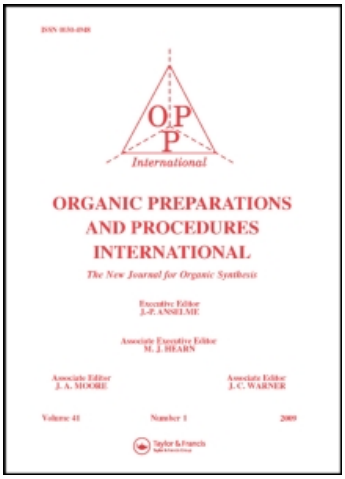

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Adama Saba[a]; Faustin Sié Sib[a]; Jean-Pierre Aycard[b]
[a] Laboratoire de Chimie Organique Structure et Réactivité, Institut de Chimie, Université de Ouagadougou, Ouagadougou, BURKINA-FASO [b] Laboratoire de Physique des Interactions Ioniques et Moléculaires, URA 773, Case 542 Université de Provence, Marseille Cedex 13, FRANCE

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SIMPLE SYNTHESIS OF ARYLALIPHATIC DIKETONES

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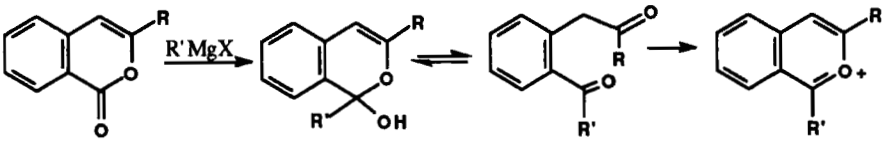
Adama Saba[†], Faustin Sié Sib[†] and Jean-Pierre Aycard*[††]

[†] *Laboratoire de Chimie Organique Structure et Réactivité*
Institut de Chimie, Université de Ouagadougou
03 B.P. 7021, Ouagadougou 03, BURKINA-FASO

[††] *Laboratoire de Physique des Interactions Ioniques et Moléculaires*
URA 773, Case 542 Université de Provence
13397 Marseille Cedex 13, FRANCE

Arylaliphatic diketones of type **3** are important intermediates in the synthesis of 2-benzopyrylium salts (**4**)[1] and precursors of isoquinolines or natural compounds such as alkaloids;[2] they were first identified in 1949 by Shriner *et al.*[3] who assumed them to be in equilibrium with the carbinol intermediates (**2**) of the addition of Grignard reagents to isocoumarins (**1**).

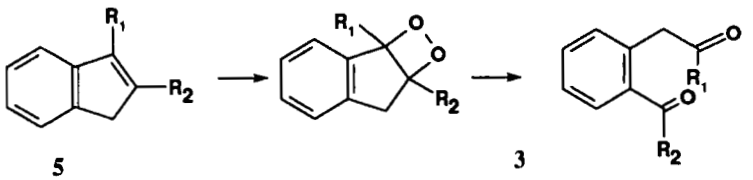


(1)

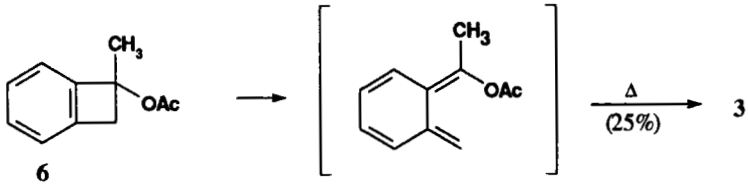
1 **2** **3** **4**

a) R = R' = CH_3 b) R = CH_3, R' = CH_3CH_2 c) R = CH_3, R' = C_6H_5 d) R = CH_3CH_2, R' = CH_3
e) R = R' = CH_3CH_2 f) R = CH_3CH_2, R' = C_6H_5 g) R = C_6H_5, R' = CH_3 h) R = R' = C_6H_5

The other methods available to obtain these diketones are a) the photooxydation of indenes (**5**)[4] (Eq. 2), b) the pyrolysis of benzocyclobutenes (**6**) (Eq. 3) and c) the degradation of polycarbonyl compounds (**7**)[6] (Eq. 4). In none of these cases was the yield higher than 5%. We now report the results of a systematic study on the formation of these 1,5-diketones (**3**) by the action of organomagnesium or organolithium compounds on isocoumarins (**1**) in anhydrous ether.[3]

