Reaction of 2-Substituted 1,3-Dicarbonyl Compounds with Nitroalkenes

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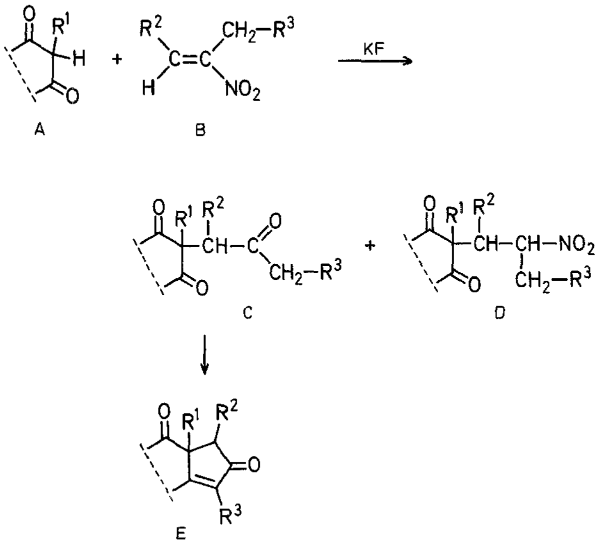
In a preliminary communication[1] it was reported that the potassium fluoride-catalyzed addition of 2-methyl-1,3-cyclohexanedione (**1**) to 2-nitropropene (**6**) leads to the formation of 2-methyl-2-(2-oxopropyl)-1,3-cyclohexanedione (**9**) in high yield. A possible reaction mechanism was derived from the isotope distribution in the product obtained from ^{18}O-labelled **1** and 2-nitropropene[2]. The reaction may be regarded as a consecutive Michael addition – Nef reaction in a formal sense: the 2-substituted dione A adds to the nitroalkenes B to give the Michael adduct D which immediately undergoes the Nef reaction to give the trione C; in some cases, the Michael adducts D are also isolated.



The reaction of 2-unsubstituted 1,3-dicarbonyl compounds with nitroalkenes has been reported earlier[3]. We describe here the results obtained with five 2-substituted 1,3-dicarbonyl compounds of different types and also the cyclization of some of the triones of the type C to cyclopentenone derivatives (E).

2-Methyl-1,3-cyclohexanedione (**1**) reacts with nitroalkenes (**6, 7, 8**) in xylene or 1,2-dimethoxyethane (DME) to give triones C (**9, 10, 11**) in high yields. On the other hand, the reaction of the (lower) cyclopentane homolog of **1**, 2-methyl-1,3-cyclopentanedione (**2**) with 2-nitropropene (**6**) in xylene in the presence of a catalytic amount of potassium fluoride using a short reaction time afforded the nitrodione **16** in 67% yield and only a low yield of the corresponding trione **12** (entry 4 in Table 1). Attempts to improve the yield of **12** by prolonged heating and by using 1 mol equiv of potassium fluoride only lowered the combined yield of **12** and **16** (entry 5). A low combined yield of trione (**13**) and nitrodione (**17**) was also obtained from 3-methyl-2,4-pentanedione (**3**) and 2-nitropropene (**6**) (entry 6). With β-oxoesters (**4, 5**) as substrates, the major products are the nitrooxoesters (**18, 19**), the dioxoesters (**14, 15**) being formed in considerably lower yields (entries 7 and 8). In conclusion it can be said that the reaction of 2-methyl-1,3-cyclohexanedione (**1**) with nitroalkenes, which are readily accessible from nitroalcohols[4,5], nitroalkyl esters[6], or alkenes[7], represents a convenient one-step procedure for the 2-(2-oxoalkylation) of **1**. To our knowledge, such a convenient method for the 2-(2-oxoalkylation) of these 1,3-diketones has hitherto not been described.

We also studied the cyclization of triones **9**, **10**, and **11** to cyclopentenones of the type E. Treatment of the triones with sodium hydride in benzene and quenching of the reaction with glacial acetic acid affords the cyclization products E in moderate yields. In the course of this study, Dauben and Hart[8] reported the cyclization of trione **9** in moderate yield using potassium fluoride in xylene containing dicyclohexyl-18-crown-6. We applied this latter method to trione **11** for comparison.

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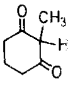
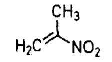
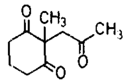
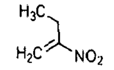
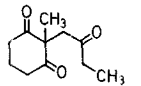
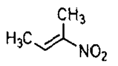
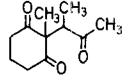
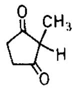
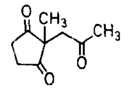
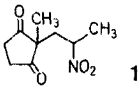
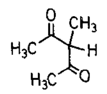
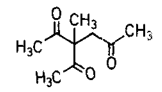
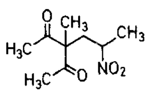
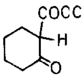
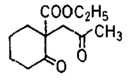
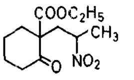
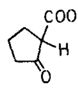
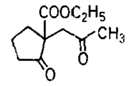
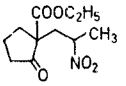
Table 1. Reaction of 2-Substituted 1,3-Dicarbonyl Compounds (A) with Nitroalkenes (B)

Entry	Dicarbonyl compound (A)	Nitro compound (B)	Reaction conditions	Tricarbonyl compound (C)	Yield[a] [%]	Nitrodicarbonyl Compound (D)	Yield[a] [%]
1	 **1**	 **6**	xylene, 120 °C, 19 h	 **9**	96	—	—
2		 **7**	xylene, 120 °C, 24 h	 **10**	96	—	—
3		 **8**	DME, 100 °C, 30 h	 **11**	63	—	—
4	 **2**	**6**	xylene, 120 °C, 1 h[b]	 **12**	5	 **16**	67
5			xylene, 120 °C, 22 h		14		13
6	 **3**	**6**	xylene, 120 °C, 100 h	 **13**	13	 **17**	17
7	 **4**	**6**	DME, 100 °C, 24 h	 **14**	11	 **18**	30[c]
8	 **5**	**6**	xylene, 120 °C, 24 h	 **15**	20	 **19**	47

[a] Yield of isolated product, based on dicarbonyl compound A.

