NOTES

1,8-DIACETYLNAPHTHALENE AND 3-METHYLPHENALENONE

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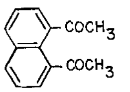
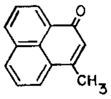
This note describes a preparation of 1,8-diacetylnaphthalene (I), which was required in another problem, and the subsequent formation of 3-methylphenalenone (II). The usual method for the preparation of I involves cleavage of 1,2-dimethylacenaphthene-1,2-diol by lead tetraacetate (1). A modified chromic acid oxidation was found to be successful and more convenient.[1]



I



II

If 1,2-dimethylacenaphthene-1,2-diol was first dissolved in warm acetic acid and then cooled to room temperature, and 1 equivalent of chromic anhydride in water added, followed immediately by addition of water, 1,8-diacetylnaphthalene (I) was obtained in yields of 85–90%, which compare favorably with those obtained with lead tetraacetate (70–75%, in our hands).

If, on the other hand, 1.5 moles of chromic anhydride was used per mole of diol at 75° and water added after 10 min, the product was 3-methylphenalenone (II) in yields of 84–90%. At room temperature the use of this same excess of chromic anhydride yielded, after 10 min, 52% of I and 28% of II. Treatment of I in hot acetic acid with an excess of chromic acid to produce II in a quantitative yield established that I was a precursor of II.[2] Though a very facile cyclization of I, with piperidine, to form II is known (1), the acid-catalyzed cyclization has not been reported.

EXPERIMENTAL

All melting points are uncorrected; infrared spectra were determined in dilute chloroform solution with a Perkin–Elmer model 421 spectrophotometer; nuclear magnetic resonance spectra were measured at 100 Mc/s in deuteriochloroform, with tetramethylsilane as internal standard ($\tau = 10$); microanalyses were performed by Dr. C. Daessle, Montreal.

1,2-Dimethylacenaphthene-1,2-diol

The procedure is that of Maxim (3), with modification. Powdered acenaphthenequinone (15 g) was added in small portions to methylmagnesium iodide (50 g methyl iodide and 8.5 g magnesium) in anhydrous ether (100 ml), and the mixture was heated under reflux for 7 h. After hydrolysis with either 10% sulfuric acid or aqueous ammonium chloride solution, the combined, dried ($MgSO_4$) ether extracts were evaporated under reduced pressure. The residue of mixed *cis*- and *trans*-diols was crystallized from acetone and then chloroform to yield 4.0 g (23%) of *cis*-diol, m.p. 193–194° (lit. m.p. 187–189° (3)), as thick colorless plates from acetone, and 10.4 g (59%) of *trans*-diol, m.p. 186–187° (lit. m.p. 182–183° (3)), as fine white needles from chloroform.

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[1] *For the preparation of large quantities of I, the lead tetraacetate method (1) requires large quantities of solvent (benzene).*

[2] *The formation of II is readily explained as an intramolecular acid-catalyzed aldol condensation. In the excellent review by Reid (2), 1,8-diacylnaphthalenes were not considered as precursors for phenalenones. In the particular case of II, the synthesis outlined here would appear to be the one of choice.*

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1,8-Diacetylnaphthalene (I)

A mixture of *cis*- and *trans*-diols (6.4 g) was dissolved in acetic acid (175 ml) with heating, and then cooled to room temperature. Chromic anhydride (3.1 g) in water (30 ml) was added dropwise, as rapidly as possible and with good mixing, followed immediately by rapid dropwise addition of cold water, with good mixing, to precipitate I. Crystallization from acetone gave 8.1 g (89%) of colorless plates, m.p. 174–175° (lit. m.p. 171–172° (1)). The infrared spectrum showed carbonyl absorption at 1 683 cm^{-1}.

3-Methylphenalenone (II)

To a hot solution (75°) of diol (6.8 g) as described above was added an excess of chromic anhydride (4.7 g) in water (50 ml). The solution was kept at 75° for 10 min, and then cold water was added slowly, with stirring, to give II as pale-yellow crystals. After crystallization from an acetone–water mixture and then from ethanol the melting point was 151–152° (lit. m.p. 152° (1)); yield 5.4 g (90%). The infrared spectrum showed carbonyl absorption at 1 640 cm^{-1}. The nuclear magnetic resonance spectrum showed three methyl protons at 7.46 τ, one olefinic proton at 3.40 τ, and six aromatic protons (multiplet, 1.4–2.5 τ).

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.56; H, 5.24. Found: C, 86.56, 87.00; H, 4.91, 5.22.

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CONCERNING *cis*- AND *trans*-3-THIOCYANOPROPENAL AND THE SYNTHESIS OF ISOTHIAZOLE

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The isothiazole ring system has received much attention lately and several methods leading to its synthesis have been developed (1). Recently, Wille *et al.* (2) reported the preparation of isothiazole by the reaction of either 3-thiocyanopropenal or sodium propenal-3-thiosulfate with liquid ammonia. This method is the most practical laboratory synthesis of this interesting compound, but full experimental details have not yet been reported. As stated by Slack and Wooldridge (3) (citing a personal communication from Wille), success is dependent on the reaction of the *cis* adducts with ammonia. The purpose of this publication is to supply practical details for obtaining optimal yields of isothiazole from both the thiocyanate and the thiosulfate.

When a solution of propynal in acetone was added to an aqueous solution of thiocyanic acid at 0°, an almost quantitative yield of 3-thiocyanopropenal, m.p. 93–94°, was obtained. The structural assignment was fully supported by the infrared spectrum and by the elemental analysis. However, when this compound was allowed to react with liquid ammonia, only a tar resulted, from which not a trace of isothiazole could be isolated. On examination of the compound's nuclear magnetic resonance spectrum (Table I), a coupling constant of 15 c.p.s. between the olefinic protons was revealed, indicating a *trans* relationship (4, 5). Attempts to isomerize *trans*-3-thiocyanopropenal (III) to the *cis* isomer were