	M.P., °C.	Yield, %	C Calcd.	C Found	H Calcd.	H Found	F Calcd.	F Found
o-Fluorophenylacetic acid	59	82		62.39		4.71		12.17
m-Fluorophenylacetic acid	38	87	62.33	62.21	4.54	4.58	12.33	12.20
p-Fluorophenylacetic acid	85	79		62.46		4.41		12.48

o-, m- and p-Fluorophenylacetyl chloride. To 23 g. (0.15 mole) of fluorophenylacetic acid in a round-bottom flask fitted with a reflux condenser was added 50 ml. of thionyl chloride. The ensuing exothermic reaction was allowed to go to completion. After removal of the excess thionyl chloride the product was fractionated.

	B.P., °C.	Yield, %	Cl Calcd.	Cl Found
o-Fluorophenylacetyl chloride	203–204	70		20.52
m-Fluorophenylacetyl chloride	201–202	72	20.58	20.46
p-Fluorophenylacetyl chloride	202–204	85		20.49

Reaction of fluorobenzoyl and fluorophenylacetyl chlorides with alkylaminoethanols. The amino alcohol (0.015 mole) was dissolved in 50 ml. of dry benzene and the solution was cooled with ice water. To this solution was added 0.015 mole of acyl chloride under efficient stirring. The white ester hydrochloride precipitated. After standing 1 hr. the reaction mixture was filtered and the precipitate was washed with a little benzene, recrystallized from ether-alcohol, and dried *in vacuo* (the products are strongly hygroscopic). The properties of the compounds are listed in Table I.

BUDAPEST, HUNGARY

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

Studies of Quinoid Structures. I. Action of Arylmagnesium Halides on Phenanthrenequinonimine

WILLIAM IBRAHIM AWAD AND ABDEL REHIM ABDEL RAOUF

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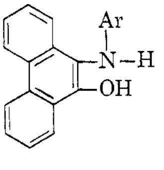
Arylmagnesium halides react with phenanthrenequinonimine by 1,2-addition and not by 1,4-addition as described by Mustafa and Kamel.[1] The constitution of the Grignard products is discussed.

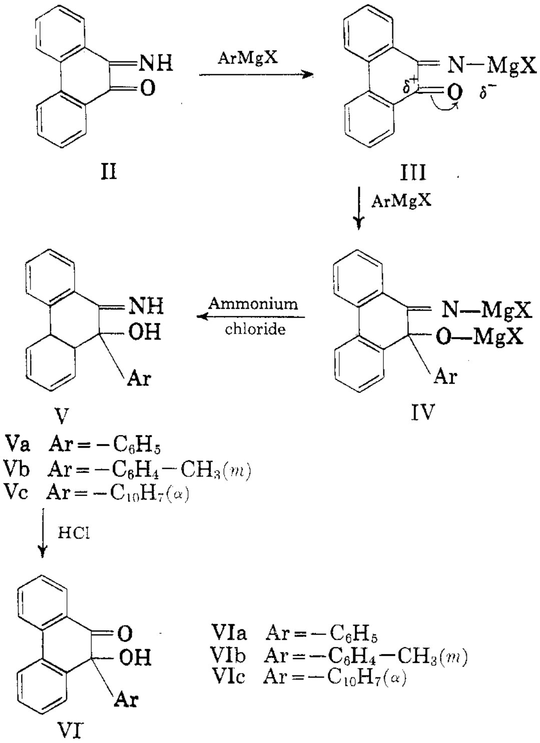
Mustafa and Kamel[1] stated that arylmagnesium halides react with phenanthrenequinonimine by 1,4-addition yielding 10-arylamino-9-phenanthrol (I). The main line of evidence was the identity of their product (from phenylmagnesium bromide and phenanthrenequinonimine) with the 10-phenylamino-9-phenanthrol obtained by Schmidt and Lumpp[2] from aniline and 9,10-dihydroxyphenanthrene. They claimed that a mixture melting point experiment gave no depression and hence structure I was assigned.



