$\gamma:\gamma'$-DIKETONIC ACIDS.

By J. B. Garner, Guy A. Reddick and Gail J. Fink.

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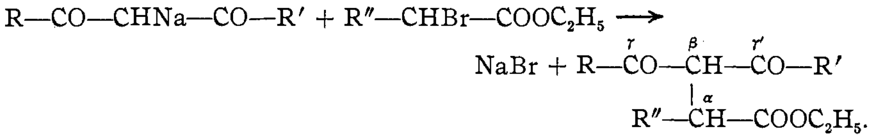
It has been shown by Dunstan and Dymond[1] and Combs,[2] that the sodium salts of β-diketones, when treated with alkyl iodides, react to produce alkylated β-diketones. It occurred to us that if the sodium salts of these diketones were treated, under the proper conditions, with α-bromacylethyl esters, a new class of substances, the $\gamma:\gamma'$-diketonic ethyl esters, would result. Our expectations have been fully realized. The reactions which occur may be represented by the following equation:



$$\mathrm{R{-}CO{-}CHNa{-}CO{-}R' + R''{-}CHBr{-}COOC_2H_5} \longrightarrow \mathrm{NaBr + R{-}\overset{\gamma}{C}O{-}\overset{\beta}{C}H{-}\overset{\gamma'}{C}O{-}R'} \quad \mathrm{\overset{|\,\alpha}{\underset{}{R''{-}CH{-}COOC_2H_5}}}.$$

In the experiments which we have carried out to the date of this paper R is methyl, R′ methyl or phenyl, and R″ hydrogen, methyl or ethyl.

The sodium salts of the β-diketones were prepared by the following methods: (*a*) to the alcoholic solution of the diketone freshly prepared sodium ethylate was added; (*b*) the benzene solution of the β-diketone was treated with sodium; (*c*) sodium was suspended in absolute ether and this treated with an ethereal solution of the β-diketone. Before the addition of the α-bromacylethyl ester the solvents were removed by distillation on the water bath. The change as above indicated progressed most rapidly when the temperature of the mixture was near the boiling point of the ester. The reaction was at an end when the characteristic odor of the ester was no longer present. The time required was from one-half hour to six hours, the change being most rapid with the ester of smallest, and slowest with that of the greatest molecular weight. Upon the completion of a reaction the mixture resulting was poured into water. The solution thus obtained was usually alkaline. This solution was extracted with ether and the ethereal extract dried over calcium chloride, and the ether subsequently removed by distillation on the water bath. The $\gamma:\gamma'$-diketonic esters which were left were fractionated under diminished pressure. It was not possible to distil any of the products at the ordinary pressure without decomposition. The yields obtained in the several cases varied, being least from the salt prepared in alcoholic solution, and greatest from that prepared in ethereal solution.

The $\gamma:\gamma'$-diketonic esters, when pure, are yellow liquids, the one of lowest molecular weight being mobile, while those of higher molecular weights are viscous. The specific gravities of all, with the exception

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[1] *Jour. Chem. Soc.*, **59**, 428.

[2] *Ann. chim. phys.* [6], **12**, 247. *Bull. soc. chim.* [3], **7**, 783.

of the one of smallest molecular weight, are greater than one. These esters are miscible in all proportions with all the ordinary solvents except ligroin. Chemically the substances are very reactive: intensely colored solutions are obtained by treatment with alcoholic or aqueous ferric chloride; alkaline solutions of chlorauric and chlorplatinic acids and ammoniacal silver nitrate are readily reduced. Unstable solid monophenylhydrazones result upon simple admixture with phenylhydrazine. These compounds readily pass with the loss of water into pyrazoles. The pyrazoles are red, viscous liquids. All of these substances show the pyrazoline reaction.[1]

I. β: β-Diacetyl Propionic Ethyl Ester, $(CH_3CO)_2CHCH_2COOC_2H_5$.—This substance is prepared by the interaction of sodium acetyl acetone and bromacetic ethyl ester. It boils at 165° at 55 mm. The following results were obtained upon analysis:

Calculated for $C_9H_{14}O_4$: C, 58.06; H, 7.52.
Found: C, 57.53; H, 7.56.

Pyrazole of β: β-Diacetyl Propionic Acid.—The pyrazole is prepared by heating the ester with excess of phenylhydrazine on the water bath for one hour. The mixture is washed with dilute acetic acid and the residue extracted with ether. The ethereal solution is dried over anhydrous sodium sulphate, the ether removed by distillation and the pyrazole fractionated under low pressure. It boils at 242° at 83 mm. The analysis gave 11.04 per cent. N; calculated, 10.85. 0.1690 gr. gave 16.8 cc. of nitrogen at 23.2° C. and 732 mm.

Calculated for $C_{15}H_{18}O_2N_2$. N, 10.85.
Found: N, 11.04.

