[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES, BROWN UNIVERSITY]

Synthesis of Dinitrobenzomorpholines and a New Ring System, Triazolobenzomorpholines[1]

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Picramides (and related compounds, 1b, 1c) of β-amino alcohols in which there are bulky groups on the α-carbon undergo ring closure with various bases to give substituted benzomorpholines (II). A nitro group in position 5 is reduced to an amine (III) and diazotization results in cyclization to a new ring system (IV), triazolobenzomorpholines.

An attempt to prepare the picryl ether of 2-amino-2-methyl-1-propanol by an adaptation of the method of Cope and Burg[3] for synthesis of sulfonate esters of amino alcohols, (1) resulted in a

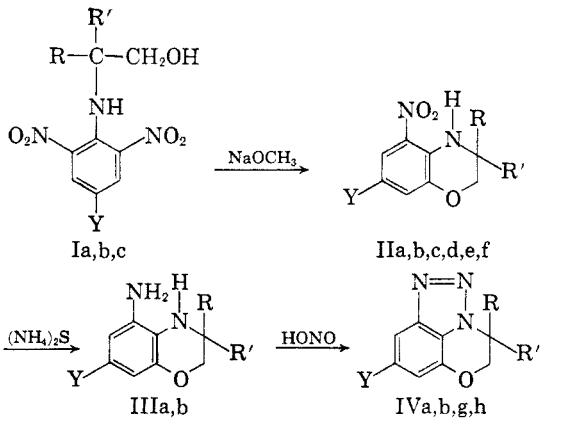
$$NaOCH_2CH_2NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_3CH_2CH_2NH_2 + NaCl \quad (1)$$

$$(CH_3)_2{-}CNH_2{-}CH_2ONa + (O_2N)_3C_6H_2Cl \longrightarrow IIa + NaCl \quad (2)$$

product in which the elements of nitrous acid had unexpectedly been lost. (2) The product was identified as 5,7-dinitro-3,3-dimethylbenzomorpholine, IIa (Chart I). This product could arise either from displacement of a nitro group by alkoxy (a well known reaction[4]) in a previously formed picramide(Ia to IIa) or from displacement of halogen by an amine in a previously formed ether. Neither reaction path has been used for benzomorpholine synthesis, where the simplest method appears to be ring closure on nitrogen, accomplished by reductive alkylation of a nitro group.[5,6] The mechanism of formation of the dinitrobenzomorpholines (II) is under study, but it will be assumed in the remainder of the present paper that the picramides (or I) are the starting compounds for the cyclization to benzomorpholines (II).

The benzomorpholine ring is only formed when compound I carries strong electron-withdrawing groups in the 4,6-positions and a nitro as leaving group in position 2. With nitro groups in positions 2 and 6, compound I will undergo ring closure when Y is $-NO_2$, $-CF_3$, $-CN$, but not when Y is $-COO^-$. With nitro groups in positions 2,4 and $-CF_3$ in position 6, ring closure could not be effected.

One arresting feature of the ring closure is that the group attached to the amino nitrogen must have a semblance to the shape or bulk of a *tert.*-butyl group which, of course, must include the β-hydroxy for the displacing group. The picramides of ethanolamine, 1-amino-2-propanol, 2-amino-3-butanol, 2-amino-1-butanol, and 1-amino-2-methyl-2-propanol[7] cannot be converted to benzomorpholines under the same conditions. Ring closures were effected in I (Y = NO_2) when R and R′ were both methyl, both hydroxymethyl, one methyl or ethyl and the other hydroxymethyl. This suggests that the present reaction is another manifestation of the unique character of geminal alkyl groups in accommodating ring closures.[8,9]



a. Y = NO_2, R = R′ = CH_3
b. Y = CF_3, R = R′ = CH_3
c. Y = CN, R = R′ = CH_3
d. Y = NO_2, R = C_2H_5, R′ = CH_2OH
e. Y = NO_2, R = CH_3, R′ = CH_2OH
f. Y = NO_2, R = R′ = CH_2OH
g. Y = NH_2, R = R′ = CH_3
h. Y = $NHCOC_6H_5$, R = R′ = CH_3

Chart I

A third factor not yet thoroughly investigated is the influence of base strength on ring closure. Sodium methoxide gave the best yields although excess of the amino alcohol (2-methyl-2-amino-1-propanol) gave a yield of 31% of IIa from the corresponding picramide, Ia. Sodium ethoxide, sodium hydride, and the sodium salts of the amino alcohols were less effective bases.