[b] A catalytic amount of potassium fluoride (0.1 mol equiv) was added whereas 1.0 mol equiv was used in all other cases.

[c] Mixture of diastereomers.

Table 2. Data of Compounds **9–19**

Compound	m.p. [°C] or b.p. [°C]/torr[a]	Molecular formula[b]		I.R. (film) ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$)[c] δ [ppm]
9	54–57°	$C_{10}H_{14}O_3$	(182.2)	1702, 1692	1.22 (3H, s); 2.10 (3H, s)
10	40–41°	$C_{11}H_{16}O_3$	(196.2)	1702, 1692	1.22 (3H, s)
11	115–125°/4	$C_{11}H_{16}O_3$	(196.2)	1698, 1688	1.18 (3H, s); 2.10 (3H, s)[d]
12	105°/2	$C_9H_{12}O_3$	(168.2)	1720, 1708	1.08 (3H, s); 2.10 (3H, s)
13	105–110°/1	$C_9H_{14}O_3$	(170.2)	1705	1.50 (3H, s); 2.17 (9H, s)
14	105–110°/1	$C_{12}H_{18}O_4$	(226.3)	1734 (sh), 1715[d]	2.18 (3H, s)
15	100°/1	$C_{11}H_{16}O_4$	(212.2)	1750, 1718	2.12 (3H, s)
16	97–98°	$C_9H_{13}NO_4$	(199.2)	1760 (sh), 1724, 1552[e]	1.15 (3H, s); 4.62 (1H, m)
17	105–110°/1	$C_9H_{15}NO_4$	(201.2)	1716 (sh), 1698, 1550	1.42 (3H, s); 4.62 (1H, m)
18	100–105°/0.07	$C_{12}H_{19}NO_5$	(257.3)	1740 (sh), 1710, 1552	4.87 (1H, m)
19	140°/2	$C_{11}H_{17}NO_5$	(243.3)	1752, 1723, 1552	4.80 (1H, m)

[a] Bath temerature in evaporative distillation.

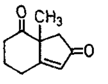
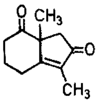
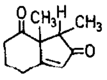
[b] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.40; H, ±0.26; N, ±0.06.

[c] 60 MHz.

[d] CCl_4 solution.

[e] $CHCl_3$ solution.

Table 3. 2,7-Dioxo-2,4,5,6,7,7a-hexahydroindenes (E) from Compounds **9**, **10**, and **11**

Starting trione	Method	Reaction time [h]	Product	Yield [%]	m.p. [°C] or bp. [°C]/torr.	Molecular formula[a] or m.p. reported [°C]	I.R. (film) ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$)[b] δ [ppm]
9	NaH/benzene (KF/xylene	1.5–3 20		37–46 30–40	liquid	m.p. 74–77°[8]	1705, 1622	1.50 (3H, s); 5.72 (1H, br s)[c]
10	NaH/benzene	1.5–2		54–55	105°/1	$C_{11}H_{14}O_2$ (178.2)	1700, 1650	1.48 (3H, s); 1.70 (3H, s)
11	NaH/benzene KF/xylene[e]	2.5 48		28 39	59–61°	$C_{11}H_{14}O_2$ (178.2)	1710, 1626[d]	1.16 (3H, d, J=7.5 Hz); 1.36 (3H, s), 5.80 (1H, br s)

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.29; H, ±0.30.

[b] 60 MHz.

[c] CCl_4 solution

[d] $CHCl_3$ solution

[e] The procedure of Ref.[8] was followed using dibenzo-18-crown-6.

Reaction of 2-Substituted 1,3-Dicarbonyl Compounds with Nitroalkenes; General Procedure:
A suspension of the dicarbonyl compound (1 mmol), potassium fluoride (1 mmol), and solvent (2.5 ml) is stirred at room temperature for 30 min under nitrogen, and then the nitroalkene (1.5 mmol) is added. The mixture is heated with stirring and then filtered through a short silica gel column with the aid of ether. The filtrate is evaporated and the residue is purified by recrystallization or silica-gel layer chromatography using ether/petroleum ether (or dichloromethane/petroleum ether) as solvent.

Cyclization of Triones 9, 10, and 11 to 2,7-Dioxo-2,4,5,6,7,7a-hexahydroindenes; General Procedure:
A solution of the trione (0.5 mmol) in dry benzene (1 ml) is added to a stirred suspension of sodium hydride (24 mg, 1 mmol) in dry benzene (1.5 ml) at room temperature under nitrogen. The mixture is refluxed with stirring and then cooled in an ice bath. Glacial acetic acid (~200 mg) is added and stirring is continued at room temperature for 30 min. The mixture is diluted with ether (20 ml) and the solution was washed with water (10 ml) and concentrated sodium chloride solution (10 ml). The residue obtained upon evaporation is purified by silica-gel layer chromatography using ether/petroleum ether or dichloromethane/petroleum ether) as solvent.

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