reactions affecting the rings probably could not be detected.

In Chart I are shown the reactions by which the compounds of the series were prepared.[6] Table I gives measured molar activities of the various members of the series. Because of the stoichiometry of the reactions some of the molar activities differ by small integral factors. The data of Table I demonstrate that for the series of compounds the agreement with the mean value is about ± 0.5%.

---

[6] See C. J. Collins and W. A. Bonner, This Journal, **77**, 92 (1955); also C. J. Collins, unpublished work.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

Acetylation of Monocarboxylic Acids with Ketene

BY R. E. DUNBAR AND FLOYD C. GARVEN

RECEIVED MARCH 16, 1955

The reaction of ketene with both aliphatic and aromatic acids as a means of preparing mixed anhydrides was first reported by Hurd and Dull[1]

$$CH_2{=}C{=}O + R{-}COOH \longrightarrow R{-}CO{-}O{-}CO{-}CH_3$$

Since this reaction usually occurs at room temperature, in the presence of inert solvents, without the aid of catalysts, it affords a convenient means of preparing and studying other anhydrides. Likewise, since inert solvents are permissible it affords a practical method of acetylating even solid organic acids.

The ketene used was generated by the pyrolysis of acetone using the lamp previously described by Dunbar and Bolstad.[2]

Thirty organic aliphatic and aromatic acids were each individually placed in the gas absorption apparatus designed by Dunbar and Bolstad.[3]

Each acid was then individually treated with ketene until a theoretical excess had been added. Dry ethyl ether was used as a solvent for the solid acids. The mixed acid anhydrides were purified by vacuum distillation or recrystallization from ligroin. Eight such mixed anhydrides, previously prepared with ketene, again were produced and formerly reported constants checked or new constants recorded. Twenty-two additional mixed anhydrides were prepared and their physical constants recorded. Of this group, nineteen have never been reported previously and the remaining three have never been produced previously by the use of ketene. These compounds and constants are recorded in Table I. Concordant elementary analyses for all new compounds are tabulated in Table II.

TABLE I

MIXED ACETIC ANHYDRIDES, $RCO{-}O{-}COCH_3$

Mixed acetic anhydride	M.p. or b.p. (mm.), °C.	$n^{20}D$ (t, °C.)	d^{20}_4 (t, °C.)
Propionic[a]	31–32 (5)	1.3963	1.013
Butyric[a]	41–43 (5)	1.405	1.00
Iso-butyric[a]	35.7–37 (5)	1.400	0.994
Valeric[a]	55–57 (6)	1.4100	.988
Iso-valeric[a]	48–60 (6)	1.4053	.982
Hexanoic[a]	56–72 (10)	1.401	.955
Benzoic[a]	.....	1.4955	1.501
Stearic[a]	54	1.427 (70)	0.885 (70)
Formic[b]	27–28 (10)	1.388	1.120
Heptanoic[c]	.....	1.414	0.943
Octanoic[c]	.....	1.421	.940
Nonanoic[c]	.....	1.422	.935
Decanoic[c]	.....	1.428	.932
Lauric[c]	.....	1.433	.914
Myristic[c]	46–47	1.432 (35)	.899 (35)
Palmitic[b]	49–51	1.432 (60)	.869 (60)
Crotonic[c]	.....	1.438	1.003
10-Undecenoic[c]	.....	1.436	0.933 (27)
Phenylacetic[c]	.....	1.496 (25)	1.090 (25)
Diphenylacetic[c]	.....	1.524	1.10
Cyclohexylacetic[c]	.....	1.444 (26)	1.019
3-Cyclohexylpropionic[c]	.....	1.449 (22)	1.01 (22)
4-Cyclohexylbutyric[c]	.....	1.450 (22)	0.994 (22)
6-Cyclohexylhexanoic[c]	.....	1.454	0.976
Cinnamic[c]	120–125	...	...
α-Naphthoic[b]	.....	1.568	1.151
o-Toluic[c]	.....	1.513	1.125
m-Toluic[c]	.....	1.504	1.102
p-Toluic[c]	.....	1.516	1.118
2,3-Dichlorophenoxyacetic[c]	.....	1.513	1.308

[a] Previously prepared with ketene but limited properties reported. [b] Previously prepared but not by the use of ketene. [c] New additional mixed anhydrides.

