95% chloroform. It was rechromatogramed on another column (48 g., *p*H 7.8) with 1% butanol, 99% $CHCl_3$, as eluent. The DMA contained considerable radioactivity, and its purity was established by the following criteria. The radioactivity and titratable acidity curves coincided as the compound was eluted from the column; the *p*-bromophenacyl ester gave the correct m.p., with no depression on admixture with a sample of authentic derivative; the specific activity of the derivative did not change upon recrystallization. The percentage of total counts added, incorporated in the DMA equalled 0.28%. DMA was degraded as follows. A Schmidt reaction gave carbon 1 as CO_2.[10] Oxidation of DMA with acid permanganate gave acetone representing carbons 3, 4 and 4′ and CO_2 representing carbons 1 and 2. The activity of carbon 2 was calculated by difference. Acetone was trapped in bisulfite and identified as the 2,4-dinitrophenylhydrazone. Degradation of acetone with NaOI provided carbon 4 and 4′ as iodoform, which was oxidized to CO_2.[11] The radioactivity in carbon 3 was obtained by subtracting the specific activity of carbons 4 and 4′ from that observed when the acetone moiety was totally oxidized. All CO_2 samples were counted as finitely thick plates of $BaCO_3$ in a gas flow counter, with appropriate corrections for self absorption.

TABLE I

	C.p.m./mmole carbon	% Isotope distribution
CH_3 CH_3 4 + 4′	3350	63.8
$_3C$	trace	..
$_2CH$	3712	35.3
$_1COOH$	168	1.6
Total oxidation calcd.	2120	
found	2100	

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The Kostanecki-Robinson Acylation of 5-Hydroxy-6-Acetyl-4-methylcoumarin

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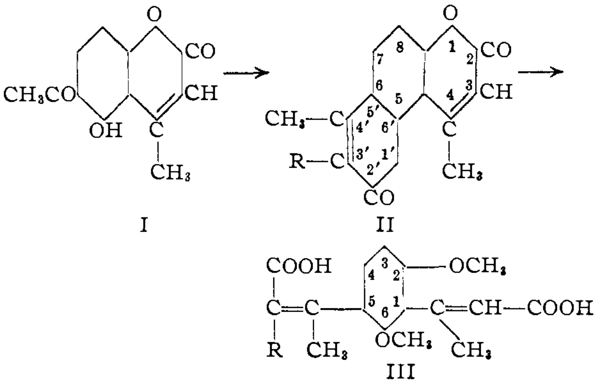
5-Hydroxy-6-acetyl-4-methylcoumarin, now easily available by the condensation of resacetophenone with ethyl acetoacetate in the presence of anhydrous aluminum chloride, is a useful substance for synthetic work. Sethna, Shah and Shah[1] carried out its Kostanecki-Robinson acetylation and benzoylation, obtaining chromono- and flavono-α-pyrones. This study now has been extended to its propionylation and butyrylation under the conditions of the Kostanecki-Robinson reaction and the results are described in this paper.

On heating 5-hydroxy-6-acetyl-4-methylcoumarin (I) with propionic anhydride in presence of its sodium salt, the product obtained was found to be insoluble in cold alkali and did not give any color with alcoholic ferric chloride. It did not give any styryl derivative with benzaldehyde. Further on treating the product with sodium ethoxide or hydroxide, the unchanged product was recovered. Hence the product has been assigned the constitution, 4,3′,4′-trimethylcoumarino-5′,6′-(6,5)-α-pyrone (II, R = CH_3).



On treating the coumarin (I) with butyric anhydride in the presence of sodium butyrate, the product obtained has been assigned the structure, 4,4′-dimethyl-3′-ethylcoumarino-5′,6′-(6,5)-α-pyrone (II, R = Et) on similar grounds.