I

Ia Ar = $-C_6H_5$
Ib Ar = $-C_6H_4\text{-}CH_3(m)$
Ic Ar = $-C_{10}H_7(\alpha)$

In contrast to Mustafa and Kamel,[1] we found that the Grignard product (Va) gave a depression in melting point with Schmidt's compound (Ia). Also, the compounds gave different colors with concentrated sulfuric acid (Schmidt's compound, after purification, was orange-brown; the Grignard compound was green.) The benzoyl derivatives of the compounds gave different colors with concentrated sulfuric acid and a depression was noted in the mixture melting point.



Scheme A

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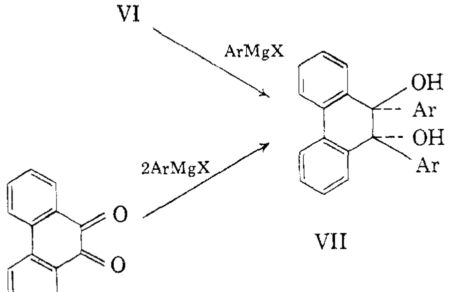
[1] Mustafa and Kamel, *J. Am. Chem. Soc.*, **76**, 124 (1954).

[2] Schmidt and Lumpp, *Ber.*, **43**, 787 (1910).

Phenanthrenequinonimine, like all other imines, was found to contain active hydrogen[3] (Zerewitinoff method). On the this basis, phenanthrenequinonimine should undergo a substitution reaction with a Grignard reagent to give a compound of the type III. The carbonyl group then is expected to react normally (1,2-addition) with an excess of the Grignard reagent to give IV. Hydrolysis of IV with ammonium chloride will then lead to 9-aryl-9,10-dihydro-10-imino-9-phenanthrol (V) according to Scheme A.

The constitution of the Grignard products was based on the fact that they are easily hydrolyzed in acid medium to give a ketonic nitrogen-free compound (VI) (compare the last step of Scheme A.) This hydrolysis is difficult to explain on the basis of the constitution given by Mustafa and Kamel, since 10-phenylamino-9-phenanthrol is stable to acid. (In its original method of preparation it is heated in a hydrochloric acid medium for one hour without change.)[2]

The constitution of the ketone VI is supported by (a) analytical data, (b) the formation of a 2,4-dinitrophenylhydrazone, (c) the reaction with arylmagnesium halide to yield *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediol (VII), identified by melting point and mixture melting point determinations with an authentic sample prepared from phenanthrenequinone and the corresponding arylmagnesium halide[4] according to Scheme B.



VIIa Ar = —C_6H_5
VIIb Ar = —C_6H_4—$CH_3(m)$
VIIc Ar = —$C_{10}H_7(\alpha)$

Scheme B

Further confirmation of the differences in constitution of the Grignard product (Va) and Schmidt's compound (Ia) is observed by comparing the ultraviolet spectrograms (Fig. 1). From these curves it is clear that Va and Ia are different.

We have also compared the ultraviolet spectrograms of Va and the corresponding keto-compound (VIa) where the shape of the curves and the longest maxima are near to each other.[5]