TABLE II

ELEMENTARY ANALYSES OF MIXED ANHYDRIDES

Mixed acetic anhydride	Carbon, % Found	Carbon, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.
Heptanoic	62.36	62.76	9.36	9.41
Octanoic	64.34	64.49	10.04	9.74
Decanoic	65.93	67.25	10.26	10.35
Lauric	70.20	69.38	10.91	10.82
Myristic	70.46	71.06	11.27	11.18
Crotonic	55.17	56.24	6.42	6.29
10-Undecenoic	68.80	68.99	10.20	9.80
Phenylacetic	66.70	67.40	6.26	5.66
Diphenylacetic	75.48	75.57	5.95	5.55
Cyclohexylacetic	64.63	65.19	8.99	8.76
3-Cyclohexylpropionic	67.38	66.63	9.45	9.15
4-Cyclohexylbutyric	67.60	67.89	9.63	9.50
6-Cyclohexylhexanoic	70.08	69.96	10.31	10.06
Cinnamic	77.29	77.44	5.42	5.05
o-Toluic	67.79	67.40	5.90	5.66
m-Toluic	67.70	67.40	6.88	5.66
p-Toluic	67.47	67.40	6.03	5.66
2,3-Dichlorophenoxyacetic	45.65	45.65	4.18	3.06

It has been reported previously,[1] and again observed, that when the size of the two alkyl or aryl groups are decidedly different, the mixed anhydrides showed a decided tendency to disproportionate into the two corresponding simple anhydrides

$$2R{-}CO{-}O{-}CO{-}R' \longrightarrow R{-}CO{-}O{-}CO{-}R + R'{-}CO{-}O{-}CO{-}R'$$

This behavior greatly complicated the purification and determination of physical constants, and frequently required the evaluation of these anhydrides immediately after preparation. As a result of this behavior, many of the constants of these mixed anhydrides have been reported variously from time to time. Fortunately, Whitford[4] has devised a satisfactory method of evaluating the purity of a mixed anhydride, and this test when applied to the freshly prepared anhydrides gave satisfactory confirmation of purity. Furthermore, pure mixed anhydrides show little reaction with sodium carbonate solution,[5] while an equal molecular mixture of two different anhydrides reacts readily. These three tests, as well as the melting points of the anilide, confirm the conclusion that the freshly prepared

---

[1] C. D. Hurd and M. F. Dull, This Journal, **54**, 3427 (1932).

[2] R. E. Dunbar and L. L. Bolstad, *J. Org. Chem.*, **9**, 219 (1944).

[3] R. E. Dunbar and A. N. Bolstad, *Anal. Chem.*, **18**, 337 (1946).

[4] E. L. Whitford, This Journal, **47**, 2934 (1925).

[5] A. Behal, *J. Chem. Soc.*, **78**, 8 (1900).

mixed anhydrides were relatively pure and were not mixtures of two distinctly different anhydrides. While a combustion analysis could not be conclusive, it is interesting to note that such results, as well as molecular refractions, substantiated the same conclusions. The mixed anhydrides, besides having considerable theoretical significance, are useful in the Friedel–Crafts reaction, for the preparation of mixed esters of polyhydroxy compounds, and by disproportionation for the synthesis of high molecular weight simple anhydrides, together with acetic anhydride as a by-product.

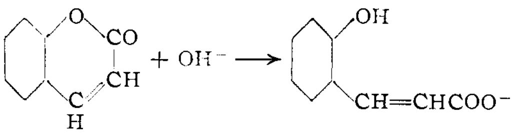
SCHOOL OF CHEMICAL TECHNOLOGY
NORTH DAKOTA STATE COLLEGE
FARGO, NORTH DAKOTA

A Sensitive and Specific Test for Coumarin through Photocatalysis[1]

BY F. FEIGL, H. E. FEIGL[2a] AND D. GOLDSTEIN[2b]

