

TABLE II  
 SODIUM 1-HYDROXY-2-ALKANESULFONATES

Compound	Yield, <sup>a</sup> %	Krafft point <sup>b</sup>	% Na		% C		% H		% S	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C <sub>10</sub> H <sub>21</sub> CH $\begin{cases} \text{CH}_2\text{OH} \\ \text{SO}_3\text{Na} \end{cases}$	68	59°	7.97	8.01	49.98	50.09	8.74	8.77	11.12	11.13
C <sub>12</sub> H <sub>25</sub> CH $\begin{cases} \text{CH}_2\text{OH} \\ \text{SO}_3\text{Na} \end{cases}$	74	73°	7.27	7.25	53.14	53.13	9.24	9.09	10.13	10.21
C <sub>14</sub> H <sub>29</sub> CH $\begin{cases} \text{CH}_2\text{OH} \\ \text{SO}_3\text{Na} \end{cases}$	64	84°	6.68	6.72	55.78	56.13	9.66	9.65	9.31	9.27
C <sub>18</sub> H <sub>33</sub> CH $\begin{cases} \text{CH}_2\text{OH} \\ \text{SO}_3\text{Na} \end{cases}$	61 <sup>c</sup>	93°	6.17	6.12	58.03	58.08	10.01	10.02	8.61	8.99

<sup>a</sup> Sum of the yield of the reduction product and the hydrolyzed ester, recovered as the disodium salt RCH(SO<sub>3</sub>Na)CO<sub>2</sub>Na = 100%. <sup>b</sup> Krafft points for corresponding monosodium salts RCH(SO<sub>3</sub>Na)CO<sub>2</sub>H are 52, 68, 83, and 94°, respectively, <sup>c</sup> Yield from C<sub>18</sub>H<sub>33</sub>CH(SO<sub>3</sub>Na)CO<sub>2</sub>CH<sub>3</sub> and NaBH<sub>4</sub> = 44%.

myristate<sup>9</sup> with an equal weight of water. The reactants were stirred with a Hershberg stirrer and heated, leading a slow stream of nitrogen over the surface to remove water vapor and exclude oxygen. As the temperature increased and water was removed, the mixture became fusible at 300°. Heating was discontinued when the mixture began to darken above 320°.

The fusion mixture was cooled, taken up in water, and acidified with sulfuric acid. Solids were filtered, washed free of inorganic salts, and taken up in hot 95% ethanol. Insoluble unconverted sodium  $\alpha$ -sulfomyristic acid, recovery 20%, was removed by filtration.

The alcoholic solution, treated with water and diethyl ether, formed two phases. Evaporation of the ether layer and crystallization of the residue from chloroform gave lauric acid (3.7 g., yield 23%) neut. equiv. 199.8 (theor. 200.3), m.p. 42.4–43.1°; confirmed by mixed melting point and infrared spectra. A gas-liquid chromatogram showed the purity of the isolated lauric acid by-product to be at least 90%.

Crystallization of the aqueous alcohol solution at 0° gave sodium tridecanesulfonate (6.0 g., yield 39%) with the analysis and Krafft point shown in Table I. Infrared spectra showed the presence of the SO<sub>3</sub><sup>-</sup> group and absence of CO and COO<sup>-</sup> groups. Sodium alkanesulfonates of 11, 15, and 17 carbon atoms prepared in the same way are recorded in Table I.

**Reduction. Sodium 1-Hydroxy-2-octadecanesulfonate.**—The general method was reduction of the lithium salt of the methyl ester of the  $\alpha$ -sulfo fatty acid, dissolved in isopropyl alcohol, by addition of a 1.25-molar ratio (theo. 0.5) of lithium borohydride. Variations in the order of addition of reactants or by use of diglyme gave lower yields.

A solution of lithium isopropyl  $\alpha$ -sulfostearate (22.6 g., 54.8 mmoles) in 270 ml. of isopropyl alcohol was heated and 50 ml. of the solvent distilled to remove traces of moisture. Lithium borohydride (Metal Hydrides, Inc.,<sup>10</sup> 89.1%; 1.48 g., 68.5 mmoles) was added during 3 min., the solution was refluxed 24 hr., 300 ml. of water was added, and the mixture was refluxed an additional hour.