Identification of IIa as 5,7-dinitro-3,3-dimethyl-

(1) This work was supported in part by a grant from the Research Corporation.

(2) Allied Chemical and Dye Fellow, 1957–1958.

(3) A. C. Cope and M. Burg, *J. Am. Chem. Soc.*, **74**, 611 (1952).

(4) F. Reverd, *Org. Syntheses*, Coll. Vol. I., 219 (1941).

(5) R. Stoermer and H. Brockerhof, *Ber.*, **30**, 1631 (1897).

(6) W. H. Strain and J. B. Dickey, U.S. Patent **2,381,935** (1945).

(7) Mr. Glenn C. Morrison carried out these experiments.

(8) E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderly, *J. Am. Chem. Soc.*, **79**, 3467 (1957).

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benzomorpholine precludes the possibility of rearrangement of the picramide Ia to an amino ether (β-amino-*tert.*-butyl 2,4,5-trinitrophenyl ether) before ring closure, as the amino ether would yield 6,8 - dinitro - 3,3 - dimethylbenzomorpholine. This pathway appeared to be in the realm of possibility as the conditions approximate those for the Smiles[10] rearrangement.

The proof of structure of IIa was accomplished by reduction of the 5-nitro group to an amine and diazotization of the 5-amino group (IIIa) to effect a second ring closure to a new ring system, IVa. Of necessity the amino group in III is in position 5 if the subsequent ring closure occurs. If a Smiles rearrangement had occurred, a nitro group at positions 6 or 8 could not be reduced and cyclized by diazotization.

Comparison of the infrared spectra of the triazolo compounds IVa, IVb, and IVg (Fig. 1)

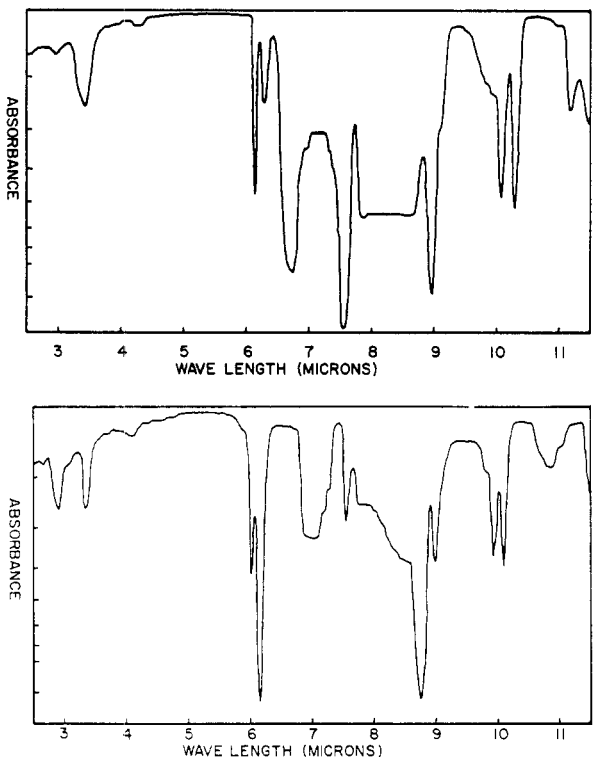

Fig. 1. Infrared spectra of 8-nitro-4,4-dimethyltriazolo-[1,5,4-d,e]benzomorpholine, IVa, and 8-amino-4,4-dimethyltriazolo[1,5,4-d,e]benzomorpholine, IVg, in chloroform (0.1% soln.) with sodium chloride prism. (Perkin-Elmer model 137 Infracord spectrophotometer)

with the aminobenzomorpholines IIIa and IIIb suggests that medium intensity bands at 10.1–10.2 μ may be characteristic of the triazolo ring in this three-ring system. Benzotriazole has a peak at 9.92 μ and Hartzel and Benson[11] suggest that characteristic absorption bands of the 4-alkyl-v-triazole ring system may lie between 9.8 and 10.3 μ.

The new triazolobenzomorpholine ring system compares in stability with the 4H-triazoloquinoline ring system, the nearest analog in the literature.[12] The triazolo ring system is aromatic in character and, indeed, very stable as is illustrated by the fact that oxidation of benzotriazoles cleaves the benzene ring in preference to the triazole ring, yielding triazoledicarboxylic acids.