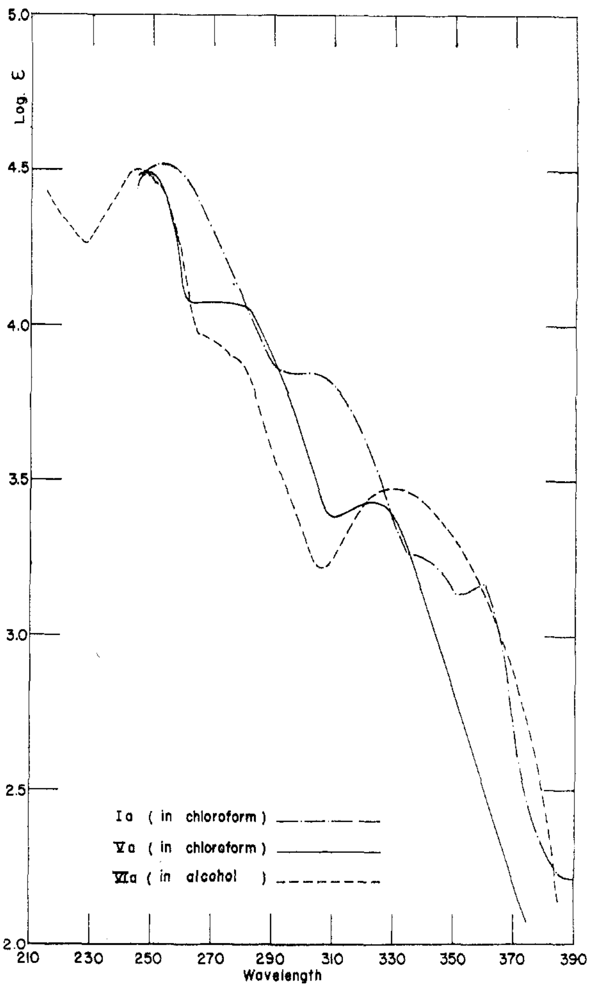


Fig. 1

EXPERIMENTAL

Melting points are not corrected. Microanalyses were carried out by Alfred Bernhardt, Germany.

Preparation of phenanthrenequinonimine. This compound was prepared according to Schmidt and Junghans,[6] and was recrystallized from anhydrous benzene.

Anal. Calcd. for $C_{14}H_9NO$: Active hydrogen, 0.48. Found: Active hydrogen, 0.45.

Action of phenylmagnesium bromide on phenanthrenequinonimine. A solution of phenylmagnesium bromide (9 g. of bromobenzene and 0.9 g. of magnesium in 50 cc. of dry ether) was prepared in the usual way. A solution of 1 g. of phenanthrenequinonimine in 30 cc. of dry benzene was added to the above solution. The pale green reaction mixture was refluxed for 2 hr. on the water bath and left overnight at room temperature.

The Grignard product was hydrolyzed using a saturated solution of ammonium chloride. The ether-benzene layer was separated, washed with water, dehydrated over anhydrous sodium sulfate, filtered, and allowed to concentrate.

The product was precipitated by the addition of petroleum ether (40–60°) and was recrystallized from benzene–petroleum ether (40–60°), as pale yellow crystals m.p. 155°, yield 0.6 g. It gave an olive-green color with concentrated sulfuric acid; this color changed gradually to a reddish-brown and finally to brown on adding a crystal of potassium nitrate or a few drops of concentrated nitric acid.

The melting point was depressed on admixture with

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(3) Compare Kharasch and Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, 1954, p. 1169.

(4) *Elsevier's Encyclopaedia of Organic Chemistry*, Elsevier Publishing Company, Inc., New York, Amsterdam, **13**, (1946), pp. 852–3.

(5) Gillam and Stern, *An Introduction to Electronic Absorption in Organic Chemistry*, Edward Arnold, London, 1955, p. 44.

(6) Schmidt and Junghans, *Ber.*, **37**, 3558 (1904).

Schmidt's compound (10-phenylamino-9-phenanthrol) (Ia).

Anal. Calcd. for $C_{20}H_{15}NO$: C, 84.2; H, 5.3; N, 4.9. Found: C, 84.1; H, 5.7; N, 4.6.

Hydrolysis of Va. A solution of 0.7 g. of Va, 50 cc. of ethyl alcohol, and 10 cc. of concentrated hydrochloric acid was refluxed for 2 hr. on the water bath. The addition of concentrated hydrochloric acid caused the substance to dissolve immediately and the solution acquired a dark brown color.

The product was precipitated after concentration and cooling and was recrystallized from methyl alcohol as colorless crystals m.p. 117–119°, yield 0.5 g. It gave a brown color with concentrated sulfuric acid, turning later to violet.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9. Found: C, 84.6; H, 5.3.

Preparation of the 2,4-dinitrophenylhydrazone derivative of VIa. A solution of 0.2 g. of VIa in 20 cc. of hot methyl alcohol was prepared. A second solution, containing 0.4 g. of 2,4-dinitrophenylhydrazine in 30 cc. of hot methyl alcohol, also was prepared, a few drops of concentrated sulfuric acid were added and the two solutions were mixed together and heated on the water bath. The color darkened and heating was continued until crystals started to separate. The product was dissolved in benzene and allowed to pass through an alumina column. The benzene solution was concentrated and the precipitate was crystallized from benzene as violet-red needles, m.p. 224°, yield 0.1 g. It gave a green color with concentrated sulfuric acid.

Anal. Calcd. for $C_{26}H_{18}O_5N_4$: N, 12.0. Found: N, 11.4.