The aqueous isopropyl alcohol solution was poured through an ion exchange column containing 400 ml. of resin sulfonic acid (Dowex 50W-X8<sup>10</sup>), neutralized with sodium hydroxide to pH 10.0, and evaporated to dryness. The residue was taken up with 1200 ml. of water, heated to boiling, allowed to crystallize at room temperature, filtered, washed, dried at 60° in a vacuum oven, and extracted twice with 3 l. of boiling methanol. The residue insoluble in

methanol was the hydrolyzed unreduced ester recovered as disodium  $\alpha$ -sulfostearate (yield 39%). Crystallization of the methanol extract gave sodium 1-hydroxy-2-octadecanesulfonate (yield 61%).

Other sodium 1-hydroxy-2-alkanesulfonates recorded in Table II were obtained in a similar manner. Infrared examination of Nujol mulls showed strong OH absorption at 3400 cm.<sup>-1</sup> and SO<sub>3</sub><sup>-</sup> absorption at 1250–1150 and 1060 cm.<sup>-1</sup>.

**1-Hydroxy-2-alkanesulfonic Acids.**—Sodium 1-hydroxy-2-hexadecane-sulfonate (2.9 g.) was dissolved in 150 ml. of isopropyl alcohol by heating and stirring in the presence of 100 ml. of resin sulfonic acid, passed through a column containing 300 ml. of the exchange medium, and eluted with 900 ml. of isopropyl alcohol.

The isopropyl alcohol solution was evaporated in a rotary evaporator at 80° and 10 mm., the residue was redissolved in 100 ml. of chloroform, and water was removed azeotropically. Crystallization at -20° and drying at 75° for 1 hr. in a vacuum oven gave 1-hydroxy-2-hexadecanesulfonic acid, neut. equiv. 322.9 (theo. 322.5) as hygroscopic crystals which soften at 106°, pass through a glassy stage and melt sharply at 113°. 1-Hydroxy-2-octadecanesulfonic acid, neut. equiv. 350.8 (theo. 350.5), obtained in a similar manner, softens at 107.5°, becomes glassy and melts sharply at 114.8°.

**Acknowledgment.**—Microanalyses for C, H, and S were performed by Mr. Ronald Campbell and Miss Oksana Panasiuk and gas-liquid chromatography by Mr. Samuel F. Herb.

### Identification of a 3-Benzylidene flavanone as a By-product of a Chalcone Synthesis

MARGARET K. SEIKEL,<sup>1</sup> MARY JANE LOUNSBURY,  
AND SU-CHU WANG<sup>2</sup>

Department of Chemistry, Wellesley College, Wellesley,  
Massachusetts, and Forest Products Laboratory, U.S.  
Department of Agriculture, Madison 5, Wisconsin

Received December 18, 1961

Although chalcones are most frequently prepared by a condensation reaction in the presence of strong

(1) Present address: Forest Products Laboratory, Madison 5, Wisconsin.

(2) Experimental work on this problem was done at Wellesley College and was started by Ann Fournier and Jane Moss.

(9) A. J. Stirton, J. K. Weil, Anna A. Stawitzke, and S. James, *J. Am. Oil Chemists' Soc.*, **29**, 198 (1952).

(10) Reference to manufactured products does not constitute recommendation by the U.S. Department of Agriculture over similar products not mentioned.

