gated the condensation of mesityl oxide and methyl vinyl ketone and concluded that the product contained, indeed, piperitenone (I) *together with* isoxylitone (IV).

We would like to clarify the situation on the basis of additional experiments carried out. While there is no doubt that piperitenone (I) is formed by the reaction in question, we concur with Naves and Conia that isoxylitone is also formed. In spite of the difference in molecular weight, I and IV can be separated only with great difficulty even in an efficient column; the boiling points reported are 92° (1.8 mm.)[2] and 90–91° (3 mm.),[8] respectively. The quantity of piperitenone (I) in the crude product and after distillation can easily be determined by the two reactions mentioned: conversion into II and III, respectively; neither of these reactions is, of course, shared by isoxylitone (IV). The ratio of I and IV in the reaction product may vary due to small differences in operating conditions. Neither the ultraviolet spectrum nor the preparation of the usual derivatives provides an easy means of differentiation between I and IV. The following figures will demonstrate this:

	Ultraviolet Spectrum	2,4-Dinitrophenylhydrazone, M.P.	Semicarbazone, M.P.
Isoxylitone (IV)	238.5 (3.36); 297 (4.12)	179; 156[a]	155–156; 180[a]
Piperitenone (I)	243 (4.10); 278 (3.90)	184–184.5; 152.5–153; 131–132	—
Our product (after distillation)	241 (3.78); 290 (3.85)	152	182

[a] J. Wiemann, B. Furth, and G. Dana, *Compt. rend.* **250**, 3674 (1960). *Cf.* also N. Bacon, S. Brewis, G. E. Usher, and E. S. Waight, *J. Chem. Soc.*, 2255 (1961).

We admit that the derivatives (dinitrophenylhydrazone, semicarbazone) obtained from our product after recrystallization, were those of isoxylitone, and it is clear that in the condensation of mesityl oxide and methyl vinyl ketone in the presence of sodium *t*-pentoxide, both piperitenone (I) and isoxylitone (IV) are formed. The thymol obtained in the palladium treatment of the product, and the acetone and 3-methylcyclohex-2-enone formed upon reaction with formic acid, have come from the piperitenone (I).

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(9) *Cf.* S. Shimizu, N. Ikeda, and H. Ueda, *Bull. Agr. Chem. Soc. Japan*, **24**, 324 (1960).

Acetyl Transfer during Alkylation Reactions

T. H. SIMPSON AND R. S. WRIGHT

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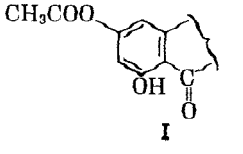
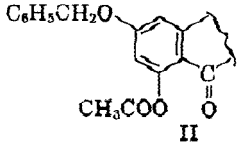
The recent publication[1] on the base-catalyzed rearrangement of *p*-aroyloxyacetophenones prompts us to record our observations on acetyl transfer in phenolic compounds. In earlier communications[2,3] it was claimed that although methylation of partially acetylated phenols possessing the partial structure I proceeded normally, benzylation under similar conditions caused migration of the acetyl group with the formation of compounds of type II. The potential usefulness of these methods in the preparation of partial ethers of complex phenols prompted this more detailed study.



I



II

In our hands, benzylation of 4-acetoxy-2-hydroxyacetophenone[3] afforded, after recrystallization, only a 10% yield of impure 2-acetoxy-4-benzyloxyacetophenone. The low yield of this compound was later confirmed by chromatography of the crude reaction product. Table I lists the compounds, with their molar yields, isolated from the product of this reaction and from the corresponding methylation reaction, performed under identical conditions.

These results showed that the methylation and benzylation reactions follow similar courses and suggested that migration of acetyl and alkylation might occur independently, giving a product whose composition would be determined by the rates of alkylation of the two hydroxyl groups relative to the rate of the base-catalyzed migration.

This suggestion was supported by the results of experiments in which 4-acetoxy-2-hydroxyacetophenone was heated with potassium carbonate and acetone. On chromatography, the product was found to contain, in addition to starting material (molar yield, 38.5%), a difficulty separable mixture of resacetophenone and 2,4-diacetoxyacetophenone (35%), 2,4-diacetoxyacetophenone (6%), 2-acetoxy-4-hydroxyacetophenone (4%), together with smaller quantities (< 2%) of 4-methylumbelliferone acetate (IV), 3-acetyl-7-hydroxy-2-methylchromone and its acetate (VII a and b).

