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THERMAL AND PHOTOCHEMICAL OXETANE FORMATION WITH α-KETOESTERS[1]

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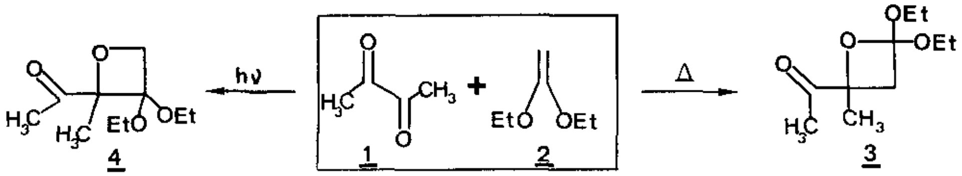
Abstract- The thermal and photochemical [2+2]-cycloadditions of ethyl pyruvate, diethyl mesoxalate and biacetyl with 1,1-diethoxyethene, 2,2-diisopropyl-1,3-dioxole and 1,1-dimethoxy-2-methylpropene have been studied. 1,1-Diethoxyethene forms oxetanes at room temperature with all carbonyl compounds as well as 1,1-dimethoxy-2-methylpropene and diethyl mesoxalate whereas the other electron-rich olefins generally react only in presence of Lewis-acids as catalysts.These observations indicate the energetic preference of the $[1_S^D+1_S^A]$ geometry of the transition state according to Houk's MO-treatement rather than the $[2_S^D+1_S^A]$ geometry for symmetrical olefins. In general the photoreaction is complementary to the thermal oxetane formation in both the reactivity and the regioselectivity. Only the electron poorest acceptor diethyl mesoxalate did not show any photochemical addition onto these olefins.

Oxetanes have been already synthesized at the beginning of our century by dehydrohalogenation of γ-halogenated alcohols or similar cyclizations[4-7]. In modern synthesis ring contraction[8] and ring expansion methods[9] have been successfully applied as well. Oxetane formation from electronically excited carbonyl compounds and olefins is a more elegant and flexible method and belongs to the most extensively studied photoreactions [10,11]. A recently reported investigation of chiral induction in the Paterno-Büchi reaction again demonstrated its importance both as a synthetic route to natural products and their precursors, respectively, and as a model for mechanistic studies [12,13]. However, during the last years the thermal [2+2]-cycloadditions under formation of oxetanes became more applicable [14-17]. Preliminary investigations of these both types of reactions were already carried out by us showing that the regiochemistry of the photochemical or thermal reactions between biacetyl and ketene acetal are complementary to each other[18] (Scheme 1).

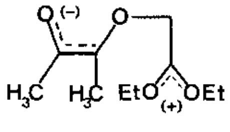
Scheme 1



In this contribution we describe further results of the thermal and photochemical [2+2]-cycloadditions between carbonyl compounds and electron rich olefins. Especially the oxetane from diethyl mesoxalate and 2,2-diisopropyl-1,3-dioxole (7,7-diethyloxycarbonyl-3,3-diisopropyl-2,4,6-trioxabicyclo[3.2.0]-heptane), which has been synthesized catalytically in 84% yield, can be used as precursor for branched-chain erythronolactones[3].

1. GENERAL REMARKS

According to Turro [19] electronically excited ketones in their $n\pi^*$-state and alkenes in their ground state form oxetanes either via an exciplex or via a radical ion pair, forming a diradical. Most recent investigations support the exciplex intermediate [20,21]. The involvement of exciplexes of some CT-character and biradicals as intermediates may explain the relatively low regioselectivity of these reactions at least for enol ethers and ketene acetals [11,22]. The exclusive formation of the oxetane 4 in nonpolar solvents, as shown in Scheme 1, was rationalized by the formation of an exciplex of high CT-character followed by photoinduced electron transfer or a contact ion pair leading to a zwitterionic intermediate 5[18].