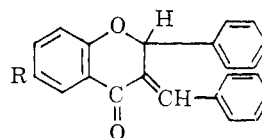
TABLE I  
 DATA ON COMPOUNDS

	Quinaceto- phenone <sup>a</sup>	2',5'-Dihydroxy- chalcone <sup>a</sup> (III)	6-Hydroxy- flavanone <sup>a</sup> (II)	3-Benzylidene- 6-hydroxy- flavanone (IV)	3-Benzylidene- 6-methoxy- flavanone
A. $R_f$ values 50% $\text{CH}_3\text{COOH}^b$	0.87	0.83	0.87	0.90	
B. Colors of spots on paper in ultraviolet <sup>c</sup>	Light orange	Pale black	Fluorescent blue-white	Light red-orange	Light orange
C. Absorption spectra, ultra- violet <sup>d</sup>					
$\lambda_{\text{max}}$ , $m\mu$ (log $\epsilon$ ) 95% alc.	365(3.51) 256(3.78) 227(4.14)	405(3.73) 316(4.36) 228(4.11)	360(3.56) <sup>e</sup> 256(3.91) 226(4.34)	395 305 230	
+ $\text{AlCl}_3$		480(3.61) 325(4.29) 230(4.16)		395 304 232	
+ $\text{NaOC}_2\text{H}_5$		500(3.35) 250(4.13)		305 230	
+ $\text{NaOOCCH}_3$		404(3.73) 315(4.37) 230(4.11)		392 305	
D. Absorption spectra, infrared <sup>f</sup>					
$\lambda_{\text{max}}$ , $\text{cm}^{-1}$					
Hydroxyl		3350	3250	3400	...
Carbonyl		1640	1680	1670	1670
Heterocyclic ether		...	1310	1320	1320
Ether		...	1070	1060	1060
Aromatic ether		...	...	...	1280
<i>trans</i> $\text{CH}=\text{CH}$		975	...	...	1010
Flavanone bands <sup>g</sup>		...	910 870	910 860	905 870
E. Melting point, $^\circ\text{C}$ .		173–3.5 <sup>h</sup>	213–214 <sup>i</sup>	211–214	117.5–118.5 <sup>j</sup>
F. Analysis					
Calcd. % C		74.99	74.99	80.45	
% H		5.04	5.04	4.92	
Found % C		74.50	74.94	80.21	
% H		4.94	5.12	4.87	

<sup>a</sup> With dilute sodium hydroxide these give unusual purple colors. <sup>b</sup> No better separation of spots was achieved in the many other solvents tried. IV is visible only when the development is carried out in the presence of strong acids such as acetic acid, formic acid, and xylene-acetic acid (1:3). <sup>c</sup> Ammonia fumes had no significant effect on these colors. <sup>d</sup> For use of reagents see M. K. Seikel and T. A. Geissman, *Arch. Biochem. Biophys.*, **71**, 17 (1957). <sup>e</sup> See S. Sakai, T. Ogata, A. Sakurai, and S. Fujise, *Nippon Kagaku Zasshi*, **78**, 653 (1957); *Chem. Abstr.*, **53**, 5259 (1959) for similar data. <sup>f</sup> Determined in a Nujol mull with a Perkin-Elmer Infracord spectrophotometer. <sup>g</sup> Strong bands for which no specific assignment could be made. <sup>h</sup> Recorded 215 $^\circ$ , footnote 14. <sup>i</sup> Recorded 220 $^\circ$ , footnote 13. <sup>j</sup> Recorded 118–119 $^\circ$ , K. v. Auwers and F. Arndt *Ber.*, **42**, 2706 (1909).

alcoholic alkali,<sup>3</sup> the yields are generally low<sup>4</sup> and the products hard to crystallize.<sup>4a,5,6</sup> The numerous by-products which have been identified include: (1) the ever-present isomeric flavanone,<sup>4a,7</sup> (2) a diacetophenone,<sup>8</sup> (3) the acid and the alcohol corresponding to the aldehyde used,<sup>3a,4a</sup> (4) the hydrated chalcone,  $\text{ArCOCH}_2\text{CHOHAr}'$ ,<sup>9</sup> (5) the flavone formed by air oxidation,<sup>10</sup> and (6) poly-

morphic forms.<sup>11</sup> In the present work a new type of by-product was identified, namely a 3-benzylidene-flavanone (I). Previously such compounds had been obtained only by the acidic condensation of flavanones and aldehydes.<sup>12</sup>


 I. R = H  
 IV. R = OH

(3) (a) T. A. Geissman and R. O. Clinton, *J. Am. Chem. Soc.*, **68**, 697 (1946); (b) E. Schraufstatter and S. Deutsch, *Chem. Ber.*, **81**, 489 (1948).

(4) (a) D. N. Dhar and J. B. Lal, *J. Org. Chem.*, **23**, 1159 (1958);

(b) K. B. Raut and S. H. Wender, *ibid.*, **25**, 50 (1960).

