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THE REGIOSPECIFIC ACYLATION OF FULVENES

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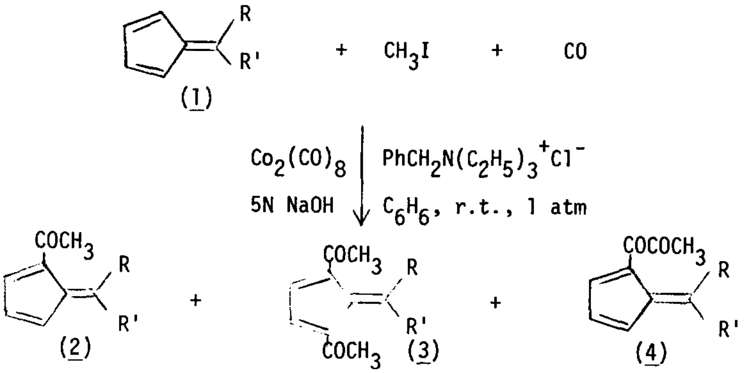
Summary: 1-Acylated fulvenes were the only monoketones formed by treatment of fulvenes with methyl iodide, carbon monoxide, catalytic quantities of benzyltriethylammonium chloride and dicobalt octacarbonyl, in a two-phase system [5N NaOH/C_6H_6].

Although there have been extensive investigations of the synthesis of fulvenes, less has been reported on the chemistry of this interesting class of compounds.[2,3] Much of the described chemistry involves the exocyclic double bond and, with the exception of the Vilsmeier reaction[2], no useful routes have been developed for the functionalization [e.g. acylation, alkylation, nitration] of the fulvene moiety. We now report a simple method for the direct, and regiospecific, acylation of fulvenes.

Fulvenes [1,R=R'=Ph,p-FC_6H_4,p-$CH_3C_6H_4$,p-$CH_3OC_6H_4$,$C_{10}H_{14}$; R=1-$C_{10}H_7$,R'=Ph] were acylated using organocobalt carbonyl and phase transfer catalysis[4]. The reactions of fulvenes were effected at room temperature and atmospheric pressure using a sodium hydroxide (5N)/benzene two-phase system, methyl iodide, carbon monoxide, and catalytic amounts of dicobalt octacarbonyl and benzyltriethylammonium chloride. After 4.5-5.5 hours, work-up afforded the 1-acetyl-6,6-disubstituted fulvenes (2) in 28-74% yields (Table 1).



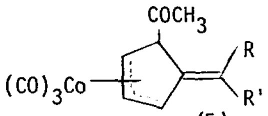
In the case of the fluorophenylsubstituted fulvene 1,R=R'=p-FC_6H_4, a 1,4-diacetylated by-product was also formed. When adamantylidenefulvene [1,R=$C_{10}H_{14}$] was used as the reactant fulvene, both 2 (R=$C_{10}H_{14}$) and the α-diketone 4 (R=$C_{10}H_{14}$) were formed, the latter resulting from a novel double carbonylation reaction. No 2-acetylated product was detected in any of these reactions. Identification of 2-4 was made on the basis of analytical and spectral [ir,nmr(^{13}C,^{1}H),ms] data, with the appearance of an ABX pattern for the protons of the cyclopentadiene ring of 2 being particularly informative.

Table 1: PRODUCTS OBTAINED BY ACYLATION OF FULVENES

1,R=,R'=	PRODUCT[a]	YIELD (%)	ν_{CO} (cm^{-1})	MS (m/e)
H,H	2,R=R'=H	74	1675	272
p-FC_6H_4,p-FC_6H_4	2,R=R'=p-FC_6H_4	46	1666	308
	3,R=R'=p-FC_6H_4	26	1676	350
p-$CH_3C_6H_4$,p-$CH_3C_6H_4$	2,R=R'=p-$CH_3C_6H_4$	49	1670	300
p-$CH_3OC_6H_4$,p-$CH_3OC_6H_4$	2,R=R'=p-$CH_3OC_6H_4$	71	1672	332
$C_{10}H_{14}$	2,R+R'=$C_{10}H_{14}$	28	1680	240
	4,R+R'=$C_{10}H_{14}$	23	1723	268
1-$C_{10}H_7$,Ph	2,R=1-$C_{10}H_7$,R'=Ph	42	1675	322

[a]Satisfactory C,H analyses (± 0.4%) were obtained for all products.

The regiospecificity of the acylation reaction can be rationalized by assuming 1,2-addition of acetylcobalt tetracarbonyl to 1 which would, after loss of carbon monoxide, give 5. The latter would be favored, for steric reasons, over the isomeric complex 6. Deprotonation of 5, followed by elimination of the cobalt carbonyl unit [i.e. regeneration of $Co(CO)_4^-$], would give 2.



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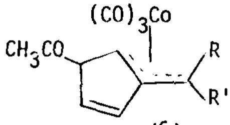

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The phase transfer catalyzed acylation of fulvenes constitutes a simple, convenient, and exceedingly mild method for the regiospecific introduction of an acyl substituent. Furthermore, 2 can be easily converted into other functionalities without affecting the fulvene skeleton [e.g. sodium borohydride gives the alcohol in 90-96% yields, and Wittig reaction with Ph_3P=CHCOOR affords the vinyl fulvene in 62-71% yields].

The following procedure is typical: A mixture of $Co_2(CO)_8$ [.044 g, .13 mmol] in benzene (20 ml) and benzyltriethylammonium chloride [0.20 g, 0.88 mmol] in 5N NaOH (20 ml) was stirred under a carbon monoxide atmosphere for 1.5 hours. Methyl iodide (2 ml) was added and, after the reaction mixture was stirred for 2 hours, 6,6-di(4-methylphenyl)fulvene [0.39 g, 1.51 mmol] in benzene (3 ml) was added and stirring was continued for two more hours. The phases were separated, the organic phase was washed (three times) with water, dried (Na_2SO_4), and concentrated. Chromatography on silica gel using 30% ether-hexane as eluant gave 0.22 g (49%) of 2,R=R'=p-$CH_3C_6H_4$, m.p. 143.5-144.0 °C.

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