composition of the native lignins of bagasse, white Scots pine and maple.

TABLE IV

COMPARISON OF THE NATIVE LIGNINS FROM BAGASSE, WHITE SCOTS PINE AND MAPLE

| | Native lignins | | |
|---|---|---|---|
| | Bagasse | White Scots pine | Maple |
| C, % | 61.5 | 64.0 | 61.0 |
| H, % | 5.7 | 6.3 | 5.6 |
| $OCH_3$, % | 15.3 | 14.5 | 17.4 |
| $OCH_3$, % of acetate | 13.3 | 10.1 | 12.8 |
| $OCH_3$, % of phenylhydrazone | 14.1 | 13.3 | 15.5 |
| Oxidation products: | | | |
| Vanillin, % | 17.8 | 19.5 | 17.2 |
| Syringaldehyde, % | 13.3 | nil | 4.5 |

Two possible considerations can be advanced from the above data: (1) Bagasse native lignin is a "guaiacyl-syringyl" lignin,[5c] the two building stones accounting for 31.1% of the polymer and only 8.2% of the total methoxyl content. Determination of the remaining 7.1% of the methoxyl group and isolation of other oxidation products will be of great importance for the elucidation of its structure. (2) Besides the "guaiacyl-syringyl" lignin, the presence of a "syringyl" lignin is also possible.[4c] Such fractionation studies are now in progress.

**Acknowledgments.**—The bagasse used in these experiments was obtained through the courtesy of the Godchaux Sugars, Inc., New Orleans, La. This work was carried out under the auspices of the Office of Naval Research.

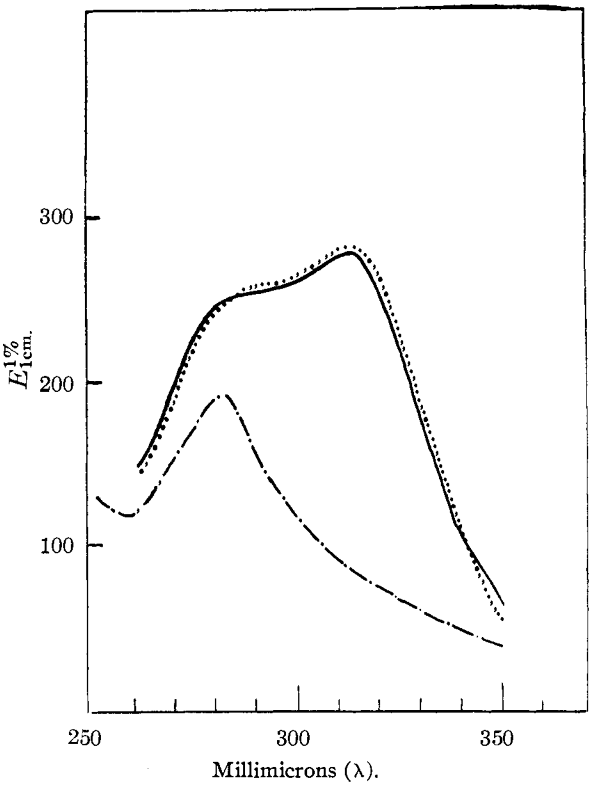

Fig. 2.—. . . . ., bagasse native lignin; ——, enzymatically liberated bagasse lignin; —·—·—, white Scots pine native lignin.

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[CONTRIBUTION NO. 816 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

# The Synthesis of Certain Beta-Diketones Containing Perfluoromethyl and Perfluoro-*n*-propyl Groups

BY LLOYD B. BARKLEY AND ROBERT LEVINE

A number of methyl ketones have been acylated with ethyl trifluoroacetate and ethyl perfluoro-*n*-butyrate in the presence of sodium methoxide to give the corresponding beta-diketones in high yields.

While considerable work has been done on the synthesis of β-diketones of the general formula $RCOCH_2COR'$, for the most part the radicals R and R′ have been aliphatic and aromatic moieties. In this Laboratory, we have prepared a variety of β-diketones in which at least one of these radicals is a heterocyclic nucleus.[1,2,3] Recently, Reid and Calvin,[4] have reported the synthesis of a number of acyltrifluoroacetones by the reaction of ketones with ethyl trifluoroacetate in the presence of sodium methoxide. With the exception of two compounds, 2-thenoyl and 2-furoyltrifluoroacetone, the β-diketones prepared by these workers[4] contained aliphatic and aromatic acyl groups.

The present paper reports our results on the synthesis of a number of β-diketones in which R is a thiophene (or substituted thiophene), a furan (or substituted furan), a thianaphthene, or benzofuran radical and R′ is the perfluoromethyl or perfluoro-*n*-propyl group. Mesityl oxide has also been converted to the corresponding 1,3-dicarbonyl compounds.