The nitro group in IVa (the last one remaining from the original starting compound, picryl chloride) was easily reduced catalytically with hydrogen in the presence of platinum to give 8-amino-4,4-dimethyltriazolo [1,5,4-d,e] benzomorpholine[13] (IVg). The amino group was easily diazotized and coupled with various reagents to give a series of dyes (Table I) related to benzomorpholine dyes,[14] patented for use in dyeing cellulose acetate rayon and nylon.

The secondary nitrogen in the morpholine ring of IIa was not alkylated by methyl iodide and no derivative could be obtained with phenylisothiocyanate, Schotten-Baumann, or Hinsberg reagents. Nitrosation could not be effected with nitrous acid nor with nitrosyl chloride in pyridine. If the benzomorpholine IIa has the properties of a dinitroaniline, one might expect to cleave the ring to an amino ether. This could not be done in aqueous media and sodium ethoxide in ethanol gave a reaction in which no fragments could be identified. The ether linkage in the benzomorpholine was not cleaved by hydrochloric or hydrobromic acid under strenuous conditions while 57% hydriodic acid and pyridine hydrochloride (at 220°) gave profound decomposition.

EXPERIMENTAL[15]

Picramides. The picramides of ethanolamine,[16] m.p. 109.5–110.5°, 2-amino-1-butanol, m.p. 90–92°, 1-amino-2-propanol, m.p. 132.5–133.5°, 2-amino-3-butanol, m.p. 100–102.5°, diethanolamine, m.p. 138–139.5°, and 1-amino-2-methyl-2-propanol, m.p. 160.6–161.6°[17] were prepared by standard procedures except for the last (see ref. 17). Other picramides, Ib and Ic were not isolated but were used directly to prepare the corresponding benzomorpholine. Indeed, these picramides could not be isolated in pure form.

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(15) Melting points are corrected. Analyses by S. M. Nagy, Microchemical Laboratory, M.I.T., Cambridge, Mass.

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TABLE I

COUPLING COMPOUNDS OF 8-AMINO-4,4-DIMETHYLTRIAZOLO[1,5,4-d,e]BENZOMORPHOLINE

Coupling Compound	M.P.	Color	Yield, %	Formula	Calcd. C	Calcd. H	Found C	Found H
Dimethylaniline	181–183[a]	or.-yel.	76	$C_{18}H_{20}N_6O$	64.26	5.99[b]	64.28	6.10
Diethylaniline	149–151	orange	82	$C_{20}H_{24}N_6O$	65.91	6.64	66.66	6.52
α-Naphthylamine	245–247	dk. red	70	$C_{20}H_{18}N_6O$	67.02	5.06[c]	67.03	5.21
Resorcinol	225 dec.	or.-red	20	$C_{16}H_{15}N_5O_3$	59.07	4.65	59.96	4.71

[a] Melting points uncorrected. [b] Calcd.: N, 24.99. Found: N, 25.10. [c] Calcd.: N, 23.45. Found: N, 22.80.

Various methods of recrystallization of compound Ia resulted in a product, m.p. 103–110°, whose nitrogen content lay between the value calculated for picramide, 18.7%, and dinitrobenzomorpholine, 16.6%. The carbon content of the product also lay between that of the picramide and the dinitrobenzomorpholine. When an attempt to prepare the picramide was made in the presence of excess amino alcohol, IIa, instead, was obtained in 31% yield.

5,7-Dinitro-3,3-dimethylbenzomorpholine, IIa. In a 2-l. three-necked flask fitted with a stirrer, dropping funnel, and a condenser carrying a calcium chloride tube was placed 60.0 g. (0.24 mole) of picryl chloride in 600 ml. of absolute methanol. To this was added 46.5 g. (0.52 mole) of 2-amino-2-methyl-1-propanol and the solution was refluxed 45 min. Thirty grams (0.55 mole) of sodium methoxide in 200 ml. of absolute methanol was added over a period of 10 min. from the dropping funnel. The mixture was stirred 30 min. longer at reflux, cooled in ice, and the product removed and washed thoroughly with water and dilute methanol. In several runs the product weighed 40.5–45.1 g., m.p. 173–175.5°. Recrystallization from 800 ml. of benzene gave 29.0–35.6 g., 47–58% yield, m.p. 174.5–176°.

