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A NEW SYNTHESIS OF FLAVONOLS

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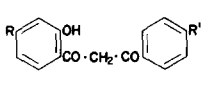
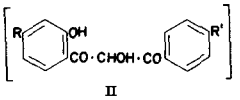
FLAVONOLS (III) are usually prepared by the Algar-Flynn-Oyamada reaction[1,2] or by the Allan-Robinson method.[3] The new synthesis here described involves the oxidation of o-hydroxydibenzoylmethanes with performic acid in chloroform. Karrer et al.[4] observed the formation of dibenzoylcarbinols



I



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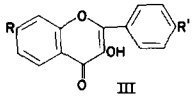

III

a=R=R'=H; b=R'=H, R=OMe; c=R=H, R'=OMe;
d=R'=H, R=OBz.

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[1] J. Algar and J. P. Flynn, Proc. Roy. Irish Acad. 42B, 1 (1934).

[2] T. Oyamada, J. Chem. Soc. Japan 55, 1256 (1934); Chem. Abstr. 29, 4358 (1935).

[3] J. Allan and R. Robinson, J. Chem. Soc. 2192 (1924).

[4] P. Karrer, J. Kebrle and R. M. Thakker, Helv. Chim. Acta 33, 1711 (1950; P. Karrer, J. Kebrle and U. Albers-Schönberg, Ibid. 34, 1014 (1951); Idem, Ibid. 35, 1498 (1952).

when dibenzolmethanes in chloroform were treated with perbenzoic acid. More recently House and Gannon[5] reported the α-hydroxylation of alkan-β-diones by monoperphthalic acid in ether.

In our experiments the o-hydroxydibenzoylmethanes (I, a, b, c, d) were shaken overnight with chloroform and performic acid. Removal of the solvent under reduced pressure yielded the corresponding flavonols (III, a, b, c, d) in yields of 20 - 50%. The intermediate dibenzoylcarbinols (II, a, b, c, d) were not isolated.

This new reaction provides an acceptable route to flavonols, since dibenzoylmethanes are readily available by Baker-Venkataraman transformation[6] of the corresponding o-aroyloxyacetophenones.

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[5] H. O. House and W. F. Gannon, J. Org. Chem. 23, 879 (1958).

[6] W. Baker, J. Chem. Soc. 1381 (1933); H. S. Mahal and K. Venkataraman, Curr. Sci. 2, 214 (1933); J. Chem. Soc. 1767 (1934); B. G. Doyle, F. Gogan, J. E. Gowan, J. Keane and T. S. Wheeler, Sci. Proc. R. Dublin Soc. 24, 291 (1948).