The heterocyclic β-diketones were prepared by the acylation of the appropriate methyl ketones with ethyl trifluoroacetate or heptafluoro-*n*-butyrate in the presence of commercial sodium methoxide. The required heterocyclic ketones were prepared by the methods developed in this Laboratory.[5,6,7,8] The following equation, in which *n* is 1 or 3, indicates the over-all reaction involved in the synthesis of these compounds.

$$RCOCH_3 + C_nF_{2n+1}CO_2C_2H_5 \xrightarrow{NaOCH_3} RCOCH_2COC_nF_{2n+1} + C_2H_5OH$$

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[1] Harris and Levine, THIS JOURNAL, **70**, 3360 (1948).

[2] Harris and Levine, *ibid.*, **71**, 1120 (1949).

[3] Sneed and Levine, *ibid.*, **72**, 5219 (1950).

[4] Reid and Calvin, *ibid.*, **72**, 2948 (1950).

[5] Heid and Levine, *J. Org. Chem.*, **13**, 409 (1948).

[6] Levine, Heid and Farrar, THIS JOURNAL, **71**, 1207 (1949).

[7] Farrar and Levine, *ibid.*, **72**, 3695 (1950).

[8] Farrar and Levine, *ibid.*, **72**, 4433 (1950).

TABLE I

SYNTHESIS OF BETA-DIKETONES OF THE TYPE $RCOCH_2COR'$

| | | | | | Analyses, % | | | | | | Copper salt | Analyses, % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Carbon | | Hydrogen | | Sulfur | | | Carbon | | Hydrogen | |
| R | R′ | Yield, % | B.p., °C./mm. | Method of isolation | Calcd. | Found | Calcd. | Found | Calcd. | Found | M.p., °C. | Calcd. | Found | Calcd. | Found |
| 2-Thienyl | B$^a$ | 88 | 99–102/5 | I | | | | | 9.95 | 9.73 | 215–216.5$^{b,c}$ | 34.03 | 33.93 | 1.14 | 1.30 |
| 2-Furyl | B | 92.5 | 95–97/10 | Ia | 39.23 | 39.41 | 1.65 | 1.77 | | | 187–188.5$^{b,c}$ | 35.65 | 35.87 | 1.20 | 1.28 |
| 5-Chloro-2-thienyl | A$^a$ | 82 | 117–119/9 | I | | | | | 12.50 | 12.24 | 243–244$^{e,c}$ | 33.43 | 33.52 | 1.05 | 1.33 |
| | | | 40–41 (m.p.)$^d$ | | | | | | | | | | | | |
| | B | 86 | 103–104/1.5 | I | | | | | 8.99 | 9.14 | 242–243$^{e,f}$ | 31.00 | 31.28 | 0.78 | 0.97 |
| | | | 45–45.5 (m.p.)$^d$ | | | | | | | | | | | | |
| 5-Bromo-2-thienyl | A | 87 | 122–124/5 | I | | | | | 10.66 | 10.73 | 254–254.5$^{b,c}$ | 28.95 | 28.70 | 0.91 | 1.17 |
| | | | 65.5–66 (m.p.)$^g$ | | | | | | | | | | | | |
| | B | 66.5 | 117–123/3.5 | I | | | | | 7.99 | 7.76 | 245.5–247$^{h,c}$ | 27.81 | 27.50 | 0.70 | 0.95 |
| | | | 38.5–39 (m.p.)$^h$ | | | | | | | | | | | | |
| 5-Iodo-2-thienyl | A | 82.5 | 73.5–74.5 (m.p.)$^{g,i}$ | IV | | | | | 9.21 | 9.37 | 262–263.5$^{e,c}$ | 25.36 | 25.43 | 0.80 | 0.93 |
| 3-Methyl-2-thienyl | A | 87.5 | 117–118/10 | I | | | | | 13.58 | 13.27 | 216–216.5$^{e,c}$ | 40.49 | 40.39 | 2.27 | 2.54 |
| | B | 86 | 104–106/3 | I | | | | | 9.54 | 9.28 | 188–189$^{b,f}$ | 36.00 | 36.17 | 1.65 | 1.75 |
| 5-Methyl-2-thienyl | A | 87 | 122–124/10 | I | | | | | 13.58 | 13.45 | 286–287.5$^{e,c}$ | 40.49 | 40.52 | 2.27 | 2.20 |
| | | | 59–60 (m.p.)$^j$ | | | | | | | | | | | | |
| | B | 81.5 | 38.5–39.5 (m.p.)$^d$ | IV | | | | | 9.54 | 9.75 | 286–288$^{e,c}$ | 36.00 | 35.80 | 1.65 | 1.54 |
| 2,5-Dimethyl-3-thienyl | A | 87.5 | 128–129/10 | I | | | | | 12.81 | 12.96 | 290–292$^{e,c}$ | 42.74 | 42.61 | 2.87 | 3.09 |
| | B | 89.6 | 141–143/14 | II | | | | | 9.16 | 9.09 | 261–262.5$^{e,f}$ | 37.83 | 37.95 | 2.12 | 1.90 |
| 2,5-Dimethyl-2-furyl | A | 85 | 107.5–108.5/10 | I | 51.28 | 51.33 | 3.88 | 4.11 | | | 257–258$^{e,c}$ | 45.33 | 45.01 | 3.04 | 3.30 |
| | B | 87.5 | 125–126/14 | II | 43.12 | 43.13 | 2.72 | 2.78 | | | 238–240.5$^{e,f}$ | 39.49 | 39.63 | 2.21 | 1.99 |
| 3-Thianaphthenyl | A | 88.5 | 143–145/2 | II | | | | | 11.78 | 11.46 | 291–293$^{e,c}$ | 47.56 | 47.37 | 2.00 | 2.17 |
| | | | 58.5–59.5 (m.p.)$^{g,k}$ | I | | | | | | | | | | | |
| | B | 97 | 59–60 (m.p.)$^d$ | III | | | | | 8.61 | 8.91 | 269–271$^{e,f}$ | 41.72 | 41.95 | 1.50 | 1.72 |
| 2-Thianaphthenyl | A | 78 | 96–96.5 (m.p.)$^{g,l}$ | I | | | | | 11.78 | 11.73 | 319–321$^{e,c}$ | 47.56 | 47.76 | 2.00 | 1.78 |
| 2-Benzofuryl | A | 61 | 74.5–75 (m.p.)$^d$ | IVa | 56.25 | 56.39 | 2.76 | 2.93 | | | 327–330$^{m,c}$ | 50.23 | 50.30 | 2.11 | 2.30 |
| | B | 95 | 54–55 (m.p.)$^g$ | IIIa | 47.20 | 47.47 | 1.98 | 2.05 | | | 295–296.5$^{e,c}$ | 43.45 | 43.31 | 1.56 | 1.20 |
| 2-Methylpropenyl | A | 83 | 104.5–106.5/60 | Ia | 49.48 | 49.40 | 4.68 | 4.74 | | | 212–214.5$^{e,c}$ | 42.72 | 42.80 | 3.59 | 3.35 |
| | B | 84.5 | 105–107.5/40 | II | 40.82 | 40.76 | 3.09 | 3.27 | | | ......$^n$ | | | | |

