Anionic Activation of Organic Compounds by Adsorption on Alumina and Alumina–KF

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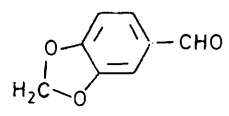
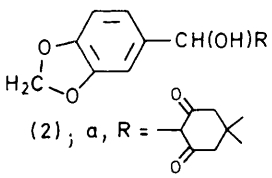
Condensations of acidic carbon compounds with piperonal (**1**) were achieved by adsorption on neutral alumina without solvent for the more acidic compounds and on Al_2O_3–KF for the less acidic compounds; dry Michael condensations also took place on Al_2O_3–KF.

Adsorptions on inorganic solids without solvent (dry reactions) have recently been used in the syntheses of organic compounds involving, *e.g.* oxidation,[1] reduction,[2] alkylation,[3] condensation,[4–6] and acetylation reactions.[7] These supported reactions[8] often involve milder conditions, easier work-up, and higher selectivity than similar reactions in solution. So far C–C bond formation by anionic activation of organic compounds in the absence of solvent has been achieved on basic silica–MeONa[4] and alumina–MeONa or neutral alumina supports with very acidic methylene-active reagents such as Meldrum's acid[6] (**4**) or malonodinitrile.[5] We report here that piperonal (**1**) reacted with indan-1,3-dione (**5**) (70%)† or with barbituric acid (**6**) (54%) by adsorption at room temperature on neutral chromatographic alumina to give the Knoevenagel products (**3a**) and (**3b**) respectively. In contrast, dimedone (**7**) (60%), dibenzoylmethane (43%), and acetylacetone (54%) gave (**2a**—**c**) respectively, without dehydration. Nitromethane after 2 h gave the nitroalcohol (35%) but prolonged contact with the support produced undesirable secondary reactions. In a typical experiment, indan-1,3-dione (**5**) (5 mmol) and (**1**) (5 mmol) were melted together and adsorbed on neutral chromatographic alumina (3 g) (Woelm 2084). The alumina was shaken at room temp. for 18 h. Products were separated by elution with CH_2Cl_2 (MeCN was used for more polar products) and recrystallised after evaporation of the solvent. The reaction also occurred when the reagents were adsorbed separately on the alumina and mixed and shaken at room temp. The condensations activated by MeONa in refluxing methanol of (**1**)

† Figures in parentheses give the yield of crystallized product. All products were characterized by elemental analysis, and by their i.r. and ^1H n.m.r. spectra.

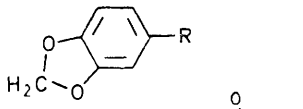


(1)

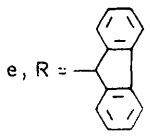


(2); a, R =

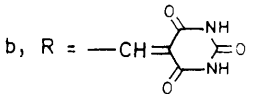
b, R = —CH(COPh)$_2$
c, R = —CH(COMe)$_2$
d, R = —C≡CPh



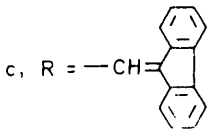
(3); a, R = —CH=



e, R =



b, R = —CH=

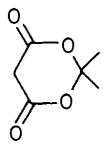


c, R = —CH=

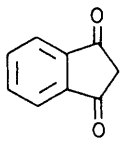
with the very reactive compounds (**5**) or (**6**) gave a mixture of products.

Michael condensation of chalcone (**8**) with (**4**) on alumina without solvent gave only a poor yield of the Michael adduct (17%). Potassium fluoride[9] on neutral alumina as described by Ando *et al.*[10] was more effective in this reaction (78% yield). On this support (**1**) condensed with the weakly acidic phenylacetylene [(**2d**), 54%] or fluorene [(**2e**), 24%; (**3c**), 64%] without solvent at room temp.

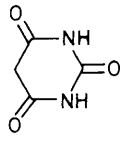
Alumina is more active than silica gel treated with soda-lime in the gas phase aldol condensation of acetaldehyde.[11] In dry reactions as in solid–gas reactions alumina and alumina–KF appear to be good supports for anionic activation of organic compounds without solvent.



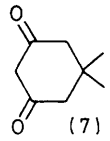
(4)



(5)



(6)



(7)

PhCH=CHCOPh

(8)

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