naphthalene. Again, the naphthalene lowered the oxidation potential sharply. The results of Figure 3 cannot be compared with those of Figure 2 since differences in chloride concentration change the potentials of the reference electrode.

In all of the runs with organic reductants, a critical current density was reached, above which the potential rose to the value observed in the absence of the organic material. Potentials in this region fluctuated and the critical current density, at concentrations of 0.1 *M* or less, varied from 1 to 5 × 10^{-3} amp./cm.^{2}. Since the previous investigators[10] worked at current densities several orders of magnitude greater than ours, there must have been at least three reacting species being simultaneously oxidized under their experimental conditions, namely acetate ions, the acetic acid molecules, and the organic reductant. The concentration of unoxidized organic reactant must have been practically zero.

Conclusions

Since naphthalene is preferentially oxidized at the electrode, the formation of naphthyl acetate would proceed *via* the formation of a naphthalene radical ion, rather than an acetoxy radical. This is in agreement with the mechanism suggested by Eberson.[15]

The absence of methylnaphthalene and of anode gas, in any significant amounts, under the experimental conditions of Linstead[10] is probably due to the naphthalene being oxidized to the radical ion, which then reacts further at potentials below those required for the formation of acetoxy radicals. Further work is now in progress, on a preparative scale.

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(15) L. Eberson, *Acta Chem. Scand.*, **17**, 2004 (1963).

Coumarin-3-carboxylic Acids

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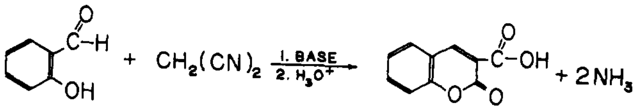
Although the method for preparing coumarin-3-carboxylic acids using basic catalysts has been known for a considerable number of years,[1,2] many of the simpler compounds have not been prepared, and none have been synthesized using malononitrile as one of the reactants in such a procedure.

In this report a procedure for the preparation of coumarin-3-carboxylic acids is given in which malononitrile is condensed with aldehydes or ketones in the presence of piperidine and described as method A. Three of the acids were also prepared by the Knoevenagel[1,2] procedure (method B) for comparison. The yields by our method (method A) are somewhat better than those of Knoevenagel which were in the range of 80%. The compounds prepared in the I–IV series are described in Table I.



Efforts were made to prepare the 4-phenyl derivative of IV by reacting 2,4-dihydroxybenzophenone with malononitrile, with diethyl malonate, and with malonic acid in the presence of piperidine. In all cases a reaction occurred, but either during the formation of the compound or during the hydrolysis the compound was decarboxylated, negating our attempt to ascertain what effect an electrophilic group in position 4 would exert on a powerfully fluorescent compound such as compound IV.

Of primary interest to us is the fluorescence of the coumarins, which in this series is most pronounced in compound IV. In view of the low but definite fluorescence levels in compounds I–III it appears that the conclusion of Seshadri[3] that a hydroxyl group must be present in a coumarin for it to fluoresce is in considerable error.

Table II gives the fluorescence in quinine reference units (g.r.u.), the ultraviolet absorption characteristics, and the *p*-bromophenacyl derivatives of the compounds of the I–IV series.

Experimental[4]

Preparation of Members of I–IV Series. Method A.—To a mixture consisting of 0.1 mole of malononitrile and 0.1 mole of the aldehyde or ketone was slowly added, with shaking, to 20 ml. of piperidine. If the mixture did not become hot and the mass become homogeneous, it was gently heated on a hot plate until homogeneity was obtained. The mixture, after cooling, was treated with 100 ml. of 6 *N* hydrochloric acid, chilled, and filtered. The precipitate was refluxed for 18 hr. in 100 ml. of 9 *N* hydrochloric acid. After chilling the mixture, it was filtered and the precipitate was dried in air.

Analytical samples were obtained either by recrystallizing the compounds twice from benzene–heptane mixtures or by dissolving the compound in ethyl acetate and then precipitating the compound with heptane. The process was repeated in either case for a second recrystallization.

Method B.—One-tenth of a mole of the aldehyde or ketone was mixed with 0.1 mole of diethyl malonate followed by 20 ml. of piperidine. The mixtures were warmed on a hot plate, if necessary, to produce complete solution of the reactants.

Acidification, hydrolysis, and purification of the compounds were effected in the same manner as in method A. Compounds which were prepared by both methods were proven to be identical by mixture melting points and by their infrared spectra.

Preparation of *p*-Bromophenacyl Derivatives of I–IV Series.—One gram each of the coumarin acid, 2′,4-dibromoacetophenone,

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(1) E. Knoevenagel, *Ber.*, **31**, 2619 (1898).

(2) E. Knoevenagel, *ibid.*, **37**, 4461 (1904).

(3) (a) S. Rangaswami and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **12A**, 375 (1940); *Chem. Abstr.*, **35**, 3526 (1941). The reference in R. C. Elderfield's, "Heterocyclic Compounds," Vol. **2**, p. 193, is in error as to the year of publication of the above article. (b) See also C. E. Wheelock, *J. Am. Chem. Soc.*, **81**, 1348 (1959), on fluorescence in coumarins.

(4) Analyses were performed by Dr. Karl Tiedcke, 705 George Street, Teaneck, N. J. All melting points were taken on Fischer-Johns melting point blocks.

