

1-CYANO-5-METHOXY-2-TETRALONE

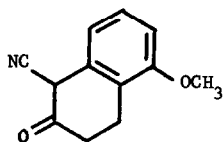
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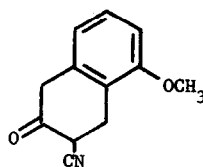
Houston, Texas

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A synthesis of 1-cyano-5-methoxy-2-tetralone (I) from 5-methoxy-2-tetralone via the hydroxymethylene derivative and the corresponding isoxazole, m.p. 137°,  $\nu_{\max}$  (Nujol) 1658, 1605, 1580  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH) 274  $\text{m}\mu$ (1,740), 280  $\text{m}\mu$ (1,950), has recently been reported by Pelletier and Parthasarathy (1).



I

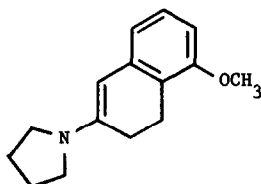


II

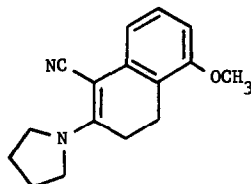
The ketonitrile obtained by this procedure melted at 175-176°,  $\nu_{\max}$  (Nujol) 3205, 2212, 1672, 1605, 1590  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH) 272  $\text{m}\mu$ (8,320), 278  $\text{m}\mu$ (7,590), and afforded a pyrrolidine enamine melting at 151-153°,  $\nu_{\max}$  (Nujol) 2174, 1613, 1582  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH) 214  $\text{m}\mu$ (11,750), 280  $\text{m}\mu$ (12,590), 289  $\text{m}\mu$ (13,180).

We understand from Professor Pelletier (2) that evidence now at hand indicates that the product in question actually possesses structure (II). In view of our own interests in (I) as a synthetic intermediate, we have been prompted to reinvestigate this matter.

When enamine (III), m.p. 79°,  $\nu_{\max}$  (Nujol) 1610, 1590, 1550  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH) 245  $\text{m}\mu$ (12,750), 322  $\text{m}\mu$ (18,100), anal. C 78.42, H 8.40, N 6.18, is treated with cyanogen chloride in dioxane solution (3), there is obtained in about 60% yield the cyano enamine (IV), m.p. 116-116.5°,  $\nu_{\max}$  (Nujol) 2172, 1600, 1581, 1539  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH), 245  $\text{m}\mu$ (14,100), 327  $\text{m}\mu$ (18,600), anal. C 75.38, H 7.10, N 10.86. Hydrolysis of (IV)



III

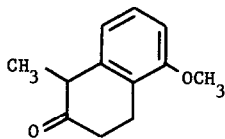


IV

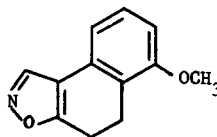
yields a cyanoketone, m.p. 181.5-182.5°,  $\nu_{\max}$  (Nujol) 3135, 2218, 1644, 1606, 1582,  $\lambda_{\max}$  (EtOH) 220  $\text{m}\mu$ (16,640), 291  $\text{m}\mu$ (8,120), anal. C 71.62, H 5.64, N 6.91, which exists essentially exclusively in the enol form. Both the enamine (IV) and the cyanoketone are clearly different from the corresponding products of Pelletier, which were prepared as described (1) for purposes of direct comparison. Assignment of structure (I) (enolic modification) to the new cyanoketone is based upon the following observation.

Catalytic hydrogenation of the substance over palladium-charcoal, followed by vapor phase chromatography of the resulting non-basic fraction,

furnished, albeit in poor yield, a crystalline sample, m.p. 39-41°, of the known 1-methyl-5-methoxy-2-tetralone (V) (4), which was identified by comparison with an authentic specimen.



V



VI

It may be noted, finally, that in repeating the work of Pelletier and Parthasarathy, we have obtained in addition to the isoxazole described by them an isomer (VI), m.p. 119-121°,  $\nu_{\max}$  (Nujol) 1630, 1593, 1568  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH) 287  $\text{m}\mu$ (1,830), 298  $\text{m}\mu$ (1,680), anal. C 71.66, H 5.51, N 6.96, convertible into (V) by palladium-catalyzed hydrogenation and into I by treatment with base.

Acknowledgment. We are grateful to Professor Pelletier for information relative to his observations in this series and to the Robert A. Welch Foundation for financial support.

#### REFERENCES

- (1) S. W. Pelletier and P. C. Parthasarathy, Tetrahedron Letters, No. 2, 103 (1964).
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- (3) M. E. Kuehne, J. Am. Chem. Soc., 81, 5400 (1959).
- (4) J. W. Cornforth and R. Robinson, J. Chem. Soc., 1855 (1949); P. Shaw, Ph.D. Dissertation, Rice University (1960).