(5) K. Matsuoka and S. Fujise, *Nippon Kagaku Zasshi*, **78**, 647 (1957), *Chem. Abstr.*, **53**, 5258 (1959).

(6) T. R. Seshadri and V. Venkateswarlu, *Proc. Indian Acad. Sci.*, **26A**, 189 (1947).

(7) (a) G. Bargellini and A. Oliverio, *Ber.*, **75B**, 2083 (1942); (b) N. B. Mulchandani and N. M. Shah, *Chem. Ber.*, **93**, 1918 (1960);

(c) G. N. Vyas and N. M. Shah, *J. Indian Chem. Soc.*, **28**, 75 (1951).

(8) H. Bablich and St. v. Kostanecki, *Ber.*, **29**, 233 (1896); A. Cornelson and St. v. Kostanecki, *ibid.*, **29**, 240 (1896).

(9) A. Romeo and G. Bargellini, *Ann. chim. (Rome)*, **42**, 361 (1952).

(10) K. G. Marathe, *J. Univ. Poona, Sci. Technol.*, no. **14**, 63 (1958); *Chem. Abstr.*, **54**, 3402 (1960).

(11) H. E. Smith and M. C. Paulson, *J. Am. Chem. Soc.*, **76**, 4486 (1954); P. Venturella and A. Bellino, *Ann. chim. (Rome)*, **49**, 2023 (1959); A. Oliverio and A. Schiavello, *Gazz. chim. ital.*, **80**, 788 (1950) (see this article for other early references).

(12) A. Katschalowsky and St. v. Kostanecki, *Ber.*, **37**, 3169 (1904); H. Ryan and P. O'Neill, *Proc. Roy. Irish Acad.*, **32B**, 167 (1915); H. Ryan and J. Algar, *ibid.*, **32B**, 185 (1915); H. Ryan and G. Cruess-Callaghan, *ibid.*, **39B**, 124 (1929).

When quinacetophenone was condensed with an equimolar amount of benzaldehyde in the presence of aqueous alkali, 6-hydroxyflavanone (II) was again found to be the chief product.<sup>13</sup> But a paper chromatographic study of the reaction (which was complete in three to four days at room temperature) revealed the presence of 2',5'-dihydroxychalcone (III) and the new by-product, 6-hydroxy-3-benzylidene flavanone (IV). With the 1:1 gram ratio of aldehyde to acetophenone suggested by Vyas and Shah<sup>14</sup> IV was often the chief crystallizable product. In fact, we propose that the yellow material, m.p. 215°, designated by them as the chalcone III was the by-product IV.<sup>15</sup> We obtained red-orange crystals, m.p. 173°, in less than a 10% yield which was shown to be the chalcone by the absorption spectrum and by conversion to II.<sup>16</sup> The structure of the by-product IV was confirmed by its synthesis from II and benzaldehyde in both acidic and basic media.

The ultraviolet and infrared absorption spectra of IV reveals its hybrid character, since they resemble both those of chalcones and flavanones. A Fisher-Hirschfelder model shows that the  $\alpha,\beta$ -unsaturated ketonic group is held rigidly in IV (unlike the situation of free rotation in chalcones) by the superimposed  $\gamma$ -pyrone ring and that steric hindrance between the two "B" phenyl rings prevents planarity of the carbonyl and ethylenic linkages. As a result, IV is lighter in color than III and has the carbonyl band at 1670  $\text{cm}^{-1}$  in the infrared, resembling that of II not of III.

#### Experimental<sup>17</sup>

**General Conditions of Reaction.**—Quinacetophenone (1–3-g. samples) and benzaldehyde were dissolved in 95% alcohol (7–60 ml.) and cooled. Simultaneously the mixture was flushed with nitrogen and 40% aqueous potassium hydroxide (7–30 ml.) was added slowly. The flask was tightly stoppered and allowed to stand 3–4 days at room temperature or in the refrigerator; paper chromatography was used to determine the disappearance of quinacetophenone. The ruby-red reaction mixture was then acidified and the resulting precipitate washed free of benzoic acid with saturated bicarbonate.

