field methoxyl is the 4-methoxy group in deuteriochloroform as expected from a simple inductive effect unperturbed by solvation.

In the case of glaucine, shifts caused by dilution were plotted relative to the peak at lowest field (Figure 2). It is again observed that the peak at highest field in 100% chloroform (δ 3.68) is the one which has moved least on dilution with benzene and is therefore nearly superimposed with the lowest field peak (δ 3.34) in pure benzene. It seems very likely that this peak is properly assigned to the 5-methoxyl adjacent to the biphenyl linkage as Goodwin, Shoolery, and Johnson[6] had earlier proposed on the basis of its chemical shift in chloroform alone.

[6] S. Goodwin, J. N. Shoolery, and L. F. Johnson, *Proc. Chem. Soc.*, 306 (1958).

Synthesis of Octamethyloxamidinium Dinitrite and Dinitrate

Wayne E. Thun

Chemistry Division, Research Department, U. S. Naval Ordnance Test Station, China Lake, California 93555

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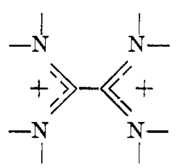
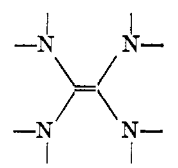
Dinitrate salts of the oxamidinium dication (1) derived from tetraaminoethylenes (2) have been prepared by oxidation of 2 with silver nitrate[1] or by metathesis of the diiodide salt of 1 and silver nitrate.[2] Pure dinitrate salts are obtained by a separation of colloidal silver or silver iodide. It is to be noted that an excess of dinitrogen tetroxide reacts with tetrakis(dimethylamino)ethylene in *n*-hexane to precipitate octamethyloxamidinium dinitrate directly. In a similar way equimolar amounts of the reactants form the dinitrite salt. This synthesis for dinitrate or dinitrite salts is believed to be a general reaction for fully substituted tetraaminoethylenes. The reactions of tetrakis(dimethylamino)ethylene with other nitrogen–oxygen compounds are extended to include tetranitromethane, nitryl perchlorate, and nitrosyl tetrafluoroborate.



1



2

During an investigation of the reaction of tetranitromethane with tetramethyl-2-tetrazene[3] or related compounds, it was observed that equimolar quantities of tetrakis(dimethylamino)ethylene and tetranitromethane produce both octamethyloxamidinium dinitrite and bis(dinitromethanenitronate).[4] In a manner analogous to the effect of excess dinitrogen tetroxide, excess tetranitromethane results in the formation of the dinitrate salt. No evidence for a mixed nitrite or nitrate–dinitromethanenitronate salt was found. The bis(dinitromethanenitronate) and dinitrite or dinitrate salts may be separated by fractional crystallization. The reaction of tetranitromethane with tetrakis(dimethylamino)ethylene is similar to the reaction of the ethylene with carbon tetrahalides,[5] but in the present case octamethyloxamidinium salts are the end products because of the increased stability of the dinitromethanenitronate ion compared with trihalomethyl carbanions.

Nitryl perchlorate or nitrosyl tetrafluoroborate react with tetrakis(dimethylamino)ethylene to give octamethyloxamidinium dinitrite or dinitrate in conjunction with the diperchlorate or bis(tetrafluoroborate) salt. Since the dinitrite or dinitrate salts are readily soluble in water, this reaction provides a novel preparation of the less soluble diperchlorate and bis(tetrafluoroborate) salts.

Experimental Section[6]

Reaction of Tetrakis(dimethylamino)ethylene with Dinitrogen Tetroxide.—Dry nitrogen was bubbled through *n*-hexane for 1 hr at room temperature. To a portion of this solvent dinitrogen tetroxide was added; the concentration of the oxide was estimated by measuring the absorption of the solution at 343 mμ.[7] A typical preparation of dinitrite salt follows. To 0.46 g of tetrakis(dimethylamino)ethylene dissolved in 15 ml of *n*-hexane and placed in a flask purged with dry nitrogen, 0.20 g of dinitrogen tetroxide in *n*-hexane was added. A white solid precipitated immediately which, when dried, gave 0.65 g of a tan solid (98% yield, based on anhydrous dinitrite salt), mp 198°. Recrystallization from ethanol gave a cream-colored solid, mp 209° dec, which exhibited an infrared spectrum identical with that obtained from the reaction of silver nitrite with tetrakis(dimethylamino)ethylene. A spectral maximum corresponding to the octamethyloxamidinium dication was observed at 275 mμ.[8] A colorimetric procedure was used to estimate the amount of nitrite present.[9]

Anal. Calcd for $C_{10}H_{24}N_6O_4 \cdot 0.5H_2O$: C, 39.86; H, 8.36; N, 27.89; NO_2^-, 30.6. Found: C, 40.25; H, 8.21; N, 27.39; NO_2^-, 31.1.