Oxime of β: β-Diacetyl Propionic Ethyl Ester.—3.5 grams of the ester were treated with 1.35 grams hydroxylamine hydrochloride and 2.9 grams dry sodium carbonate in 25 cc. of 50% aqueous alcohol solution. The mixture was heated four hours and then evaporated to dryness on the water bath. The residue was taken up in water and the aqueous solution extracted with ether, both in alkaline and acid solutions. The oxime was obtained from the ethereal extract from the acid solution. Yield, 2.3 grams. The substance crystallizes from benzene or alcohol and melts at 120°. It is readily soluble in warm glacial acetic acid but insoluble in ligroin. Analysis gave 6.54 and 7.02 per cent. N; calculated, 6.96.

II. α-Ethyl β: β-Diacetylpropionic Ethyl ester, $(CH_3CO)_2CH(C_2H_5)COOC_2H_5$.—This substance results from the interaction of sodium acetylacetone and α-brombutyric ethyl ester. The mixture of the substances is heated on a metal bath at 175–85°. The substance obtained boils at 205° at 27 mm. The ester was not analyzed but was converted into the pyrazole, the analysis of which is given below.

The Pyrazole of α-Ethyl β: β-Diacetyl Propionic Acid.—This pyrazole is prepared by the method given above. It boils at 237° at 45 mm. An analysis gave 10.85 per cent. N; calculated, 10.85.

III. α: α-Dimethyl β: β-Diacetylpropionic Ethyl Ester, $(CH_3CO)_2C(CH_3)_2COOC_2H_5$.—The method used in the preparation of this ester is the same as that given for the preceding. The temperature of the reaction was 166–70° and six hours were required for its completion. The ester boils at 180° at 22 mm. The pyrazole, which boils at 215° at 20 mm., upon analysis, gave a percentage of nitrogen which agrees with the formula $C_{17}H_{22}O_2N_2$:

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[1] Knorr, *Berichte*, 26, 100.

Calculated for $C_{17}H_{22}O_2N_2$, 10.85 per cent. N; found, 10.83 per cent. N.

IV. β-Acetyl β-Benzoylpropionic Ethyl Ester, $C_6H_5COCH(COCH_3)CH_2COOC_2H_5$.—Ten grams of benzoyl acetone were dissolved in anhydrous benzene, to this were added 1.43 grams sodium and the reaction completed by heating on the water bath. The benzene was removed by distillation and the sodium benzoyl acetone treated with 12.2 grams bromacetic ethyl ester. The mixture was heated on the water bath for four hours, at the end of which period there is no longer the characteristic odor of the bromacetic ester. The mixture resulting was treated with water. This solution gave an alkaline reaction. It was extracted with ether and the ethereal extract dried over calcium chloride. The ether was removed and the substance remaining boiled at 194° at 44 mm. An analysis gave:

Calculated for $C_{14}H_{16}O_4$: C, 67.74; H, 6.45.
Found: C, 67.50; H, 6.39.

Pyrazole of β-acetyl-β-benzoylpropionic Acid.—One molecule of the ester is treated with an excess of phenylhydrazine in alcoholic solution. The mixture is heated for eight hours on the water bath, and the alcohol removed by distillation. The residue crystallized in large white cubes which were slightly impure, and melted at 101–106°. If this substance be permitted to stand, it gradually loses water and passes into the pyrazole, a red liquid which boils at 270° at 47 mm. The white crystalline substance is undoubtedly the mono-phenylhydrazone, but is so unstable as to render an analysis unsatisfactory. The pyrazole gave 9.80 per cent. N; calculated for the acid $C_{18}H_{16}O_2N_2$, 9.59 per cent.; for the ester $C_{20}H_{20}O_2N_2$, 8.75 per cent.

V. α-Methyl β-acetyl-β-benzoylpropionic Ethyl Ester, $C_6H_5COCH(COCH_3)CH(CH_3)COOC_2H_5$.—In the preparation of this substance sodium benzoylacetone and α-brompropionic ethyl ester are mixed in molecular quantities and the method employed is analogous to the one given under IV above. It boils at 205° at 69 mm. The pyrazole is prepared by heating a mixture of phenylhydrazine and the ester, without the use of a solvent. This pyrazole boils at 250°–3° at 55 mm. An analysis gave 9.80 per cent. N; calculated for the acid $C_{19}H_{18}O_2N_2$, 9.15 per cent.

VI. α-Ethyl β-Acetyl-β-benzoylpropionic Ethyl Ester, $C_6H_5COCH(COCH_3)CH(C_2H_5)COOC_2H_5$.—This ester is prepared by the action of α-brombutyric ethyl ester on sodium benzoylacetone. It boils at 198° at 37 mm. Its pyrazole boils at 250°–3° at 46 mm. The analysis gave 9.06 per cent. N; calculated for the acid $C_{20}H_{20}O_2N_2$, 8.75 per cent.

This work is being continued in this laboratory. Mr. Guy A. Reddick carried out the experimental work with acetylacetone, and Mr. Gail J. Fink that with benzoylacetone.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES.[1]

II. LAUROLENE.

BY W. A. NOYES AND C. G. DERICK.

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Two fairly well-defined hydrocarbons, C_8H_{14}, derived from camphor are known. Laurolene, which boils at 120–122°, has been obtained by

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[1] For the first paper, see THIS JOURNAL, **31**, 278.