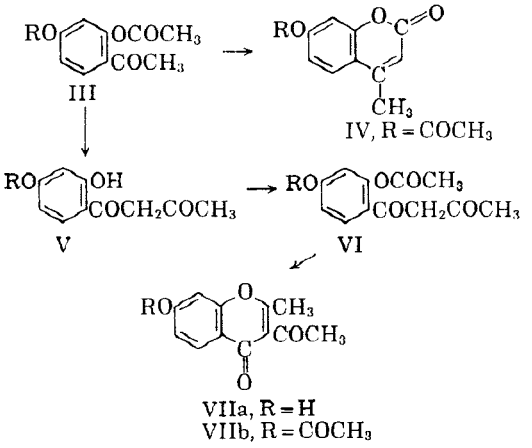
(1) L. Jurd, *Chem. & Ind. (London)*, 965 (1960).
(2) L. Jurd, *Chem. & Ind. (London)*, 1452 (1957).
(3) L. Jurd and L. A. Rolle, *J. Am. Chem. Soc.*, **80**, 5527 (1958).

TABLE I

BENZYLATION OF 4-ACETOXY-2-HYDROXYACETOPHENONE METHYLATION OF 4-ACETOXY-2-HYDROXYACETOPHENONE

	Products	M.P.	Yield, %		Products	M.P.	Yield, %
1.	4-Benzyloxy-2-hydroxyacetophenone	103–104°[a]	24	1.	2-Hydroxy-4-methoxyacetophenone	47–49°[a]	25
2.	4-Acetoxy-2-hydroxyacetophenone	72.5–74°[a]	19	2.	4-Acetoxy-2-hydroxyacetophenone	72–73°[a]	19
3.	2,4-Dibenzyloxyacetophenone		—	3.	2,4-Dimethoxyacetophenone	36–37.5°[a]	2
4.	4-Acetoxy-2-benzyloxyacetophenone	54–55.5°	11	4.	4-Acetoxy-2-methoxyacetophenone	32.5–34.5°[a]	19
5.	2-Acetoxy-4-benzyloxyacetophenone	115–116.5°[a]	14	5.	2-Acetoxy-4-methoxyacetophenone	40–44°[a]	6
6.	2,4-Diacetoxyacetophenone	35–37°[a]	20	6.	2,4-Diacetoxyacetophenone	34.5–37°[a]	24
7.	2-Acetoxy-4-hydroxyacetophenone	105–108°	2	7.	2-Acetoxy-4-hydroxyacetophenone	106–109°	0.5

[a] And mixed melting point.



The coumarin presumably arises by a direct cyclization of III. The chromones are presumably formed by a Baker-Venkataraman rearrangement[4,5] of III to the diketone (V. R = H or $COCH_3$), followed by intermolecular acetylation to give VI and subsequent cyclization.

That acetyl migration between non-vicinal hydroxyl groups may occur intermolecularly was proved by chromatographic examination of the products from the potassium carbonate-catalyzed reactions of equimolar quantities of 4-acetoxyacetophenone, and 4-benzyloxy-2-hydroxyacetophenone and of *p*-hydroxyacetophenone with 2-acetoxy-4-benzyloxyacetophenone. It was found that in less than three hours an equilibrium was established in which approximately 90% of the available acetyl was present as 4-acetoxyacetophenone. The addition of benzyl chloride and potassium iodide to the first set of reactants, in a second experiment, resulted in only a small increase in the amount of 2-acetoxy-4-benzyloxyacetophenone formed. This presumably reflects the disturbance to the equilibrium caused by benzylation blocking the small amount of *p*-hydroxyacetophenone formed in the reaction.

A further demonstration of the intermolecular nature of the acetyl migration reaction in acetone and potassium carbonate was afforded by a study of the interaction of 7-acetoxyflavone with 5-hydroxyflavone and of 7-hydroxy- with 5-acetoxyflavone. Analysis of the products showed that in three hours an equilibrium was reached in which 75%, of the 7-hydroxyflavone was acetylated. Similarly, 7-acetoxyflavone and 3′-hydroxyflavone or 7-hydroxy flavone and 3′-acetoxyflavone reacted to give an equilibrium mixture in which approximately 85% of the available acetate was located on the 3′-hydroxyl group. In all cases, in agreement with theory, the acetyl migrated from the oxygen atom of least to the oxygen atom of greatest electron availability.

