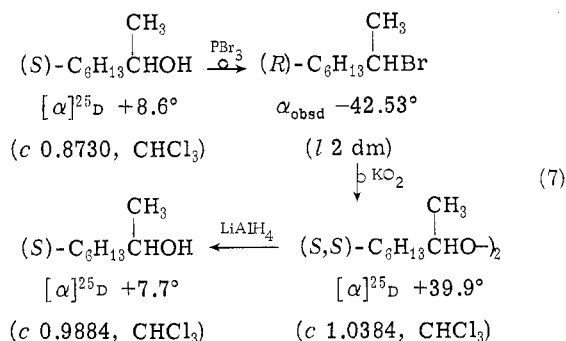


mation of these equations gives eq 2. Two displacements of bromide are seen in these equations and it was suggested⁵ that these occurred by SN2 mechanisms. We have examined the stereochemistry of the reaction as outlined below.



The entire three-step reaction sequence (7) proceeds with a net 94% retention of configuration. Since the first step is known to proceed with complete inversion at the asymmetric carbon¹³ and the last step¹⁴ proceeds with retention of configuration, we conclude that the conversion of 2-bromooctane to di-2-octyl peroxide must occur with inversion at the asymmetric carbon. This result is consistent with the SN2 mechanism postulated for the reaction steps depicted in eq 4 and 6.

The yields of primary dialkyl peroxides obtained by the present method are comparable with, and in some cases better than, those reported for the generally used methods of peroxide synthesis.¹⁵ Yields of secondary dialkyl peroxides, except for the cyclohexyl example, are better than those obtained by other methods. The procedure is considerably simpler than the generally used method of displacement of mesylates with alkaline hydrogen peroxide.¹⁶

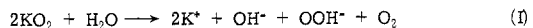
The formation of alcohols as significant by-products in these reactions is not completely understood as yet and remains under investigation.

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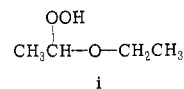
salts in organic media: (a) C. J. Pederson, *J. Am. Chem. Soc.*, **89**, 7017 (1967); (b) D. J. Cram and J. M. Cram, *Science*, **183**, 803 (1974); (c) B. Dietrich, J. M. Lehn, and J. Simon, *Angew. Chem., Int. Ed. Engl.*, **13**, 406 (1974); (d) C. L. Liotta, H. P. Harris, M. McDermott, T. Gonzalez, and K. Smith, *Tetrahedron Lett.*, 2417 (1974); (e) C. L. Liotta, and H. P. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974); F. L. Cook, C. W. Bowers, and C. L. Liotta, *J. Org. Chem.*, **39**, 3416 (1974); (f) D. J. Sam and H. E. Simmons, *J. Am. Chem. Soc.*, **96**, 2252 (1974); (g) H. D. Durst, *Tetrahedron Lett.*, 2421 (1974); (h) J. W. Zubrick, B. I. Dunbar, and H. D. Durst, *ibid.*, 71 (1975).

(8) Supplied by the Ventron Corporation, Beverly, Mass. 01915, as small chunks of a caked yellow powder. Potassium superoxide reacts rapidly with water, producing peroxide, hydroxide, and oxygen according to the eq 1.⁵ Care should be taken to avoid reaction of large quantities of KO₂



with water in the presence of organic materials. Precautions similar to those used with hydrogen peroxide are recommended.⁹ In the present experiments, excessive contact with atmospheric moisture was avoided by using larger pieces of the solid and quickly covering them with dry solvent. More rigorous anhydrous conditions could be attained in a dry-box.

(9) "Kirk-Othmer Encyclopedia of Chemical Technology", Vol. 14, 2nd ed, Wiley, New York, N.Y., 1967, pp 748-749, 762-764.
 (10) Peroxides and hydroperoxides can be visualized on silica gel tic plates by spraying with a freshly prepared (remains effective for about 1 day) solution of ammonium thiocyanate (0.625 g), concentrated sulfuric acid (0.125 ml), and ferrous ammonium sulfate [FeSO₄(NH₄)₂SO₄, 0.875 g] in water (12.5 ml).¹¹ With this spray, peroxidic materials give a rust-red-colored spot.
 (11) R. D. Mair and R. T. Hall, in "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1971, pp 553-560.
 (12) Extraction of several reactions with ether resulted in formation of a peroxidic product tentatively considered to have structure i. Since i is an



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Experimental Chemistry Research
 The Upjohn Company
 Kalamazoo, Michigan 49001

Roy A. Johnson*
 Eldon G. Nidy

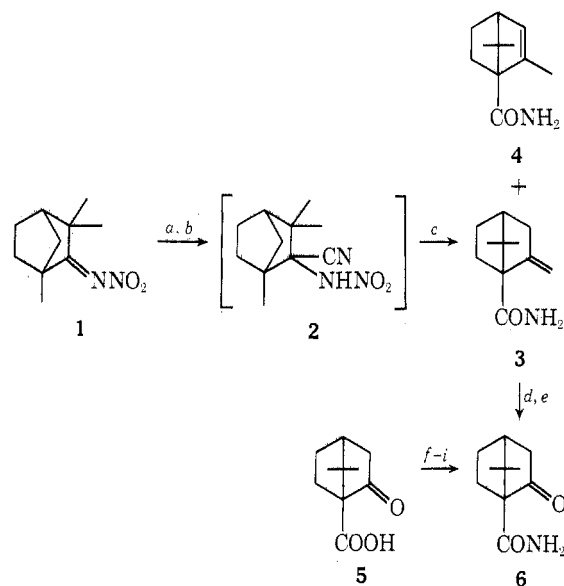
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Reaction of Nitrimes with Cyanide Ions

Summary: The nitrimes of fenchone, menthone, camphor, and benzophenone were treated with KCN in aqueous methanol to give unstable cyanonitrime intermediates which decompose with the loss of N₂O to afford α-fenchene-1-carboxamide, ρ-menth-3-ene-3-carboxamide, camphene-1-carboxamide, and α-methoxydiphenylacetamide, respectively.