In the preparation of the dinitrate salt a threefold excess of dinitrogen tetroxide was added to the tetrakis(dimethylamino)ethylene. The precipitate, 3.17 g (96% yield), was washed with ethanol and gave a white solid, mp 266° dec. The ultraviolet spectrum of the material had a maximum at 275 mμ and the infrared spectrum was the same as that of the material produced from the reaction of tetrakis(dimethylamino)ethylene with silver nitrate.

Anal. Calcd for $C_{10}H_{24}N_6O_6$: C, 37.03; H, 7.46; N, 25.91. Found: C, 36.98; H, 7.55; N, 25.72.

Reaction of Tetrakis(dimethylamino)ethylene with Tetranitromethane.—To 1.70 g of tetrakis(dimethylamino)ethylene in *n*-hexane under a protective atmosphere of dry nitrogen, 1.59 g of tetranitromethane in *n*-hexane was added. The resulting solid, 3.28 g (99% yield), was recrystallized from water to give 1.92 g of the bis(dinitromethanenitronate) salt (95% yield), mp 122–124° dec.

Anal. Calcd for $C_{12}H_{24}N_{10}O_{12}$: C, 28.80; H, 4.83; N, 27.99. Found: C, 29.13, 28.85; H, 4.71, 4.86; N, 26.97, 27.10.

An alternative procedure for the separation of the dinitrite or dinitrate salts involved precipitation of these relatively in-

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[1] D. M. Lemal, R. A. Lovald, and K. I. Kawano, *J. Am. Chem. Soc.*, **86**, 2518 (1964).

[2] D. M. Lemal and K. I. Kawano, *ibid.*, **84**, 1761 (1962); R. L. Pruett, *et al.*, *ibid.*, **72**, 3646 (1950).

[3] W. E. Thun, D. W. Moore, and W. R. McBride, *J. Org. Chem.*, **31**, 923 (1966).

[4] Since tetramethyl-2-tetrazene is a nitrogen analog of tetrakis(dimethylamino)ethylene [N. Wiberg and J. W. Buchler, *Z. Naturforsch.*, **19b**, 9 (1964)], it was thought that the ethylene analog of 1,1,4-trimethyl-4-(β,β-dinitrovinyl)-2-tetrazene[3] might be formed.

[5] W. Carpenter, *J. Org. Chem.*, **30**, 3082 (1965).

[6] Infrared spectra were obtained from potassium bromide disks (Perkin-Elmer Model 137) and ultraviolet spectra of salts from aqueous solutions (Cary Model 11 MS). Chemical analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn.

[7] C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 3142 (1958).

[8] N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3223 (1963).

[9] B. F. Rider and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **18**, 96 (1946).

soluble salts from acetone solutions of the initial product of the reaction.

Reaction of Tetrakis(dimethylamino)ethylene with Nitryl Perchlorate or Nitrosyl Tetrafluoroborate.—A solution containing 3.20 g of tetrakis(dimethylamino)ethylene in *n*-hexane was stirred for 6 hr with 2.20 g of nitryl perchlorate in a dry nitrogen atmosphere. The resulting solid, 4.54 g (84% yield), was a mixture of the dinitrate and diperchlorate salts and after recrystallization from water 2.50 g of the diperchlorate salt (95% yield) was recovered. This material had an infrared spectrum identical with that of an authentic sample of the diperchlorate salt and melted with decomposition at 277–279° (lit.[10] 279°).

Anal. Calcd for $C_{10}H_{24}Cl_2N_4O_8$: C, 30.08; H, 6.06; Cl, 14.04; N, 17.76. Found: C, 30.34; H, 6.09; Cl, 14.09; N, 17.64.

In the same way, 4.50 g of tetrakis(dimethylamino)ethylene and 3.00 g of nitrosyl tetrafluoroborate produced 4.35 g of solid (58% yield) which was recrystallized from methanol–water to give 2.03 g of the bis(tetrafluoroborate) salt (62% yield), mp 280–282° dec (lit.[11] 273°).

Anal. Calcd for $C_{10}H_{24}B_2F_8N_4$: C, 32.12; H, 6.47; N, 14.98. Found: C, 32.45; H, 6.70; N, 15.24.

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[10] K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964).

[11] N. Wiberg and J. W. Buchler, *Angew. Chem. Intern. Ed. Engl.*, **1**, 406 (1962).