In the light of these experiments, alkylation of fully acetylated phenols, a well known[6] method of etherifying readily oxidizable phenols, must depend on the presence in the reaction mixture of a suitable acetate acceptor, presumably the small quantity of water which is formed by the base-catalyzed self-condensation of acetone. Although acetyl transfer and alkylation are both controlled by the electron availability at the various oxygen atoms, the high degree of selectivity claimed[2,7] for the preparation of monoalkyl ethers from quercetin pentaacetate seemed difficult to explain. In our hands, moreover, the procedure was much less satisfactory, quercetin pentaacetate yielding, on methylation and saponification, rhamnetin (molar yield, 24%) 3,3′,5-trihydroxy-4′,7-dimethoxyflavone (18%), 3′,5-dihydroxy-3,4′,7-trimethoxyflavone (15%), 3′-hydroxy-3,4′,5,7-tetramethoxyflavone (11%) quercetin pentamethyl ether (5%) in addition to some quercetin and unidentified compounds. The di-, tri- and tetramethyl ethers of quercetin were not available to us and were therefore identified by comparison of their ethylation products with authentic samples of quercetin ethyl methyl ethers, prepared by Allan-Robinson condensation[8] of the appropriate intermediates and suitable alkylation of the products.

EXPERIMENTAL

Potassium carbonate was dried at 400° for 4 hr. before use and stored over phosphorus pentoxide in a vacuum desic-

(4) W. Baker, *J. Chem. Soc.*, 1381 (1953).

(5) H. S. Mahal and K. Venkataraman, *J. Chem. Soc.*, 1767 (1934).

(6) P. S. Rao and T. R. Seshadri, *Proc. Indian Acad. Sci.*, 9A, 365 (1939).

(7) L. Jurd, *J. Am. Chem. Soc.*, 80, 5531 (1958).

(8) J. Allan and R. Robinson, *J. Chem. Soc.*, 2192 (1924).

cator. Acetone was dried over magnesium sulfate and then over anhydrous calcium sulfate or over anhydrous potassium carbonate.

Methylation and benzylation of 4-acetoxy-2-hydroxyacetophenone. Rearrangement of this compound in acetone potassium carbonate. A solution of 4-acetoxy-2-hydroxyacetophenone[7] (2 g.) in acetone (50 ml.) containing potassium carbonate (4 g.) was refluxed, either alone or with the addition of methyl iodide (2 ml.) or benzyl chloride (2 ml.) and potassium iodide (200 mg.). After 3 hr., the mixtures were filtered, the potassium salts repeatedly extracted with boiling acetone and the combined filtrates and washings evaporated *in vacuo*. The residues were then dissolved in benzene, dried over magnesium sulfate and adsorbed on a column packed with a silicic acid-Celite mixture (2:1). The various components were eluted, in the orders given in Table I, with benzene containing increasing proportions of ether (0–40%). They were identified (melting point and mixed melting point) with authentic samples.

2-Acetoxy-4-hydroxyacetophenone was eluted impure (m.p. 105–108°) with benzene–20% ether. A portion (60 mg.) of this material was hydrolyzed in 4% aqueous sodium hydroxide during 1 hr. Acidification and crystallization of the precipitate furnished resacetophenone, m.p. and mixed m.p., 143°. A further portion (10 mg.) after acetylation furnished 2,4-diacetoxyacetophenone, m.p. and mixed m.p., 35–37°.

The fraction of the benzylation reaction product eluted by benzene –2% ether, after crystallization from petroleum ether (b.p. 40–60°), furnished *4-acetoxy-2-benzyloxyacetophenone* in colorless needles, m.p. 54–55.5°, giving a negative ferric reaction in ethanol.

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.8; H, 5.7. Found: C, 72.2; H, 5.7.

2-Benzyloxy-4-hydroxyacetophenone. Saponification of the last-named compound (28 mg.) in ethanol (1 ml.) and aqueous sodium hydroxide (4%, 1 ml.) at room temperature during 2 hr. and acidification of the mixture furnished the phenol in colorless needles (20 mg.), m.p. 168–170° which gave no ferric reaction in ethanol.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.3; H, 5.8. Found: C, 74.0; H, 6.0.

2-Benzyloxy-4-methoxyacetophenone. (a) The last-named compound (20 mg.) was methylated with excess diazomethane in ether containing a trace of methanol and the product isolated, after 3 hr., by evaporation of the solvent. After elution from silicic acid-Celite with benzene–10% ether and crystallization from ethanol, the ether was obtained in colorless rhombs (10 mg.) m.p. 82.5–84°, undepressed on admixture with material from part (b).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.0; H, 6.3. Found: C, 75.0; H, 6.3.