[a] A represents the trifluoromethyl group; B represents the perfluoro-*n*-propyl group. [b] Recrystallized from 95% ethanol. [c] Melts with decomposition. [d] Recrystallized from 60–70° petroleum ether which was cooled in a Dry Ice–acetone-bath. [e] Recrystallized from benzene. [f] Melts without apparent decomposition. [g] Recrystallized from 60–70° petroleum ether. [h] Recrystallized from 95% ethanol and obtained in anhydrous form by fusion in vacuum. [i] Observed a hydrate, m.p. 126–128°. [j] Recrystallized from 30–35° petroleum ether. [k] Melted first at 50–51°, then changed on standing to another form with m.p. 58.5–59.5°. [l] Observed hydrate, m.p. 115–116°; one melting of the hydrate gave the anhydrous form with m.p. 94.5–96°; the hydrate gave a weak color test with alcoholic iron(III) chloride, which became strong on standing. [m] Recrystallized from acetone. [n] While this compound appeared to give a copper salt with copper(II) acetate, the salt could not be obtained in the crystalline state.

The compounds and their physical properties are found in Table I. It may be seen that high yields of condensation products are obtained in all cases. It is of interest to note that while the copper salts of the $\beta$-diketones containing the perfluoromethyl group melted with decomposition, several of the homologous perfluoro-*n*-propyl derivatives gave copper chelates which melted without apparent decomposition.

Work is now in progress in our laboratory to extend this work to the acylation of a variety of ketones containing alpha methylene and methinyl groups.

## Experimental[9]

**Starting Materials (a) Ethyl Trifluoroacetate.**—This ester was purchased from the Dow Chemical Company, Pittsburg, California.