TABLE I

COUMARIN-3-CARBOXYLIC ACIDS

Compd.[a]	Aldehyde or ketone used	Method used	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
I	Salicylaldehyde	A, B	190–191	100	$C_{10}H_6O_4$	63.16	63.34	3.18	3.38		
II	5-Chlorosalicylaldehyde	A, B	214–215	100	$C_{10}H_5ClO_4$	53.47	53.69	2.24	2.24	15.78	15.94
III	2′-Hydroxyacetophenone	A	194.5–196	44	$C_{11}H_8O_4$	64.70	64.50	3.94	4.14		
IV	2,4-Dihydroxybenzaldehyde	A, B	264–265	85	$C_{10}H_6O_5$	58.26	57.99	2.93	3.14		

[a] I, 3-carboxycoumarin, lit.[2] m.p. 187–188°; II, 3-carboxy-6-chlorocoumarin; III, 3-carboxy-4-methylcoumarin; IV, 3-carboxy-7-hydroxycoumarin, P. C. Mitter and S. K. Saha [*J. Indian Chem. Soc.*, **11**, 257 (1934); *Chem. Abstr.*, **28**, 5069 (1934)] reported m.p. 262°.

TABLE II

SPECTRAL CHARACTERISTICS AND *p*-BROMOPHENACYL DERIVATIVES OF I–IV SERIES

Compd.	Q.r.u.[a]	Ultraviolet absorption, mμ[b] (log ε)	*p*-Bromophenacyl ester formula	M.p., °C.	Bromine, % Calcd.	Bromine, % Found
I	0.432	267.4 (3.90), 300.5 (4.02)	$C_{18}H_{11}BrO_5$	122–123	20.68	20.97
II	1.16	295 (4.00), 340 (3.85)	. . .	. . .	. . .	. . .
III	2.30	266.4 (3.84), 302.3 (4.03)	$C_{19}H_{13}BrO_5$	151–152	19.91	19.49
IV	196.6	263.7 (3.56), 346 (4.14)	$C_{18}H_{11}BrO_6$	122–123.5	19.81	19.67

[a] See L. L. Woods and J. Sapp, *J. Chem. Eng. Data*, **8**, 235 (1963), for the method of calculating quinine reference units. [b] Spectra were run on a Bausch and Lomb 505 spectrophotometer in Spectrograde methanol.

and calcium carbonate were refluxed together for 90 min. in 50 ml. of absolute ethanol. The mixture was then filtered while boiling hot. The filtrate was diluted with an equal volume of water, chilled for 2–3 hr. in the freezer, and the precipitate was collected and recrystallized twice from absolute ethanol.

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N-H Stretching Frequency in Alkylaminotriphenylphosphonium Salts

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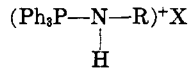
Participation of N–H in hydrogen bonding to anions had been studied quite extensively in the recent years. Most work in this field has been done with ammonium salts.[2] Fujita, *et al.*,[3] and Larsson[4] obtained evidence of hydrogen bonding of the type N–H. . .anion from the lowering of the N–H stretching frequency in hexammine cobalt(III) complexes. Most recently, similar studies on hexammine and pentammine complexes of chromium(III) have been reported.[5]

No hydrogen bond studies in alkylaminotriphenylphosphonium salts (I) have been reported. As recently, some alkylaminotriphenylphosphonium salts, such as chlorides,[6] bromides,[7] iodides,[7] and tetrafluoroborates,[8] became available to us, it was decided to investigate systematically the possible presence of N–H. . .anion-type hydrogen bond in them. This report deals with the results of the investigation and their interpretation.



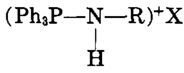
$$(Ph_3P\text{—}\underset{\overset{|}{H}}{N}\text{—}R)^+X^-$$

I

The results obtained in the present investigation (Table I, Figure 1) can be conveniently discussed under the following two headings.

TABLE I

INFRARED DATA OF ALKYLAMINOTRIPHENYLPHOSPHONIUM SALTS



$$(Ph_3P\text{—}\underset{\overset{|}{H}}{N}\text{—}R)^+X^-$$

	N-H stretching frequency, cm.$^{-1}$			
	X^-			
R	Cl^-	Br^-	I^-	BF_4^-
CH_3	2945	2950	2954	3294
C_2H_5	2942	2948	2952	3278
$CH(CH_3)_2$	2938	2946	2952	3257
$C(CH_3)_3$	2934	2941	2948	3241

Effect of the Anion.—Alkylaminotriphenylphosphonium salts possess a secondary N–H group. It is well known that the free N–H moiety of the secondary amines absorbs in the 3500–3200-cm.$^{-1}$ region,[9] whereas, if N–H participates in hydrogen bonding, its absorption is shifted to a lower frequency and the absorption band becomes broader.[9,10] This is actually what was observed especially in the case of alkylaminotriphenylphosphonium chlorides, bromides, and iodides (Figure

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[2] G. Gray and T. C. Waddington, *Trans. Faraday Soc.*, **53**, 901 (1957); A. Tramer, *Compt. rend.*, **249**, 2755 (1959); P. Sauvageau and C. Sandorfy, *Can. J. Chem.*, **38**, 1901 (1960); G. Tsoucaris, *Acta Cryst.*, **14**, 917 (1961).

[3] J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Am. Chem. Soc.*, **78**, 3295 (1956).

[4] R. Larsson, *Acta Chem. Scand.*, **16**, 2460 (1962).

[5] N. Tanaka, M. Kamada, J. Fujita, and E. Kyuno, *Bull. Chem. Soc. Japan*, **37**, 222 (1964).

[6] H. Zimmer and G. Singh, *Angew. Chem.*, **75**, 574 (1963); *Angew. Chem., Intern. Ed. Engl.*, **2**, 395 (1964).

[7] H. Zimmer and G. Singh, *J. Org. Chem.*, **28**, 483 (1963).

[8] H. Zimmer and G. Singh, *ibid.*, **29**, 3412 (1964).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 215.

[10] G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," Reinhold Publishing Corp., New York, N. Y., 1960, p. 75.