(b) A mixture of peonol (80 mg.), benzyl chloride (1 ml.), potassium carbonate (2 g.) and potassium iodide (100 mg.) in acetone (50 ml.) was heated under reflux for 20 hr., filtered and the filtrate and washings evaporated *in vacuo*. After crystallization from methanol, the residue yielded colorless rhombs, m.p. 82.5–84°.

Interaction of 4-acetoxyacetophenone and 4-benzyloxy-2-hydroxyacetophenone in acetone-potassium carbonate. 4-Acetoxyacetophenone (890 mg., 0.005 mole) and 4-benzyloxy-2-hydroxyacetophenone[8] (1.12 g., 0.005 mole) and, in a second experiment, 4-hydroxyacetophenone (660 mg.) and 2-acetoxy-4-benzyloxyacetophenone (1.42 g.) were refluxed in acetone (50 ml.) and potassium carbonate (4 g.) for 3 hr. and the products were isolated and separated exactly as in the experiments above.

Interaction of hydroxy- and acetoxyflavones. 7-Acetoxyflavone (200 mg., 0.0007 mole) and 3′-hydroxyflavone (170 mg. 0.0007 mole) were dissolved in acetone (25 ml.) and refluxed with potassium carbonate for 3 hr. The crude mixture, isolated as in the previous experiments was dissolved in toluene and separated by elution from a silicic acid-Celite packed column with benzene-ether (0–20% ether) and benzene-ethanol (1–5%) mixtures. Reactions between 3′-acetoxyflavone and 7-hydroxyflavone, 7-acetoxyflavone and 5-hydroxyflavone and between 7-hydroxyflavone and 5-acetoxyflavone were carried out and the products isolated in the same way. The components from the interaction of 3′- and 7-substituted flavones were eluted in the order 7-acetoxy-, 3′-acetoxy-, 3′-hydroxy-, and 7-hydroxyflavone and had melting points and mixed melting points of 129–130°, 96–97°, 208–210° and 232–234° respectively.

From the second pair of reactions the elution order was 5-hydroxy-, 5-acetoxy-, 7-acetoxy- and 7-hydroxyflavone and the melting points and mixed melting points were 152–153°, 141–143°, 129–130°, and 232–234°.

Methylation of quercetin pentaacetate. A solution of quercetin pentaacetate[10] (2.5 g.) and methyl iodide (5 ml.) in dry acetone (50 ml.) was refluxed with anhydrous potassium carbonate (6 g.) for 20 hr., and the combined filtrate and acetone washings evaporated *in vacuo*. The resulting residue was then hydrolyzed in hot ethanol (250 ml.) and concentrated hydrochloric acid (25 ml.) for 15 min. and the product isolated by evaporation. This was dissolved in hot, aqueous acetic acid (50%, 300 ml.) and extracted first with boiling benzene (six 150-ml. portions) and then repeatedly with chloroform. Evaporation of these furnished benzene-soluble and -insoluble fractions (990 mg. and 495 mg., respectively) which were worked up separately.

The benzene-soluble fraction was adsorbed from benzene on a column packed with silicic acid–Celite (1:1) and eluted first with benzene and then with benzene-ethanol mixtures (0.1% ethanol up to 20%). The four major bands from this column were then further purified by chromatography, using the same system. 3,3′,5-Trihydroxy-4′,7-dimethoxyflavone formed yellow prisms (300 mg.), m.p. 230–231° and 240–241° (dimorphic) (lit.[11] m.p. 229–230°) from aqueous acetic acid.

Anal. Calcd. for $C_{13}H_5O_5(OCH_3)_2$: C, 61.8; H, 4.3; OCH_3, 18.8. Found: C, 61.7; H, 4.3; OCH_3, 18.7.

Its acetate formed colorless needles, m.p. 212–213° (lit.[11] m.p. 212°).

Anal. Calcd. for $C_{23}H_{20}O_{10}$: C, 60.5; H, 4.4. Found: C, 60.6; H, 4.3.

On methylation it furnished quercetin pentamethyl ether, m.p. and mixed m.p., 149–150°, and on ethylation with excess ethyl sulfate and potassium carbonate in acetone it yielded 3,3′,5-triethoxy-4′,7-dimethoxyflavone, colorless prisms, m.p. 138–139° (lit.[10] m.p. 146–148°), undepressed on admixture with authentic material.