(b) **Ethyl Perfluoro-*n*-butyrate.**—This ester, b.p. 93–94°, was prepared in 75–85% yield by the reaction of perfluorobutyric acid with absolute ethanol in the presence of concentrated sulfuric acid following the method developed by the Minnesota Mining and Manufacturing Company.[10]

(c) **Heterocyclic Ketones.**—The necessary thiophene and furan ketones were prepared by methods developed in this Laboratory.[5,6,7,8]

**Methods for Preparing Fluorinated $\beta$ Diketones. Procedure I.**—The apparatus used in these condensations consisted of a 1000-ml. three-neck, round-bottom flask equipped with ground-glass joints, a mercury-sealed stirrer, an addition funnel and a reflux condenser (protected from atmospheric moisture by a drying tube filled with Drierite). To 0.315 mole (18 g.) of commercial 95% sodium methoxide,[11] suspended in 300 ml. of anhydrous ether, was added 0.3 mole (36.2 g.) of ethyl trifluoroacetate over a period of 30 minutes. To the rapidly stirred mixture, 0.3 mole of the appropriate ketone, dissolved in 50 ml. of anhydrous ether, was added over a fifteen minute period. Stirring was continued for two hours longer and then the mixture was allowed to stand for twelve hours at room temperature. Then, 0.36 mole (20.6 ml.) of glacial acetic acid, dissolved in 100 ml. of water, was added. This was followed by the addition of 0.22 mole (21.4 g.) of anhydrous magnesium acetate, dissolved in 125 ml. of water. The reflux condenser was replaced by a condenser set up for downward distillation and the ether removed by distillation on a steam bath. The magnesium chelate, which precipitated, was filtered and washed with 100 ml. of water. The chelate was placed in a 2 liter round-bottom flask, covered with 500 ml. of water and the mixture steam-distilled to remove any unreacted ketone. After the ketone had been removed, as indicated by the fact that the distillate no longer consisted of two phases, 0.3 mole (16.6 ml.) of concentrated sulfuric acid, dissolved in 30 ml. of water, was added to the flask and steam distillation continued until the distillate no longer gave a positive color test with alcoholic iron(III) chloride solution. The distillate was extracted with ether, the extracts dried over Drierite, the solvent distilled and the residue fractionated in vacuum to give the $\beta$-diketone.

**Procedure Ia.**—This procedure is identical with Procedure I except that the diketone was chelated by means of copper(II) acetate.

**Procedure II.**—This method is similar to Procedure I except that after the acetic acid is added, the mixture is extracted with ether until the extracts no longer give a positive test with iron(III) chloride. The extracts are dried over Drierite, the solvent distilled and the residue fractionated in vacuum.

**Procedure III.**—This method is identical with Procedure I except that after the magnesium chelate is filtered, it is placed in a 2-liter separatory funnel, 500 ml. of 15% sulfuric acid is added and the mixture shaken and extracted with ether. The extracts are then treated as described in Procedure II.

**Procedure IIIa.**—This method is identical with Procedure III except that copper(II) acetate is used in place of magnesium acetate.

**Procedure IV.**—This method is identical with Procedure I except that after the diketone had been steam distilled, it was filtered and recrystallized.

**Procedure IVa.**—This method is identical with Procedure IV except that copper(II) acetate is used in place of magnesium acetate.

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[9] All analyses were performed by Mr. George Stragand of the Microanalytical Laboratory of the University of Pittsburgh.

[10] Private communication from Mr. J. M. Rogers, Minnesota Mining and Manufacturing Co., Saint Paul, Minnesota.

[11] Purchased from the Mathieson Chemical Corporation, Niagara Falls, N. Y.

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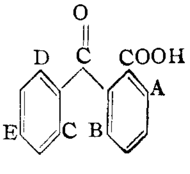
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

# Normal and Pseudo Esters of 2-Benzoylbenzoic Acid Types. III

BY MELVIN S. NEWMAN AND CHESTER W. MUTH[1]

A study of the Fischer–Speier esterification of all of the substituted 2-benzoylbenzoic acids of formula shown, with or without methyl groups at positions A, B, C and D has been completed. Generalizations concerning the effect of structure on the formation of normal and pseudo methyl esters are made.



The impetus for the work herein reported arose from the observation that 2-benzoyl-1-naphthoic acid[2] formed the pseudo methyl ester on esterification by the Fischer–Speier method whereas 2-benzoylbenzoic acid had been shown to form entirely the normal ester under similar conditions.[3] In order to learn more about the structural features responsible for the formation of normal and pseudo esters, we undertook to study the esterification of the twelve possible 2-benzoylbenzoic acids with or without methyl groups at the lettered positions, A, B, C and D. In certain cases, a methyl group at E was also included because of greater ease of preparation.[4] In this paper, we summarize our findings to date in Table I which includes data from previous publications,[4,5] together with new

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[1] Taken from Ph.D. thesis of C. W. M., 1949. Present address: Department of Chemistry, West Virginia University, Morgantown, W. Va.

[2] L. F. Fieser and M. S. Newman, THIS JOURNAL, **58**, 2376 (1936).

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[5] M. S. Newman and C. D. McCleary, *ibid.*, **63**, 1537 (1941).