Action of phenylmagnesium bromide on VIa. Magnesium (0.1 g.) and bromobenzene (0.5 g.) were used in the preparation of phenylmagnesium bromide in the usual way. A solution of 0.5 g. of VIa in 10 cc. of dry benzene was added to the above reagent and the reaction was allowed to proceed to completion. The Grignard product was hydrolyzed in the usual way.

The ether-benzene mixture was evaporated and the residue was triturated with petroleum ether (40–60°) and recrystallized from a small amount of ethyl alcohol as colorless prisms, m.p. 179–180°, yield 0.3 g.

The melting point was not depressed on admixture with an authentic sample prepared as in Ref. 4. It gave an orange color with concentrated sulfuric acid.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.7; H, 5.5. Found: C, 85.5; H, 5.6.

Benzoylation of Va. Va (0.2 g.), 5 cc. of pyridine, and 3 cc. of benzoyl chloride were heated on the water bath for 2 hr. and then poured into 25 cc. of dilute hydrochloric acid. An oil separated out which was extracted with ether, washed with sodium carbonate solution, then with water, and then was dehydrated over anhydrous sodium sulfate. The ether was evaporated and the oily residue was triturated with benzene–petroleum ether (40–60°); it was recrystallized from benzene–petroleum ether (40–60°) to give pale yellow crystals m.p. 214°, yield 0.15 g. It gave an olive-green color with concentrated sulfuric acid. The m.p. was depressed on admixture with the benzoyl derivative of Schmidt's compound (Ia).

Anal. Calcd. (for monobenzoyl) $C_{27}H_{19}NO_2$: C, 83.3; H, 4.9; N, 3.6; (for dibenzoyl) $C_{34}H_{23}NO_3$: C, 82.8; H, 4.7; N, 2.8. Found: C, 83.5; H, 5.1; N, 3.1.

It is clear that the analytical data of the mono and the dibenzoyl derivatives are very similar. However, we believe that it is a dibenzoyl derivative, as is clear from the analytical data for the *o*-chlorobenzoyl derivative (shown below).

Preparation of the o-chlorobenzoyl derivative of Va. Va (0.2 g.), 5 cc. of pyridine, and 3 cc. of *o*-chlorobenzoyl chloride were heated on the water bath for 2 hr. and treated as before. The product was recrystallized from benzene–petroleum ether (40–60°) as colorless crystals, m.p. 219°, yield 0.15 g. It gave an olive-green color with concentrated sulfuric acid.

Anal. Calcd. (for monobenzoyl) $C_{27}H_{18}ClNO_2$: C, 76.5; H, 4.3; N, 3.3; Cl, 8.4; (for dibenzoyl) $C_{34}H_{21}Cl_2NO_3$: C, 72.6; H, 3.7; N, 2.5; Cl, 12.6. Found: C, 73.0; H, 3.9; N, 2.6; Cl, 12.3.

Comment on the purification of 10-phenylamino-9-phenathrol (Schmidt's compound) (Ia).[2] Schmidt and Lumpp[2] obtained the above compound in green prisms from alcohol, m.p. 165°. This compound gave a green color with concentrated sulfuric acid; on adding a crystal of potassium nitrate or a few drops of concentrated nitric acid, it immediately changed to a persistent, intense red color.

In order to compare Schmidt's product (Ia) with the Grignard product (Va), Ia was recrystallized (using charcoal) from the same solvent as Va (benzene–petroleum ether, 40–60°) in grey crystals; the green color of the crystals completely disappeared, m.p. 169° (not depressed on admixture with the above sample). This pure compound gave an orange-brown color with concentrated sulfuric acid which changed rapidly to intense red on adding a crystal of potassium nitrate or a few drops of concentrated nitric acid.

It should be noted that on dissolving Ia in alcohol for the examination of the ultraviolet spectrum, the solution changed its color gradually from colorless to greenish-violet, a fact which forced us to carry out the examination of the ultraviolet spectrum of Ia in a nonhydroxylic solvent such as chloroform.