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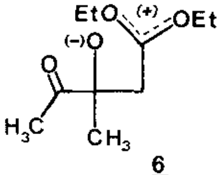

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In contrast to the photoreactions the thermal cycloadditions proceed better in polar solvents. Based on a frontier MO treatment of cycloadditions by Houk[23] the HOMO (2)-LUMO (1) interaction ($1_S^D + 1_S^A$) should lead to 3 (Scheme 1) via the dipolar intermediate 6 which is stabilized in polar solvents. On the other hand symmetrical substituted alkenes such as 1,3-dioxoles should prefer a three centered transition state ($2_S^D + 1_S^A$)[23].

2. RESULTS AND DISCUSSION

The photochemical and thermal reactions of biacetyl, ethyl pyruvate and diethyl mesoxalate as acceptor partners and ketene acetal, 2,2-diisopropyl-1,3-dioxole and 1,1-dimethoxy-2-methyl propene as donor partners have been investigated. The results such as products and yields are summarized in Table 1 together with the reaction conditions and leave the following conclusions:

2.1. THERMAL REACTIONS

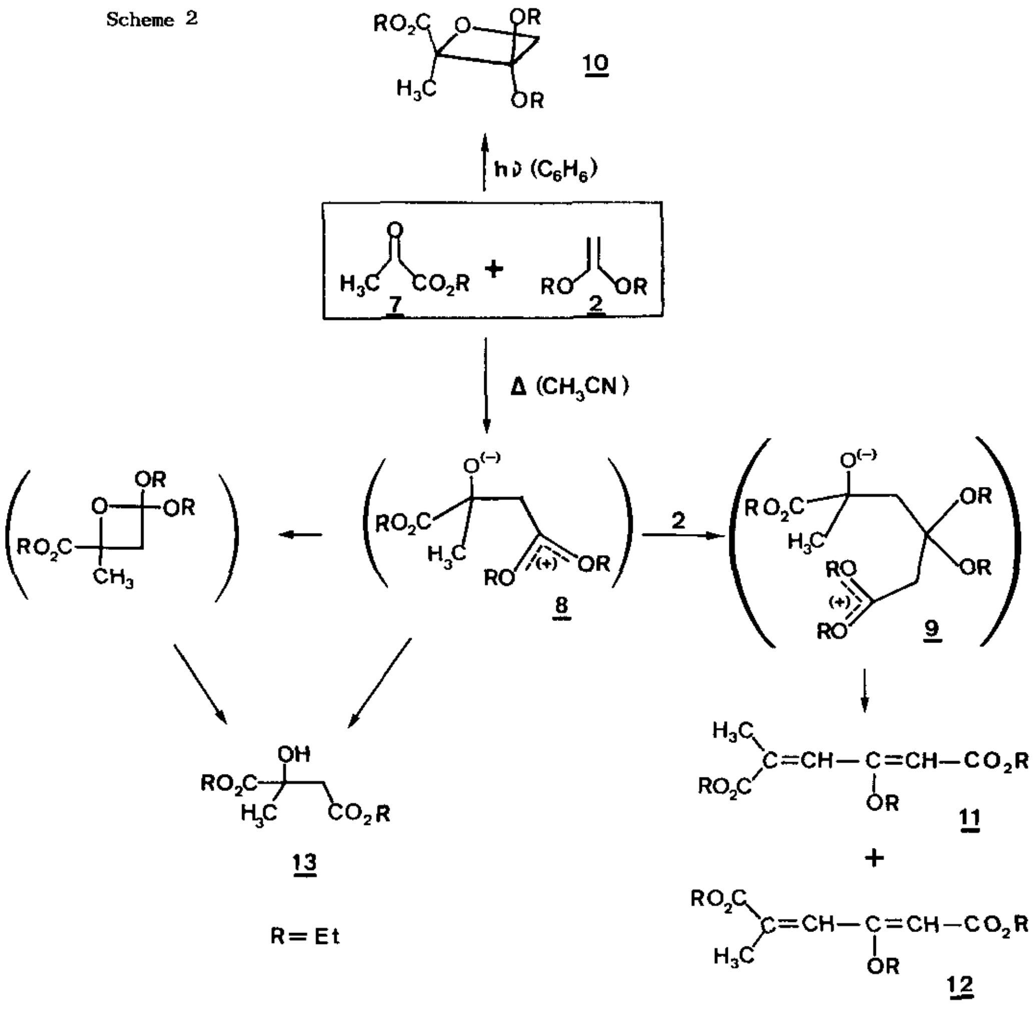
2.1.1 Reactions with 1,1-diethoxyethene 2