Anal. Calcd. for $C_{10}H_{11}N_3O_5$: C, 47.40; H, 4.35; N, 16.61. Found: C, 47.73; H, 4.50; N, 16.21.

The compound took up the calculated amount of hydrogen in the presence of platinum oxide for two nitro groups but the product rapidly decomposed in air and was not further characterized.

7-Nitro-5-amino-3,3-dimethylbenzomorpholine, IIIa. A mixture of 31.1 g. (0.123 mole) of IIa in 400 ml. of 95% ethanol and 200 ml. of 28% ammonium hydroxide was stirred mechanically at 45–55° while a slow stream of hydrogen sulfide was introduced at the bottom of the suspension over a 2.5-hr. period. The red solution was cooled in ice and the red product removed by filtration. Concentration of the filtrate at reduced pressure to 250 ml. gave a total of 18 g. of product. The product was washed with carbon disulfide and recrystallized from toluene to yield 15.6g. (57%) of 7-nitro-5-amino-3,3-dimethylbenzomorpholine, m.p. 180.5–183.5° dec. The reaction was carried out with some dispatch since it oxidized rapidly in solution.

Vacuum sublimation gave an analytical sample and the compound was reasonably stable after purification; m.p. 182.5–184.5° dec.

Anal. Calcd. for $C_{10}H_{13}N_3O_3$: C, 53.81; H, 5.87; N, 18.83. Found: C, 53.65; H, 6.17; N, 18.67.

A benzal derivative was prepared by the method of Vogel[18] and recrystallized from 95% ethanol, m.p. 160–163°.

Anal. Calcd. for $C_{17}H_{17}N_3O_3$: C, 65.58; H, 5.51; N, 13.50. Found: C, 65.32; H, 5.78; N, 13.64.

A monoacetyl derivative prepared by the method of Vogel[19] was sublimed *in vacuo* to give an analytical sample, m.p. 195–196.5°.

Anal. Calcd. for $C_{12}H_{15}N_3O_4$: C, 54.34; H, 5.70; N, 15.84. Found: C, 53.80; H, 5.58; N, 15.76.

8-Nitro-4,4-dimethyltriazolo[1,5,4-d,e]benzomorpholine, IVa. Five grams (0.022 mole) of 7-nitro-5-amino-3,3-dimethylbenzomorpholine (IIIa) was dissolved in 50 ml. of warm 20% sulfuric acid and then cooled to 0°. The solution was stirred mechanically during the addition of a solution of 1.7 g. (0.025 mole) of sodium nitrite in 10 ml. of water over a 10-min. period. The resulting mixture was stirred for 15 min. longer at 0–10°. Filtration and recrystallization from dilute ethanol yielded 4.9 g. (93%) of dark needles, m.p. 147–153°. Vacuum sublimation gave an analytical sample of yellow needles, m.p. 151.5–153.5°.

Anal. Calcd. for $C_{10}H_{10}N_4O_3$: C, 51.28; H, 4.30; N, 23.92. Found: C, 51.43; H, 4.51; N, 24.36.

Comparison of the infrared spectra of compounds IVa and IVg is afforded in Fig. 1.

8-Amino-4,4-dimethyltriazolo[1,5,4-d,e]benzomorpholine, IVg. A sample of 8-nitro-4,4-dimethyltriazolo[1,5,4-d,e]-benzomorpholine (0.92 g., 0.0039 mole) was dissolved in 30 ml. of absolute methanol and reduced with hydrogen at 1 atm. in the presence of 0.25 g. of platinum oxide (prereduced). The theoretical volume of hydrogen was taken up. Removal of the solvent gave a slightly discolored product but vacuum sublimation at 186° (1 mm.) gave 0.50 g. (62%) of white cubic crystals, m.p. 217.5–220.5° dec. (darkens 214°).

Anal. Calcd. for $C_{10}H_{12}N_4O$: C, 58.81; H, 5.91; N, 27.43. Found: C, 59.17; H, 6.07; N, 27.39.

A benzoyl derivative, IVh, was recrystallized from dilute methanol and sublimed at 215° (1 mm.), m.p. 219.5–221.5°.

Anal. Calcd. for $C_{17}H_{16}N_4O_2$: C, 66.22; H, 5.23; N, 18.17. Found: C, 66.28; H, 5.16; N, 18.01.