The bright pink fluorescent band "B" yielded 3′,5-dihydroxy-3,4′,7-trimethoxyflavone in pale yellow needles (290 mg.), m.p. 172–173° (lit.[11] m.p. 172–173°), λ_{max}^{CHSOH} 354 mμ, giving a brown ethanolic ferric coloration.

Anal. Calcd. for $C_{13}H_7O_4(OCH_3)_3$: C, 62.8; H, 4.7; OCH_3; 27.1. Found: C, 63.3; H, 4.5; OCH_3, 27.0.

Its diacetate formed colorless leaflets, m.p. 177–179.5° (lit.[12] m.p. 176–177°). On methylation it furnished quercetin pentamethyl ether, m.p. and mixed m.p. 149–150°. Ethylation afforded 3′,5-diethoxy-3,4′,7-trimethoxyflavone in cream colored needles, melting point and melting point on admixture with a synthetic sample, 162–163°.

Anal. Calcd. for $C_{22}H_{24}O_7$: C, 66.0; H, 6.0. Found: C, 65.8; H, 6.0.

The blue florescent band C yielded quercetin pentamethyl ether in colorless needles (83 mg.) from ethanol;

(9) K. C. Gulati, R. Seth, and K. Venkataraman, *J. Chem. Soc.*, 1765 (1934).

(10) Simokoriyama, *Bull. Chem. Soc. Japan*, **16**, 284 (1941).

(11) G. B. Marini-Bettolo, V. Delofeu, and E. Hug, *Gazz. chim. ital.*, **80**, 63 (1950).

(12) F. E. King, T. J. King, and K. Sellars, *J. Chem. Soc.*, 92 (1952).

no ferric coloration in ethanol, m.p. and mixed m.p. 149–150°.

Band D on crystallization from ethanol furnished 3'-hydroxy-3,4',5,7-tetramethoxyflavone in yellow prisms (190m g.), m.p. 223–224.5° (lit.[11] m.p. 220–222°) $\lambda_{max}^{C_2H_5OH}$ 343 mμ, $\lambda_{max}^{0.002M\ NaOC_2H_5\ in\ C_2H_5OH}$ 380, 333 mμ, giving no ferric coloration in ethanol.

Anal. Calcd. for $C_{15}H_6O_2(OCH_3)_4$: C, 63.7; H, 5.1; OCH_3, 35.0. Found: C, 63.9; H, 5.0; OCH_3, 34.1.

The *acetate* of this compound separated from ethanol in colorless needles, m.p. 214–216°.

Anal. Calcd. for $C_{21}H_{20}O_8$: C, 63.0; H, 5.0; Found: C, 63.2; H, 5.1.

On ethylation with excess of ethyl iodide and potassium carbonate in boiling acetone during 4 hr. it furnished 3-ethoxy-3,4',5,7-tetramethoxyflavone in cream colored needles, m.p. 156.5–158° undepressed on admixture with an authentic sample.

Anal. Calcd. for $C_{21}H_{22}O_7$: C, 65.3; H, 5.7. Found: C, 65.0; H, 5.5.

The benzene insoluble fraction of the methylation product of quercetin pentaacetate was repeatedly crystallized from aqueous ethanol, furnishing rhamnetin in yellow needles (340 mg.) m.p. 291–294°, undepressed on admixture with authentic amaterial. Paper chromatography of the mother liquors showed the presence of quercetin.

3'-Ethoxy-5,7-dihydroxy-3,4'-dimethoxyflavone. A mixture of ω-methoxyphloracetophenone[13] (3 g.), sodium 3-ethoxy-4-methoxybenzoate (3 g.) and 3,3'-diethoxy-4,4'-dimethoxybenzoic anhydride[14] was heated *in vacuo* to 180° for 4 hr. and the product hydrolyzed in boiling alcoholic sodium hydroxide (10%, 200 ml.) during 20 min. The solution was then evaporated to one-third bulk, diluted with water (2 l.) and neutralized by the addition of solid carbon dioxide. The resulting solid was crystallized from aqueous acetic acid and then from ethanol, furnishing the flavone in yellow needles (5.0 g.) m.p. 217.5–218.5°.

Anal. Calcd. for $C_{19}H_{18}O_7$: C, 63.7; H, 5.1. Found: C, 63.5; H, 5.0.

Its *diacetate* formed colorless needles, m.p. 167–168.5°.

Anal. Calcd. for $C_{23}H_{22}O_9$: C, 62.4; H, 5.0. Found: C, 62.4; H, 5.3.