Benzoylation of 10-phenylamino-9-phenanthrol [Schmidt's compound (Ia)]. Ia (0.5 g.), 15 cc. of pyridine, and 8 cc. of benzoyl chloride were heated for 2 hr. on the water bath and treated as before. The product was recrystallized from benzene–petroleum ether (40–60°) as colorless crystals m.p. 217°, yield 0.3 g. It gave a pale lemon-yellow color with concentrated sulfuric acid. The melting point was depressed on admixture with the benzoyl derivative of Va.

Anal. Calcd. for $C_{34}H_{23}NO_3$: C, 82.8; H, 4.7; N, 2.8. Found: C, 82.9; H, 5.1; N, 2.97.

Action of m-tolylmagnesium bromide on phenanthrenequinonimine. Magnesium (0.7 g.) and *m*-bromotoluene (6 g.) were used in the preparation of *m*-tolylmagnesium bromide by the same procedure as in the preparation of phenylmagnesium bromide. A solution of 1.5 g. of phenanthrenequinonimine in 60 cc. of dry benzene was added and the reaction was allowed to proceed to completion as before. The product was recrystallized from benzene as pale yellow crystals m.p. 179°, yield 1.2 g. It gave a green color with concentrated sulfuric acid, rapidly changing to a brown-violet color.

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.3; H, 5.7; N, 4.7. Found: C, 84.4; H, 5.8; N, 4.5.

Hydrolysis of Vb. The compound (0.5 g.) in 50 cc. of ethyl alcohol was hydrolyzed with 10 cc. of concentrated hydrochloric acid in the same manner as before. The product was precipitated by the addition of water and was recrystallized from petroleum ether (40–60°) as colorless crystals m.p. 145°, yield 0.3 g. It gave a green color with concentrated sulfuric acid, changing to brown.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.4. Found: C, 83.6; H, 5.4.

Action of m-tolylmagnesium bromide on VIb. Magnesium (0.1 g.) and *m*-bromotoluene (1 g.) were used in the preparation of *m*-tolylmagnesium bromide as before. A solution of 0.3 g. of VIb in 20 cc. of dry benzene was added and the reaction completed as before. The product in form of an oil was triturated with a chloroform–methyl alcohol mixture. The solid obtained was recrystallized by dissolving in hot methyl alcohol and adding a few drops of chloroform to help solution; it was filtered and left to evaporate slowly whereby colorless crystals came down, m.p. 149°, yield 0.2 g. It gave a yellow-orange color with concentrated sulfuric acid.

The melting point was not depressed on admixture with an authentic sample prepared as in Ref. 4.

Action of α-naphthylmagnesium bromide on phenanthrenequinonimine. Magnesium (1.2 g.) and α-bromonaphthalene (10 g.) were used in the preparation of α-naphthylmagnesium bromide in the usual way. A solution of 2 g. of phenanthrenequinonimine in 60 cc. of dry benzene was added to the

Grignard reagent and the reaction was completed as before. The product was recrystallized from benzene–petroleum ether (40–60°) as colorless crystals, m.p. 177°, yield 1.8 g. It gave a blue-violet color with concentrated sulfuric acid.

Anal. Calcd. for $C_{24}H_{17}NO$: C, 85.9; H, 5.1; N, 4.2. Found: C, 86.3; H, 5.3; N, 4.0.

Hydrolysis of Vc. The compound (0.5 g.) in 50 cc. of ethyl alcohol was hydrolyzed with 8 cc. of concentrated hydrochloric acid as before. The product was precipitated by the addition of water and recrystallized from petroleum ether (80–100°) as colorless crystals, m.p. 168°, yield 0.4 g. It gave a purple color with concentrated sulfuric acid.

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.7; H, 4.8. Found: C, 85.2; H, 5.1.

Action of α-naphthylmagnesium bromide on VIc. Magnesium (0.3 g.) and α-bromonaphthalene (2 g.) were used in the preparation of α-naphthylmagnesium bromide as before. A solution of 1 g. of VIc in 30 cc. of dry benzene was added and the reaction was completed as before. The product was recrystallized from benzene as colorless crystals, m.p. 261°, yield 0.8 g. It gave a brown color with concentrated sulfuric acid.

The melting point was not depressed on admixture with an authentic sample prepared as in Ref. 4.

Anal. Calcd. for $C_{34}H_{24}O_2$: C, 87.9; H, 5.2. Found: C, 88.4; H, 5.5.