The above structures were confirmed by converting the coumarino-α-pyrones into the corresponding methoxycinnamic acid derivatives, *viz.*, 2,6-dimethoxy-5-(α-carboxy-α,β-dimethylvinyl)-β-methylcinnamic acid (III, R = CH_3) and 2,6-dimethoxy-5-(α-carboxy-α-ethyl-β-methylvinyl)-β-methylcinnamic acid (III, R = Et), using the modified method of Shah and Shah.[2]

5-Hydroxy-6-acetyl-4-methylcoumarin (I) also was treated with acetic anhydride in presence of fused sodium phenyl acetate; the product obtained has been assigned the structure, 4,4′-dimethyl-3′-phenyl-5′,6′ (6,5)-α-pyrone (II, R = Ph) on grounds similar to those mentioned above. However, its methoxycinnamic acid derivative could not be prepared satisfactorily.

The above results show that α-pyrone ring does not affect the course of the Kostanecki-Robinson reaction, as the results are in line with those of the observations of the previous investigators.[3]

Experimental

4,3′,4′-Trimethylcoumarino-5′,6′(6,5)-α-pyrone.—5-Hydroxy-6-acetyl-4-methylcoumarin (5 g.), freshly fused sodium propionate (4 g., 2 molar equivalents) and propionic anhydride (10 ml., 4 molar equivalents) were refluxed at 160–170° for 12 hours. The cooled mixture was then decomposed with ice-water. The pasty mass that separated was washed with cold dilute alkali and then with water. The solid obtained was crystallized from acetic acid, lustrous short needles, m.p. 225°, yield 2.0 g.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.32; H, 4.7. Found: C, 70.02; H, 4.6.

Action of Alkali.—The product dissolved in alcohol (10 ml.) was treated with potassium hydroxide (20 ml., 10%) on steam-bath for 3 hours. It was acidified and the solid obtained was crystallized from acetic acid; m.p. 225° undepressed in mixture with the original product. It also was treated similarly with sodium ethoxide with the same result.

2,6-Dimethoxy-5-(α-carboxy-α,β-dimethylvinyl)-β-methylcinnamic Acid.—To the product (1 g.) dissolved in minimum acetone, potassium hydroxide (10 ml., 3 *N*) was added and refluxed on hot water-bath for some time. Dimethyl sulfate (10 ml.) was added, keeping the mixture alkaline; 5 ml. of dimethyl sulfate and 10 ml. of alkali were added every half-hour. Heating was continued for four hours, the

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(1) S. M. Sethna, N. M. Shah and R. C. Shah, *J. Chem. Soc.*, 228 (1938).

(2) N. M. Shah and R. C. Shah, *J. Univ. Bombay*, **7**, 213 (1938).

(3) I. M. Heilbron, D. H. Hey and B. Lythgoe, *J. Chem. Soc.*, 1581 (1934).

solution was then acidified and the solid obtained was treated with sodium bicarbonate when it dissolved with effervescence. It was filtered and the filtrate acidified. The acid crystallized from acetic acid as white plates, m.p. 285°, yield 0.4 g.

Anal. Calcd. for $C_{17}H_{20}O_6$: equiv., 160; C, 63.75; H, 6.25. Found: equiv. (by titration), 159.4; C, 63.57; H, 6.32.

4,4'-Dimethyl-3'-ethylcoumarino-5',6'(6,5)-α-pyrone.—Butyric anhydride (12 ml.), fused sodium butyrate (5 g.) and 5-hydroxy-6-acetyl-4-methylcoumarin (5 g.) were refluxed at 160–170° as before. The product isolated as before crystallized from acetic acid, needles, m.p. 205°; yield, 3 g.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.19. Found: C, 70.94; H, 5.18.

The product was treated with potassium hydroxide and sodium ethoxide as before, but the original compound was recovered unchanged.

The 2,6-Dimethoxy-5-(α-ethyl-α-carboxy-β-methylvinyl)-β-methylcinnamic Acid.—The above coumarino-α-pyrone was treated with dimethyl sulfate and alkali as before. The acid isolated as before crystallized from acetic acid; white needles, m.p. 305°.

Anal. Calcd. for $C_{18}H_{22}O_6$: equiv., 167; C, 64.67; H, 6.58. Found: equiv. (by titration), 166.6; C, 64.58; H, 6.50.