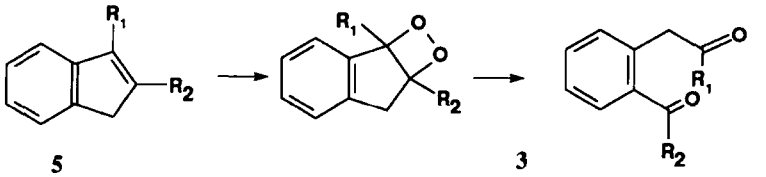


5 **3** (2)



6 (3)

The results are summarized in the Table. Yields vary from 40 to 60% with organomagnesium compounds, but increase to 70-95% with organolithium after purification by column chromatography on silica gel or by recrystallization. The action of protic acids such as tetrafluoroboric acid on diketones **3** generates 2-benzopyrylium salts (**4**) quantitatively.



5 **3** (2)

EXPERIMENTAL SECTION

Mps are uncorrected. The diketones were identified by IR recorded as KBr pellets or as films on a Beckman 250 type spectrometer. ^{1}H NMR spectra were obtained on a Varian EM 360 apparatus using TMS as an internal reference.

TABLE.

Cmpd	Yield (%) RMgX	Yield (%) RLi	mp (°C)	lit.	IR (cm^{-1})	^{1}H NMR (δ)
3a	60	83	35-37	ref 2, 4	1700, 1600	2.2 (s, 3H), 2.5 (s, 3H), 4.0 (s, 2H), 7-7.9 (m, 4H)
3b	60	–	39-40		1700, 1670	1.1 (t, 3H), 2.2 (s, 3H), 2.9 (q, 2H)
3c	50	90	<30		1720, 1655	1.2 (s, 3H), 4.0 (s, 2H), 7.1-7.7 (m, 7H), 7.8-8 (m, 2H)
3d	40	75	<30		1700, 1660	1.1 (t, 3H), 2.6 (q, 2H), 2.5 (s, 3H), 4.0 (s, 2H), 7-8 (m, 4H)
3e	45	–	40-42		1700, 1660	1.1 (t, 3H), 1.2 (t, 3H), 2.5 (q, 2H), 2.9 (q, 2H), 4.0(s, 2H), 7.2-7.9 (m, 4H)
3f	–	98	<30		1710, 1650	1.0 (t, 3H), 2.4 (q, 2H), 4.9 (s, 2H), 7-8 (m, 4H)
3g	–	80	100-102	103[2]	1660	2.6 (s, 3H), 4.7 (s, 2H), 7.2-7.7 (m, 5H), 7.8-8.2 (m, 4H)
3h	–	83	<30	liquid[2]	1680, 1650	4.7 (s, 2H), 7-8 (m, 4H)

Anal. Calcd. for $C_{12}H_{14}O_2$ (**3b**): C, 75.79; H, 7.37. Found: C, 75.80; H, 7.40

Anal. Calcd. for $C_{16}H_{14}O_2$ (**3c**): C, 80.67; H, 5.88. Found: C, 80.70; H, 5.83

Anal. Calcd. for $C_{12}H_{14}O_2$ (**3d**): C, 75.79; H, 7.37. Found: C, 75.79; H, 7.78

Anal. Calcd. for $C_{13}H_{16}O_2$ (**3e**): C, 76.47; H, 7.85. Found: C, 76.40; H, 7.80

Anal. Calcd. for $C_{17}H_{16}O_2$ (**3f**): C, 80.95; H, 6.35. Found: C, 81.00; H, 6.40

General Procedure[7].- To a solution of 0.18 g (0.001 mole) of isocoumarin in 20 ml of ether in a 100 ml two-necked flask fitted with a condenser and a dropping funnel place under nitrogen atmosphere, cooled to minus 30°, was added dropwise a solution of 0.002 mole of organolithium in ether. The temperature of the reaction mixture was allowed to become ambiant. The reaction mixture was stirred for 2 hrs and then it was cooled to 0° in ice bath before hydrolysis by a 10% aqueous solution of sodium chloride. The organic layer was separated and the aqueous phase was extracted with 2 x 20 ml of ether. The organic phases were combined, dried over $MgSO_4$ and evaporated under vacuum. The crude product was purified by column chromatography on a silica gel by using a 1:1 mixture of ether-pentane as an eluent or by recrystallisation from the same mixture of solvents.

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7. In case $R_1 = C_6H_5$, the reaction mixture was brought to reflux 1 hr prior to hydrolysis.

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