Benzoylation of Vc. Vc (0.5 g.), pyridine (10 cc.), and benzoyl chloride (8 cc.) were heated on the water bath for 2 hr., then poured into 60 cc. of dilute hydrochloric acid. The product was treated as in the case of benzoylation of Va.

The oily product was triturated with petroleum ether (40–60°), cooled in ice to solidify, and filtered from the oily part. It was recrystallized from benzene–petroleum ether (40–60°) in colorless crystals, m.p. 241°, yield 0.3 g. It gave an emerald-green color with concentrated sulfuric acid.

Anal. Calcd. (for monobenzoyl) $C_{31}H_{21}NO_2$: C, 86.7; H, 4.8; N, 3.2; (for dibenzoyl) $C_{38}H_{25}NO_3$: C, 84.0; H, 4.6; N, 2.6. Found: C, 84.2; H, 4.7; N, 2.6.

Acknowledgment. The authors are indebted to Dr. F. G. Baddar, Assistant Professor, Chemistry Department, Faculty of Science, Cairo University, for his valuable help in the determination of the ultraviolet spectrograms.

ABBASSIA, CAIRO, EGYPT

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, INSTITUTE OF SCIENCE]

Substitution in the Benzopyrone Series. IV. Sulfonation of Coumarin Derivatives

J. R. MERCHANT AND R. C. SHAH

Received November 19, 1956

The sulfonation of 7-hydroxy-3,4-dimethylcoumarin, its methyl ether, 7-hydroxy-4-methyl-6-ethylcoumarin, its methyl ether, 7-hydroxy-3,4-dimethyl-6-ethylcoumarin and its methyl ether, with chlorosulfonic acid is described. The structures of the sulfonated products have been established, by oxidation, bromination, or nitration to give known compounds.

The present work was undertaken with a view to studying the reactivity of some substituted 7-hydroxycoumarins and their methyl ethers upon sulfonation.[1]

The products of sulfonation were characterized as described previously[2] by their conversion to crystalline derivatives. Table I describes the experimental conditions and the results obtained on the sulfonation of different coumarin derivatives with chlorosulfonic acid. From the results of the sulfonation, it is observed that in 7-hydroxycoumarins, the *6* position is the most reactive, positions *3* and *8* being next in order of reactivity. It is also interesting to note that the *8* position is not favorable for the formation of sulfonyl chlorides. In the case of 7-methoxycoumarins also, the order of reactivity is $6 > 3$. The substitution in the *8* position is always accompanied by demethylation.

It was observed that the sulfonation of 7-hydroxy-3,4-dimethylcoumarin at 100° or at lower temperatures gave monosulfonated products I and II, while the disulfonic acid III was obtained with excess of chlorosulfonic acid at higher temperatures. Experiments to prove the constitution of I by the hydrolysis, nitration, and methylation of its sodium salt failed to give definite products. Since the sulfonic acid I could be easily obtained by the hydrolysis of the sulfonyl chloride II, attempts were made to establish the structure of the latter. It is known[3] that halogenation and nitration of sulfonyl chlorides can be effected without modifying the sulfonyl chloride group. Consequently, the bromination of II was carried out and a bromo sulfonyl chloride was obtained. The chlorosulfonation of the known[4] 7-hydroxy-6-bromo-3,4-dimethylcoumarin was attempted under a variety of conditions; however, the product, in all cases, was a sulfonic acid (IV). This bromosulfonic acid was different from that obtained by hydrolysis of the bromo sulfonyl chloride and was assigned the structure, 7-hydroxy-6-bromo-3,4-dimethylcoumarin-8-sulfonic acid. The position of the sulfonyl chloride group in II, however, was determined by demethylation of

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[1] C. M. Suter, *Organic Chemistry of Sulfur*, John Wiley and Sons, Inc., New York, 1948, p. 316.

[2] D. V. Joshi, J. R. Merchant, and R. C. Shah, *J. Org. Chem.*, 21, 1104 (1956); J. R. Merchant and R. C. Shah, *J. Ind. Chem. Soc.*, **34**, 35 (1957).

[3] Reference 1, p. 512.

[4] D. Chakravarty and S. M. Mukherjee, *J. Ind. Chem. Soc.*, **14**, 729 (1937).