4,4'-Dimethyl-3'-phenylcoumarino-5',6'(6,5)-α-pyrone.—The coumarin (3 g.), acetic anhydride (10 ml.) and dry sodium phenylacetate (3 g.) were refluxed at 160–170° as before. The product, as obtained previously, crystallized from acetic acid as lustrous needles, m.p. > 300°, yield 2.0 g.

Anal. Calcd. for $C_{20}H_{14}O_4$: C, 75.47; H, 4.40. Found: C, 75.50; H, 4.47.

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The Behavior of Triphenylmethyl Chloride in Nitromethane

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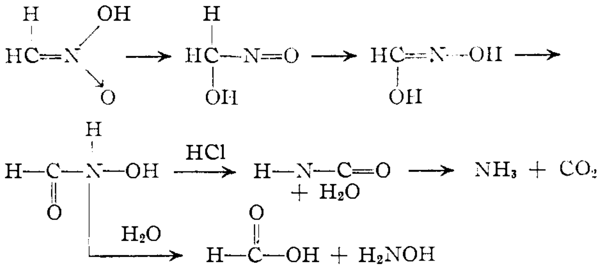
The formation of ion-pairs by triphenylmethyl chloride in nitromethane has been studied spectrophotometrically and the equilibrium constant reported by Bentley, Evans and Halpern.[1] As a preliminary to other work contemplated by us, the equilibrium constant for ion-pair formation has been redetermined by the same method. We find that the optical density of solutions of triphenylmethyl chloride in nitromethane changes with time and that the optical density extrapolated to zero time, from which we have calculated the apparent equilibrium constants for ion-pair formation, depends very much on the method used for purifying the nitromethane.

Using a commercial sample of nitromethane dried over phosphorus pentoxide and distilled (method I), the values of the equilibrium constant are in good agreement with those cited.[1] But some doubt is cast on the interpretation of those values by the fact that ammonium chloride precipitates if the solution is allowed to stand for several days and that the supernatant liquid after evaporation and hydrolysis gives triphenylmethane as well as triphenylcarbinol. Since the sample of triphenylmethyl chloride used was entirely free from triphenylmethane, that product is very likely the result of a reaction with formic acid present as an impurity in the nitromethane. Formic acid has a boiling point very close to that of nitromethane and is known to reduce triphenylmethyl chloride to triphenylmethane.[2]

Even when the nitromethane is purified more elaborately[3] and dry-box or vacuum-line technique is used in making up the solutions the drift in optical density is still observed. Triphenylmethane is no longer detectable as a product but the decay in optical density is even faster and the precipitation of ammonium chloride begins in a few minutes at room temperature rather than after several hours. Another product of the reaction is triphenylmethylamine.

The average value of the apparent equilibrium constant for ion-pair formation in carefully purified nitromethane at a room temperature near 25° is 1.75×10^{-4}, about half that reported in the literature and about half that found by us for the less elaborately purified solvent. Formic acid causes a notable intensification of the color when it is added to the solution.

The disproportionation of nitromethane in the presence of hydrogen chloride at 130° to give carbon dioxide and ammonium chloride has been known for some time.[4] The following appears to be a plausible reaction path, especially in view of the observation that formylation of hydroxyl compounds takes place and that hydroxylamine hydrochloride rather than ammonium chloride is produced in the presence of water



We believe that the decay in the color of triphenylmethyl chloride in pure nitromethane is due to a similar reaction in the presence of triphenylmethyl chloride. Although participation of hydrogen chloride produced by the action of traces of water cannot be excluded as a possibility, it is significant that ammonium chloride is produced faster in the more carefully prepared and drier solutions in which hydrolysis of the triphenylmethyl chloride should be at a minimum. Triphenylcarbonium ions perhaps may themselves promote the rearrangement of the hydroxamic acid. On the other hand, the reaction of tris-(*p*-anisyl)-carbinol and perchloric acid in nitromethane is reported to give 1,1,1-tris-(*p*-anisyl)-2-nitroethane.[5] No analogous product was found in our triphenylmethyl chloride–nitromethane reaction mixtures.

Experimental

Triphenylmethyl chloride was prepared from the carbinol.[6]

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