[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HOLY CROSS COLLEGE]

PHENACYL AND PARA-BROMOPHENACYL ESTERS OF DIBASIC ORGANIC ACIDS[1]

BY T. LEONARD KELLY AND PIERRE A. KLEFF

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The use of phenacyl and *p*-bromophenacyl esters was introduced by Reid and co-workers[2] as a means of identifying acids. Since derivatives of acids are desirable as an aid in their identification the present investigation was undertaken.

Experimental

The procedure for the preparation of the esters was essentially the same as that of Reid. All melting points are uncorrected, having been taken in a Fisher melting point apparatus, with the aid of a set of Anschütz thermometers which gave correct melting points with various pure reagents.

Results

The results are expressed in tabular form, the first column giving the melting point of the ester and the second the percentage yield obtained.

TABLE I

PHENACYL ESTERS

Ester	M. p., °C.	Yield, %	Ester	M. p., °C.	Yield, %
Adipate	87.6	82	Suberate	102.4	93
Pimelate	72.4	90	Azelate	69.7	84
Sebacate	80.4	100	Phthalate	154.4	78
Isophthalate	191	57	Terephthalate	192.2	38

TABLE II

p-BROMOPHENACYL ESTERS

Ester	M. p., °C.	Yield, %	Ester	M. p., °C.	Yield, %
Glutarate	136.8	80	Phthalate	152.8	62
Adipate	154.5	85	Isophthalate	179.1	53
Pimelate	136.6	78	Terephthalate	225	71
Suberate	144.2	84	Itaconate	117.4	70
Azelate	130.6	86	*l*-Malate	179	65

It was found impossible to prepare a crystalline ester of malonic acid with either of the reagents, both giving an oil. In general the solubility of the phenacyl esters is much higher than that of the *p*-bromophenacyl esters. The *p*-bromophenacyl esters of the aliphatic acids have higher melting points than the phenacyl esters of these same acids. Acetone was used as solvent for the recrystallization of all the *p*-bromophenacyl esters. Two

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[1] This paper is constructed from a thesis submitted by Pierre A. Kleff to the Faculty of Holy Cross College in partial fulfilment of the requirements for the degree of Master of Science.

[2] Reid and co-workers, THIS JOURNAL, **41,** 75 (1919); **42,** 1043 (1920).

of the *p*-bromophenacyl esters, *viz.*, those of adipic and suberic acids, were analyzed for bromine by means of the Parr peroxide bomb and the results checked with the calculated percentages.

Summary

A number of dibasic organic acids have been converted to the phenacyl and *p*-bromophenacyl esters and their melting points determined.

WORCESTER, MASSACHUSETTS

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

REARRANGEMENTS OF POLYINES. II. TETRAPHENYLDIPHENYLETHINYLETHANE

BY H. E. MUNRO AND C. S. MARVEL

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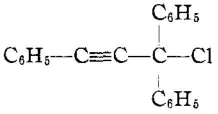
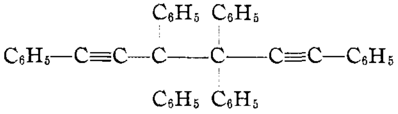
Several years ago a hydrocarbon, $C_{42}H_{30}$, was prepared by the action of iron on diphenylphenylethinylchloromethane (I) and assigned the formula tetraphenyldiphenylethinylethane[1] (II).



$C_6H_5{-}C{\equiv}C{-}\overset{C_6H_5}{\underset{C_6H_5}{C}}{-}Cl$

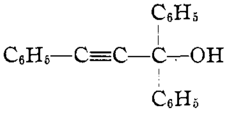
I



$C_6H_5{-}C{\equiv}C{-}\overset{C_6H_5}{\underset{C_6H_5}{C}}{-}\overset{C_6H_5}{\underset{C_6H_5}{C}}{-}C{\equiv}C{-}C_6H_5$

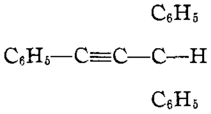
II

The preparation of this same hydrocarbon has also been reported by Wieland and Kloss,[2] who used not only the original method of treating diphenylphenylethinylchloromethane with a metal, but two other methods, namely, the reduction of diphenylphenylethinylcarbinol (III) with titanium trichloride and the oxidation of phenylethinyldiphenylmethane (IV) with potassium permanganate solution.



$C_6H_5{-}C{\equiv}C{-}\overset{C_6H_5}{\underset{C_6H_5}{C}}{-}OH$

III



$C_6H_5{-}C{\equiv}C{-}\overset{C_6H_5}{\underset{C_6H_5}{C}}{-}H$

IV

Some recent work[3] in this Laboratory on the closely related hydrocarbon tetraphenyl-di-*tert.*-butylethinylethane (V) has demonstrated that it has properties which are altogether unlike those reported for Moureu's hydrocarbon. The *tert.*-butyl derivative is easily cleaved by 40% sodium amalgam, absorbs oxygen rapidly and undergoes rearrangement in solution at room temperature to give an isomeric hydrocarbon, $C_{38}H_{38}$. This re-

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[1] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).

[2] Wieland and Kloss, *Ann.*, **470**, 217 (1929).

[3] Stampfli and Marvel, THIS JOURNAL, **53**, 4057 (1931).