Ethyl pyruvate 7 reacts with 2 even at room temperature but the oxetane intermediate was not isolable. On the basis of the products (Scheme 2) and according to the above mentioned ($1_S^D + 1_S^A$)- geometry of the transition state we assume first the formation of the dipolar intermediate 8 (see Scheme 2) which leads either directly to 13 - eventually via the oxetane after intramolecular ring closure or which may be scavenged by a second olefin under formation of 9. Alternative mechanisms especially concerning the consecutive reactions leading to the 1:2 products have been discussed earlier for the biacetyl/1,1-diethoxyethene system[25]. The corresponding photoreaction exclusively leads to the regioisomeric oxetane 10. Diethyl mesoxalate 14 and biacetyl 1 also form 1:1 and 1:2 adducts with 2 under similar conditions (Scheme 1, 3 and Ref.[25]). However the oxetane 25 is isolable only in benzene as solvent.

2.1.2 Reactions with 1,1-dimethoxy-2-methylpropene 26

Alkyl-substituted ketene acetals such as 1,1-dimethoxy-2-methylpropene 26 only react thermally with the electron poorest carbonyl compound 14 forming the oxetane 20 (see Scheme 3). Weaker electron acceptors such as biacetyl require catalytic conditions even with the less substituted 1,1-dimethoxypropene[24].