5-Nitro-7-cyano-3,3-dimethylbenzomorpholine, IIc. 3,5-Dinitro-4-chlorobenzoic acid was obtained in 95% yield from *p*-chlorobenzoic acid as described in the literature.[20] The acid was converted to an amide (m.p. 186°) by way of the acid chloride (m.p. 58°) according to directions of Lindemann and Wessel[21] in 83% yield.

A finely powdered mixture of 12.4 g. (0.051 mole) of 3,5-dinitro-4-chlorobenzamide was heated with 12 g. (0.084 mole) of phosphorus pentoxide for 15 min. in a metal bath at 300–350°. The resulting pale yellow nitrile was distilled from the reaction flask, b.p. 220–225° (15 mm.). Recrystallization of the solidified product from methanol gave 5.5 g. (48%) of short needles, m.p. 137–141°. The analytical sample by repeated recrystallizations from methanol melted at 143–144.5°.

Anal. Calcd. for $C_7H_2N_3O_4Cl$: C, 36.94; H, 0.89; N, 18.46. Found: C, 37.01; H, 1.35; N, 18.30.

Three grams (0.013 mole) of 3,5-dinitro-4-chlorobenzonitrile was refluxed for 0.5 hr. with 2.5 g. (0.028 mole) of 2-amino-2-methyl-1-propanol in 60 ml. of absolute methanol. Addition of 1.6 g. (0.028 mole) of sodium methoxide in 60 ml. of absolute methanol and refluxing 0.5 hr. longer gave 1.5 g. of orange product after evaporation of most of the solvent. Recrystallization from methanol yielded 1.2 g.

(18) A. I. Vogel, *A Textbook of Practical Organic Chemistry,* Longmans, Green and Co., New York (1951), 2nd Ed., p. 625.

(19) Ref. 12, pp. 556–7.

(20) F. Ullmann and N. Wosnessensky, *Ann.,* **366,** 92 (1909).

(21) H. Lindemann and W. Wessel, *Ber.,* **58B,** 1221 (1925).

(39%) of 5-nitro-7-cyano-3,3-dimethylbenzomorpholine, fluffy orange crystals, m.p. 176–181°. A sublimed sample (160°, 1 mm.) was used for analysis, m.p. 180–181.5°.

Anal. Calcd. for $C_{11}H_{11}N_3O_3$: C, 56.65; H, 4.76; N, 18.02. Found: C, 56.47; H, 4.92; N, 17.82.

By a procedure similar to that described for compound IIa above, the following dinitrobenzomorpholines were obtained:

3-Hydroxymethyl-3-ethyl-5,7-dinitrobenzomorpholine, IId, orange crystals, m.p. 139.5–141°, 37%.

Anal. Calcd. for $C_{11}H_{13}N_3O_6$: C, 46.64; H, 4.63; N, 14.84. Found: C, 46.51; H, 4.78; N, 14.90.

3-Hydroxymethyl-3-methyl-5,7-dinitrobenzomorpholine, IIe, orange crystals, m.p. 147.2–148.6°, 47%.

Anal. Calcd. for $C_{10}H_{11}N_3O_6$: C, 44.61; H, 4.12; N, 15.61. Found: C, 44.84; H, 3.95; N, 15.80.

3,3-Dihydroxymethyl-5,7-dinitrobenzomorpholine, IIf, yellow powder, m.p. 158.5–160 dec., 31%.

Anal. Calcd. for $C_{10}H_{11}N_3O_7$: C, 42.11; H, 3.89; N, 14.73. Found: C, 41.93; H, 4.05; N, 14.64.

5-Nitro-7-trifluoromethyl-3,3-dimethylbenzomorpholine, IIb. Two nitro groups are best introduced into 4-chlorobenzotrifluoride one at a time as described by Friedrich and Schniepp.[22] The first nitration gave 3-nitro-4-chlorobenzotrifluoride in 84% yield[23] and the second 3,5-dinitro-4-chlorobenzotrifluoride[24] in 85% yield. Seven grams (0.026 mole) of the dinitro compound was dissolved in 50 ml. of absolute methanol. The solution was refluxed with 4.65 g. (0.05 mole) of 2-amino-2-methyl-1-propanol for a few minutes, 4.0 g. of sodium methoxide was added in 50 ml. of methanol, and refluxing was continued 10 min. The product was precipitated by adding 50 ml. of water and recrystallized from 90% methanol to yield 4.8 g. (67%) of 5-nitro-7-trifluoromethyl-3,3-dimethylbenzomorpholine, golden needles, m.p. 107–109°. A sublimed analytical sample melted at 108–109.5°.