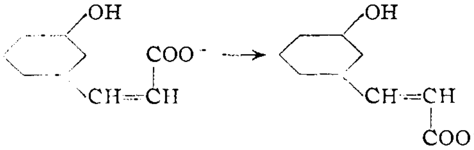
RECEIVED MARCH 11, 1955

When coumarin is dissolved in dilute alkali, the pyrone ring opens with production of the alkali salt of *o*-hydroxycinnamic acid. We have found



that freshly prepared alkaline solutions show no fluorescence at first if observed under a quartz lamp, but continued exposure produces gradually a yellow-green fluorescence, whose intensity increases to a maximum. This effect can be strikingly demonstrated. A small quantity of coumarin is dissolved in 1 N alkali and a drop of the solution is placed on filter paper. After one or two minutes of irradiation, the fleck begins to fluoresce yellow-green. Alternatively, a part of the fleck may be covered with a coin or black paper and then exposed, for 3–8 minutes, to the action of the ultraviolet rays. When the shielded area is uncovered, a crescent-shaped zone or segment of a circle displaying intense yellow-green fluorescence stands out sharply from the non-fluorescing area. If the irradiation is then continued, the part of the fleck originally covered begins to fluoresce and after sufficient exposure the entire surface of the fleck displays a uniform fluorescence intensity

If a freshly prepared solution of coumarin in alkali is protected from the light, no fluorescence is observed even after several months. In contrast, alkaline solutions exposed to diffused daylight show a faint but distinct fluorescence even within 10–12 hours. Accordingly, the fluorescence of an alkaline solution of coumarin is initiated by irradiation and it seems that the action of the ultraviolet accelerates the change of a non-fluorescing into a fluorescing compound, a change that normally proceeds at an immeasurably small rate. It seems logical to suppose that when coumarin is dissolved in alkali, the initial product is the non-fluorescing *cis* form I of *o*-hydroxycinnamic acid, which is rearranged by the ultraviolet irradiation into the fluorescing isomeric *trans* form II



I II

Our trials thus far show that the light effect observed with coumarin also occurs with alkaline solutions of those coumarin derivatives which have no free OH groups in the benzene ring. Substituents appear to have an influence on the speed with which the fluorescence becomes visible. For example, when a drop of an alcohol basic solution of bergapten is placed on filter paper and subjected to ultraviolet irradiation, the fluorescence does not appear until after about 10 minutes' exposure, and furthermore the intensity of the fluorescence increases much more slowly than with a coumarin solution of the same molarity.

Coumarin derivatives, such as umbelliferone, esculetin, daphnetin, etc., which have free OH groups in the benzene ring, fluoresce deep blue in the solid state and in basic solution. No photo effect could be found in alkaline solutions of these compounds.

The fluorescence after irradiation with ultraviolet light of drops of alkaline solutions of coumarin placed on filter paper will reveal the presence of as little as 0.005 γ of coumarin. This corresponds to a dilution limit of 1:10,000,000. However, this type of test is not reliable for detecting coumarin because alkaline solutions of its derivatives without OH groups show the same behavior and because the self-fluorescence of hydroxycoumarins makes it difficult to see the yellow-green-fluorescence produced by the irradiation with ultraviolet light. (Within certain concentration limits, it appears possible to detect compounds, which fluoresce blue or yellow-green, by capillary (absorptive) separation on filter paper. This points to a possible employment of the coumarin test in paper chromatography.)

A specific test for coumarin can be achieved if advantage is taken of the fact that only coumarin has an appreciable vapor tension at room temperature or when gently warmed. Consequently, it is possible to allow the coumarin vapor to come into contact with a solution of alkali to yield compound I which can then be irradiated to produce the isomeric fluorescing compound II. The procedure in this case is: A drop of the ether test solution is evaporated in a micro test-tube or a tiny sample of the solid is taken. The open end of the tube is covered with a piece of filter paper moistened with alkali solution and the bottom of the tube is plunged into hot water. After several minutes, the paper is held under a quartz lamp. If coumarin is present, a yellow-green fluorescence appears in a short time. Leaves and other plant parts can be tested for coumarin by this simple method.

The following experiment is worth noting. A bean of *Torresia cearensis* (coumarin content about 0.3%) is cut in two with a sharp knife and the face of the section is pressed for several seconds against filter paper moistened with alkali. If the paper is then exposed under the quartz lamp, the impression begins to fluoresce intensively after 1–2 minutes. If the imprint is previously half covered with black paper, the photoeffect (lack of fluorescence of the covered portion) is very striking. If an uncut bean is pressed against paper

---

(1) Translated from the German manuscript, by Ralph E. Oesper, University of Cincinnati.

(2) (a) Deceased. (b) Laboratorio da Produçao Mineral, Ministerio da Agricultura, Rio de Janeiro, Brazil.