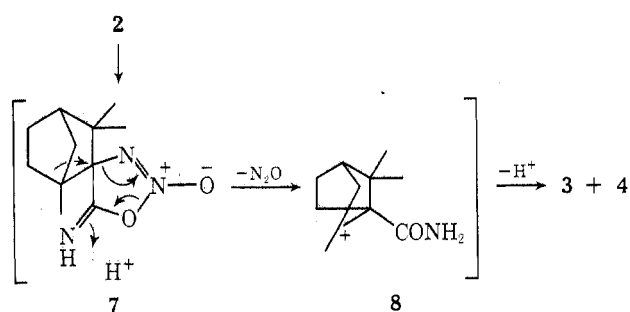
Sir: The reaction of fenchone nitrime (1) with cyanide ion was reported by Passerini to afford a mixture of isomeric fenchone cyanohydrins.¹ We have reinvestigated this reaction duplicating the conditions of Passerini and have found that the products actually isolated are the rearranged amides 3 and 4 formed in 80% yield in a ratio of 85:15, respectively. The structure of the major product 3 was deduced from the spectral data [NMR (CDCl₃) δ 1.05 (s, 3 H), 1.10 (s, 3 H), 4.91 (m, 1 H), 5.07 (m, 1 H); ir (CHCl₃) 3520, 3400, 1665, 895 cm⁻¹] and by conversion to ketopinic amide (6) which was prepared independently from ketopinic acid (5)² as shown in Scheme I.

Scheme I



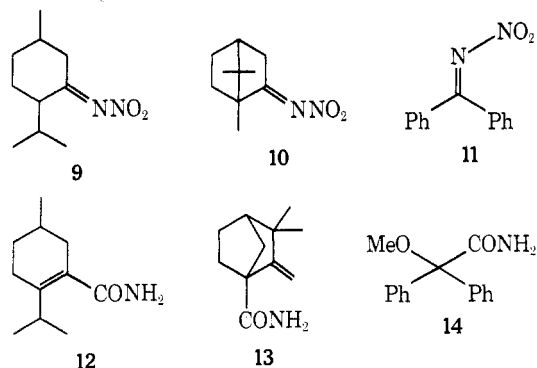
^a KCN/MeOH, room temperature. ^b HOAc. ^c CHCl₃, reflux 20 min. ^d O₃/MeOH, -60°. ^e Me₂S/MeOH. ^{f-i} SOCl₂/benzene, reflux 45 min. ^g NH₄OH/MeOH, room temperature, 30 min. ^h O₃/MeOH, -60°. ⁱ Me₂S/MeOH.

When the above reaction was conducted at room temperature in aqueous methanol for 20 min, acidification of the reaction mixture gave an unstable crystalline cyanonitramine intermediate 2 (mp 81–83° dec) in virtually quantitative yield which gradually decomposed at 25° with gas evolution to afford the same mixture of amides 3 and 4 cited above. The structure of 2 (exclusive of stereochemistry) was assigned on the basis of the spectral data:³ NMR (CDCl₃) δ 1.08, 1.40, 1.47 (s, 3 H each); ir (CHCl₃) 3360, 2240, 1585, 1330 cm⁻¹. Since the decomposition of the cyanonitramine 2 takes place readily in inert solvents, the formation of the amide products suggests an internal transfer of oxygen from the nitro group to the nitrile via the intermediate 7. Loss of N₂O, accompanied by rearrangement



of the carbon skeleton, and finally loss of a proton account for the products observed.

To demonstrate the synthetic potential of this unusual transformation, the nitrimines of menthone (9),⁴ camphor (10),⁴ and benzophenone (11)⁵ were treated with cyanide ion to afford the amides 12,⁶ 13,⁷ and 14,⁸ respectively.⁹ In



each case, the formation of a cyanonitramine adduct analogous to 7 followed by elimination of N₂O as depicted above can be invoked to explain the formation of the products. The fact that skeletal rearrangement, loss of an adjacent proton to generate an olefin, and the capture of an external nucleophile were observed variants provides additional evidence in support of the ionic mechanism proposed.

Since the above reactions proceed under mild conditions (MeOH, room temperature) to afford the amides in 50–85% isolated yield, the synthetic utility of this reaction is being further investigated, and will be reported in a later paper.

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- (7) Mp 206–208° (lit.⁴ mp 208°); ir (CH₂Cl₂) 3545, 3420, 1675, 1585, 1380, 885 cm⁻¹; NMR (CCl₄) of corresponding nitrile (prepared by *p*-toluenesulfonyl chloride/pyridine dehydration) δ 1.12 (s, 6 H), 1.48–2.32 (m, 7 H), 4.80 (s, 1 H), 5.15 (s, 1 H).
- (8) Mp 147–149°. Compared with an authentic sample: D. A. Petgunin and M. S. Kodyrera, *Zh. Obshch. Khim.*, **33** (3), 755 (1961), who report mp 146–148°.
- (9) The cyanonitramine intermediates were too unstable to permit isolation.

Department of Chemistry
State University of New York
at Binghamton
Binghamton, New York 13901

P. J. Kocienski*
M. Kirkup

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