Anal. Calcd. for $C_{11}H_{11}N_2O_3F_3$: C, 47.83; H, 4.01; N, 10.14. Found: C, 48.09; H, 4.19; N, 10.13.

5-Amino-7-trifluoromethyl-3,3-dimethylbenzomorpholine, IIIb. In the presence of 0.30 g. of platinum oxide (prereduced) 1 g. of 5-nitro-7-trifluoromethylbenzomorpholine was reduced quantitatively in 40 ml. of absolute methanol at 1 atm. of hydrogen pressure in 1 hr. After removal of solvent the product was sublimed at 70° (1 mm.) to give 0.80 g. (90%) of white 5-amino-7-trifluoromethyl-3,3-dimethylbenzomorpholine, m.p. 80–82°.

Anal. Calcd. for $C_{11}H_{13}N_2OF_3$: C, 53.65; H, 5.37; N, 11.38. Found: C, 53.88; H, 5.43; N, 11.30.

8-Trifluoromethyl-4,4-dimethyltriazolo[1,5,4-d,e]benzomorpholine, IVb. A sublimed sample (0.27 g., 0.0011 mole) of 5-amino-7-trifluoro-3,3-dimethylbenzomorpholine, IIIb, was dissolved in 30 ml. of warm 50% sulfuric acid and then cooled in ice. An ice-cold solution of 0.12 g. (0.0017 mole) sodium nitrite in 10 ml. of water was added slowly over a 10-min. period with stirring. The reaction mixture was poured into 100 ml. of water and the white precipitate was collected. Recrystallization from dilute methanol gave 0.10 g. (35%) of short white needles, m.p. 101–102.5°.

Anal. Calcd. for $C_{11}H_{10}N_3OF_3$: C, 51.36; H, 3.92; N, 16.34. Found: C, 51.16; H, 4.09; N, 16.01.

Azo Dyes from 8-Amino-4,4-dimethyltriazolo[1,5,4-d,e]-benzomorpholine, IVg. Standard procedures for diazotization of 8-amino-4,4-dimethyltriazolo[1,5,4-d,e]benzomorpholine and coupling with various compounds in sodium acetate solution were employed to obtain the dyes described in Table I. The dyes were all recrystallized from 95% ethanol.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, M. S. UNIVERSITY]

Chloromethylation of Some Coumarin Derivatives

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Several coumarin derivatives have been chloromethylated and the structures of the chloromethyl derivatives established by direct comparison of the methyl derivatives, obtained on reduction, with the known compounds or authentic specimens synthesized for this purpose.

The chloromethylation of coumarins has not been studied so far. As chloromethyl derivatives are useful for the synthesis of a variety of compounds, the present work was undertaken. Coumarin, 4-methylcoumarin, 4′-methyl-1,2-naphtha-α-pyrone, and 7,8-dimethoxy-4-methylcoumarin on chloromethylation with paraformaldehyde and hydrogen chloride gave the corresponding 3-chloromethyl derivatives. Higher chloromethyl derivatives could not be obtained. The chloromethyl derivatives were reduced to the corresponding 3-methylcoumarin derivatives and directly compared with the authentic specimens.

7-Methoxy-4-methylcoumarin with one mole of paraformaldehyde gave a mixture from which only the 6-chloromethyl derivative could be isolated in a pure state. This was reduced to 7-methoxy-4,6-dimethylcoumarin. With 2.3 moles of paraformaldehyde a mixture was obtained from which both the 3,6- and the 3,8-dichloromethyl derivatives were isolated. These were reduced to the corresponding 3,4,6-trimethyl- and 3,4,8-trimethylcoumarin, which were synthesized for comparison by the Pechmann condensation of ethyl-α-methyl acetoacetate with 4-methyl- and 2-methylresorcinol respectively and subsequent methylation of the hydroxycoumarins formed. The 3,6,8-trichloromethyl derivative was obtained by the further chloromethylation of the above dichloromethyl derivatives and by the chloromethylation of 7-methoxy-4-methylcoumarin in ethylene dichloride in presence of zinc chloride.