Synthetic Furocoumarins. VIII. The Pechmann Condensation of 2-Alkylhydroquinones

KURT D. KAUFMAN, ROBERT C. KELLY, AND DAVID C. EATON

Department of Chemistry, Kalamazoo College, Kalamazoo, Michigan

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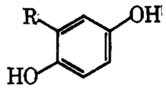
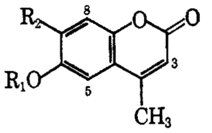
Earlier syntheses of furocoumarins have involved the use of the Pechmann condensation of hydroquinone (Ia) with acetoacetic ester to obtain 6-hydroxy-4-methylcoumarin (IIa).[1] As an extension of the earlier work, the present paper describes the preparation of two new furocoumarins from 2-methylhydroquinone (Ib). To establish their structures, it was necessary to reinvestigate the Pechmann condensation of acetoacetic ester with mono-substituted hydroquinones. Desai and Mavani[2] have studied that reaction, using 2-methyl- and 2-ethylhydroquinone. They assumed that condensation occurred at the 5 position to produce 7-alkyl-6-hydroxy-4-methylcoumarins (II, R_1 = H), but obtained no experimental evidence to exclude the isomeric 5-alkyl or 8-alkyl possibilities. Other workers[3] have made the same assumption in similar reactions. A contrary result has recently been reported[1] when 2-allylhydroquinone (Id) was treated with acetoacetic ester in the presence of concentrated sulfuric acid. It was shown that the Pechmann condensation occurred in the 3 position followed by cyclization of an intermediate *o*-allylhydroxycoumarin to produce the angular dihydrofurocoumarin (IV), although the yield was only 18% and the rest of the reaction mixture was not identified.

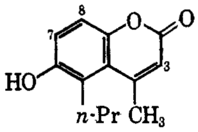
Experimental evidence has now been obtained to establish that acetoacetic ester undergoes sulfuric acid catalyzed Pechmann condensation with 2-methylhydroquinone (Ib) in the 5 position to produce 4,7-dimethyl-6-hydroxycoumarin (IIb) as originally assumed. Similar results were obtained with 2-*n*-propylhydroquinone (Ic).



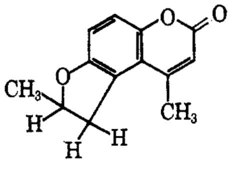
Ia, R=H
b, R=CH_3
c, R=n-C_3H_7
d, R=allyl



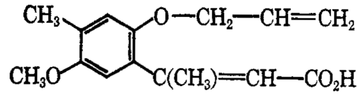
IIa, R_1=R_2=H
b, R_1=H; R_2=CH_3
c, R_1=H; R_2=n-C_3H_7
d, R_1=R_2=CH_3



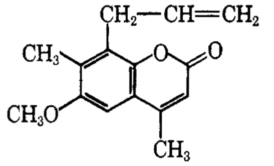
III



IV



V



VI

The nmr spectrum of 4,7-dimethyl-6-hydroxycoumarin shows two aromatic hydrogens as singlets (δ 7.02 and 7.07) The aromatic hydrogen spectrum of the coumarin from 2-*n*-propylhydroquinone is quite similar (δ 7.12 and 7.15). For comparison, the spectrum of 6-hydroxy-4-methyl-5-*n*-propylcoumarin[1] (III) was obtained and its aromatic hydrogen absorption appears as an AB multiplet (J = 9 cps, δ 7.15 and 7.17) because the two *ortho* hydrogens (7 and 8) split each other by spin coupling.[4] Since no splitting was observed in the spectra of the Pechmann condensation products, they were judged to be 7-alkylcoumarins (IIb and c), although the unknown 8-alkyl isomers could not be completely ruled out (*meta* hydrogens give weak couplings of 1–3 cps[4] which are not always seen).

Additional evidence, to eliminate the 8-alkyl possibility, was obtained from 4,7-dimethyl-6-hydroxycoumarin (IIb) by carrying out a synthetic sequence which requires that the 8 position be unsubstituted. It was converted to a methyl ether (IId), which was treated with allyl bromide and sodium hydroxide to obtain the allyloxycinnamic acid (V). When heated in boiling diethylaniline, V produced a compound ($C_{15}H_{16}O_3$) with an ultraviolet spectrum typical of 6-methoxycoumarins.[5] It must be 8-allyl-4,7-dimethyl-6-methoxycoumarin (VI) formed by *ortho* Claisen rearrangement and lactonization.

With its structure established, 4,7-dimethyl-6-hydroxycoumarin (IIb) was converted to its allyl ether (VIIa), which underwent the Claisen rearrangement in boiling diethylaniline to produce 5-allyl-4,7-dimethyl-6-hydroxycoumarin (VIIb) Ozonization, followed by catalytic hydrogenation, gave the hemiacetal (VIII)

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[1] K. D. Kaufman, J. F. W. Keana, R. C. Kelly, D. W. McBride, and G. Slomp, *J. Org. Chem.*, **27**, 2567 (1962).

[2] R. D. Desai and C. K. Mavani, *Proc. Indian Acad. Sci.*, **15A**, 11 (1942).

[3] (a) D. H. Mehta, R. S. Salimath, and N. M. Shah, *J. Indian Chem. Soc.*, **33**, 135 (1956); (b) P. B. Russell, A. R. Todd, S. Wilkinson, A. D. MacDonald, and G. Woolfe, *J. Chem. Soc.*, 169 (1941).

[4] H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

[5] A. Mangini and R. Passerini, *Gazz. Chim. Ital.*, **87**, 243 (1957).