**6-Hydroxyflavanone (II)** was obtained as the main product (32.5%) when a mole to mole ratio of benzaldehyde to quinacetophenone was employed and concentrated hydrochloric acid was used to precipitate the yellow product. After repeated recrystallizations from 95% alcohol, the last traces of yellow color (due to III) were removed from this material by passing it through a column packed with a washed<sup>18</sup>

mixture of nylon<sup>19</sup> powder and Celite<sup>20,21</sup> (2:1). When the 30% methanolic eluate<sup>22</sup> was allowed to stand several days in the refrigerator, pure white crystals of II separated.

**2',5'-Dihydroxychalcone (III)** could be isolated in 4–9% yields from a similar reaction mixture if the acidification was done with 6 *N* hydrochloric acid and the yellow-orange precipitate was extracted with methanol. On evaporation of the methanol crude chalcone was deposited; this was obtained as orange-red crystals after repeated recrystallization from benzene. When III was refluxed with dilute alcoholic hydrochloric acid for 10 hr., it was converted into II.

**6-Hydroxy-3-benzylidene flavanone (IV)** was obtained as the main product (28–37%) when equal weights of quinacetophenone and benzaldehyde were used (a 1:1.3 molar ratio). A larger excess of benzaldehyde (up to 7 moles) increased the yields, a 50% yield being isolated after recrystallization from methanol. The same compound was obtained in a 70% yield by substituting 6-hydroxyflavanone (II) for quinacetophenone in the standard procedure with excess benzaldehyde and running the reaction for 1 day. The same compound was also isolated in 29% yield when an alcoholic solution of 0.184 g. of 6-hydroxyflavanone and 0.6 g. of benzaldehyde was saturated with hydrogen chloride and allowed to stand for 4 days at room temperature. Mixed melting points proved the identity of the three samples of IV. The yellow methyl ether of this compound was prepared by means of dimethyl sulfate and anhydrous potassium carbonate in anhydrous acetone. When IV was refluxed for 10 days with dilute alcoholic hydrochloric acid, no color change occurred and the melting point of the product was little changed. Paper chromatography showed a second spot appearing.

(19) Polypenco Nylon Powder, The Polymer Corp., Reading, Pa.

(20) Johns Manville.

(21) R. Neu, *Nature*, **182**, 660 (1958).

(22) III eluates only with 75% methanol.

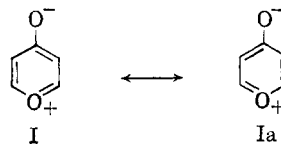
#### Diels-Alder Reaction. Experiments with 2,6-Distyryl- $\gamma$ -pyrone and 2-Styrylchromones

GAMIL AZIZ

Department of Chemistry, Faculty of Science,  
University of Cairo, Giza, Egypt, U.A.R.

Received November 21, 1961

$\gamma$ -Pyrone s differ from *p*-quinones to which they bear structural resemblance as the former do not function as dienophiles in the Diels-Alder reaction. This may be attributed to the important contribution of structures I and Ia to the actual state of the molecule.<sup>1,2</sup>



The use of 2,6-distyryl- $\gamma$ -pyrone as a diene component in the Diels-Alder reaction seems not to have been investigated so far. In the present in-

(13) A. Robertson, V. Venkateswarlu, and W. B. Whalley, *J. Chem. Soc.*, 3137 (1954).

(14) G. N. Vyas and N. M. Shah, *J. Indian Chem. Soc.*, **26**, 273 (1949).

(15) The methyl ether of IV melts relatively close to that reported by Vyas and Shah<sup>14</sup> for their chalcone.

(16) Vyas and Shah<sup>14</sup> report no such reaction for their supposed chalcone although the reaction was reported for all other chalcones in their paper.

(17) Melting points are uncorrected.

(18) Washed with benzene, ether, ethyl acetate, acetone, methanol, and hot water (R. Birzgalis, M.A. thesis, Wellesley College, 1960, p. 43).

(1) K. Alder in "Newer Methods of Preparative Organic Chemistry," New York, 1948, p. 501.

(2) B. Eistert, "Tautomerie und Mesomerie," F. Enke, Stuttgart, 1938, p. 56 ff.