3'-Ethoxy-3,4',5,7-tetramethoxyflavone. A mixture of the foregoing compound (500 mg.) methyl sulfate (2 ml.) and potassium carbonate in acetone (40 ml.) was refluxed for 4 hr., filtered, and the combined filtrate and washings evaporated to low bulk. The remaining solid was dissolved in benzene, washed with water, dried, and chromatographed on alumina. Elution with benzene-ethanol (99.5:0.5) and crystallization from ethanol furnished cream colored needles, m.p. 158°.

Anal. Calcd. for $C_{21}H_{22}O_7$: C, 65.3; H, 5.7. Found: C, 65.3; H, 5.8.

3'-Ethoxy-5-hydroxy-3,4',7-trimethoxyflavone. 3'-Ethoxy-5,7-dihydroxy-3,4'-dimethoxyflavone (900 mg.) was methylated with 1.1 equivalents of methyl sulfate (0.35 g.) and the product isolated by the above method. After purification by elution from silicic acid–Celite (2:1) with benzene-ethanol (99.5:0.5) and crystallization from ethanol, yellow needles (690 mg.), m.p. 138–139°, were obtained, giving a brown ethanolic ferric reaction.

Anal. Calcd. for $C_{22}H_{22}O_7$: C, 64.5; H, 5.4. Found: C, 64.4; H, 5.4.

Its *acetate* formed colorless needles, m.p. 164–165° from ethanol.

Anal. Calcd. for $C_{24}H_{24}O_8$: C, 63.8; H, 5.4. Found: C, 63.8; H, 5.5.

3',5-Diethoxy-3,4',7-trimethoxyflavone. The foregoing hydroxyflavone (250 mg.) was ethylated with excess ethyl sulfate and potassium carbonate in acetone and the product isolated and purified by elution from neutral alumina with benzene-chloroform (1:1). Crystallization from ethanol furnished colorless needles (250 mg.) m.p. 162.5–164°.

Anal. Calcd. for $C_{23}H_{24}O_7$: C, 66.0; H, 6.0. Found: C, 65.8; H, 5.8.

3,3'-Diethoxy-5-hydroxy-4',7-dimethoxyflavone. 3,3'-Diethoxy-5,7-dihydroxy-4'-methoxyflavone[14] (1.3 g.) was monomethylated and the product purified as in the previous partial methylation experiment, furnishing yellow prisms (1.1 g.), m.p. 130–131° giving a dark brown ferric coloration.

Anal. Calcd. for $C_{21}H_{22}O_7$: C, 65.3; H, 5.7. Found: C, 65.4; H, 5.9.

Its *acetate* formed colorless needles, m.p. 153–154.5° from ethanol.

Anal. Calcd. for $C_{23}H_{24}O_8$: C, 64.5; H, 5.7. Found: C, 64.1; H, 5.5.

3,3',5-Triethoxy-4',7-dimethoxyflavone. The foregoing compound (800 mg.) was alkylated with excess ethyl sulfate and the product isolated by the standard method. Elution from neutral alumina with benzene-chloroform (1:1) and crystallization from benzene–petroleum ether (b.p. 80–100°) furnished colorless needles (600 mg.), m.p. 138–139°.

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(13) R. Robinson and K. Venkataraman, *J. Chem. Soc.*, 61 (1929).

(14) S. R. Gupta and T. R. Seshadri, *J. Chem. Soc.*, 3063 (1954).

The Sulfonation of 2-6-Dinitronaphthalene

D. C. MORRISON

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In a previous report,[1] the sulfonation of 1,3-dinitronaphthalene was described. The present work is concerned with the sulfonation of the 2,6-isomer.

This reaction proceeded at room temperature with oleum as the sulfonating agent, and was complete in less than seven hours. Conventional orientation rules[2] would indicate that the 4-sulfonic acid should be formed (3,7-dinitronaphthalene-1-sulfonic acid, I), and this was found to be the case. Reaction of the sodium salt of I with phosphorus pentachloride at moderate temperatures gave the sulfonyl chloride, while at higher temperatures, 1,3,7-trichloronaphthalene was formed. The infrared spectrum of the latter was identical to that of an authentic specimen, and provides evidence for the assigned structure.

Contrary to expectation, the sulfonic acid I did not appear to be formed in the nitration of 7-nitronaphthalene 1-sulfonic acid,[3] other isomers

(1) D. C. Morrison, *J. Org. Chem.*, 26, 1661 (1961).

(2) H. W. Armstrong and W. P. Wynne, *Ber.*, 24R, 718 (1891).