitrile solutions of 1-ethyl-4-carbomethoxypyridinyl (∽0.01 - .02 M) have been stored for many months with little apparent decomposition.

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