Scheme 2

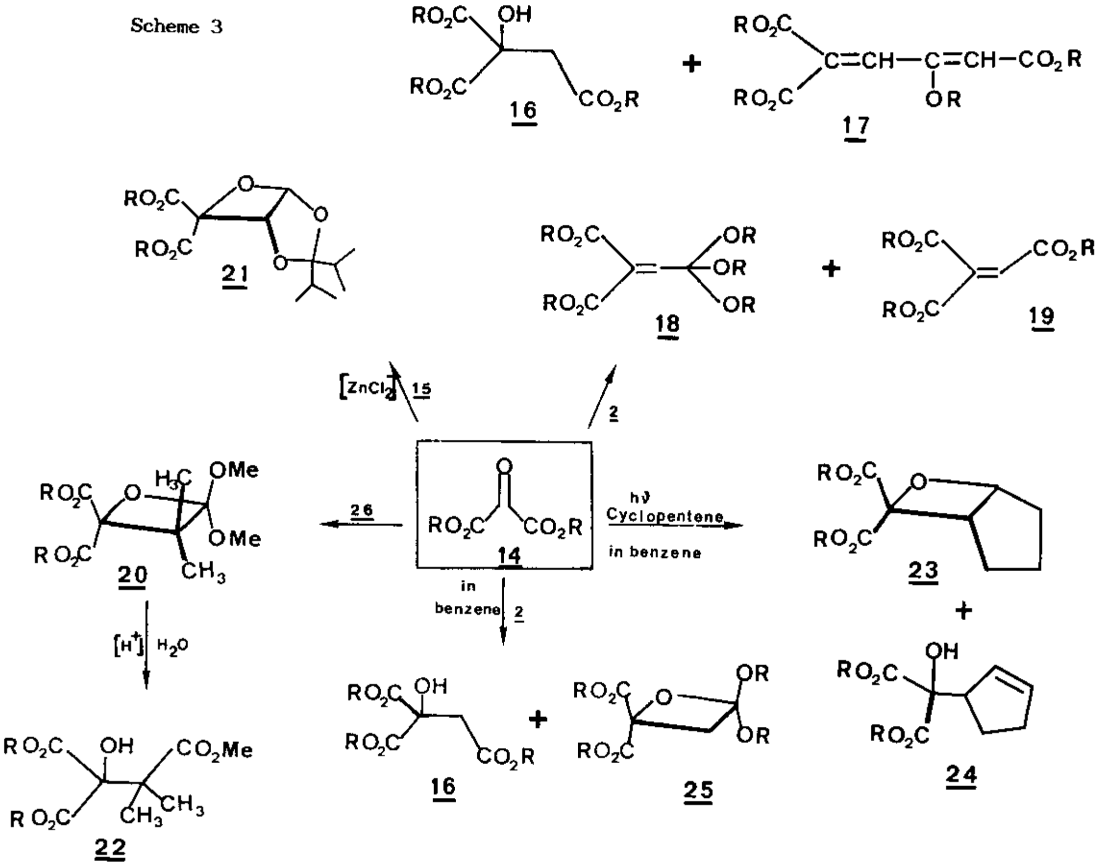


2.1.3 Reaction with 2,2-diisopropyl-1,3-dioxole 15

A thermal cycloaddition of the symmetrical cyclic olefin 15 is observed only with 14 in the presence of a Lewis-acid as catalyst. In order to optimize the yields of 21 several experiments have been carried out by varying the reaction conditions such as reaction times and temperatures and by using different catalysts. The yields and product ratios are listed in Table 2 leaving the conclusion that here $ZnCl_2$ is the catalyst of choice.

Summarizing these observations both the charge-transfer (CT) character and the substitution pattern of the starting materials have to be considered in thermal reactions of carbonyl

Scheme 3



compounds with olefins: In general only carbonyl compounds which are strong electron acceptors may add thermally to electron rich olefins. The $(1_S^D + 1_S^A)$ geometry of the transition state seems to be favoured energetically rather than the corresponding $(2_S^D + 1_S^A)$ geometry[23], since symmetrically substituted olefins require the support of a catalyst even with the strongest acceptor used here. Only the highly unsymmetrical 1,1-diethoxy ethene add thermally to all carbonyl compounds even in the absence of a catalyst.

2.2 PHOTOREACTIONS

In general the corresponding photoreactions are complementary to the thermal additions. High yields of oxetanes are observed under photochemical conditions preferentially in systems which are thermally inert[11,20]. As examples, even the strong donor 15 only forms oxetanes

Table 1: Products and yields of photochemical and thermal reactions of biacetyl 1, ethyl pyruvate 7 and diethyl mesoxalate 14 with electron-rich olefins 2, 15 and 26
(NR = no reaction)

Olefin	Method	14	7	1
2	Δ	(25°C, CH_3CN) 16(53%) 17(10%) 18(6%) 19(25%)	(25°C, CH_3CN) 11(45%) 12(32%) 13(8%)	(25°C, CH_3CN) 3(34%) [18,25]
	Δ	(25°C, benzene) 16(42%) 25(58%)		
	hν	(25°C, benzene) NR	(25°C, benzene) 10(79%)	(25°C, benzene) 4(69%) [18,25]
26 a)	Δ	(25°C, CH_3CN) ($R_1, R_2=CH_3$) 20(68%)		(25°C, CH_3CN) ($R_1, R_2=CH_3$) NR
	Δ			(80°C, CH_3CN) ($R_1=H, R_2=CH_3$) Oxetane catalyst(60%)[24]
	hν	(25°C, benzene) ($R_1, R_2=CH_3$) NR		(25°C, benzene) ($R_1, R_2=CH_3$) NR
15 R = iPr	Δ	(80°C, CH_3CN, $ZnCl_2$ catalyst) 21(84%)	(0-80°C, CH_3CN, catalyst) NR	(10-80°C, CH_3CN, catalyst) NR
	hν	(25°C, benzene) NR	(25°C, benzene) 27, 28 (4:1)	(25°C, benzene) NR

a) 26: $R_1R_2C{=}C(OCH_3)_2$

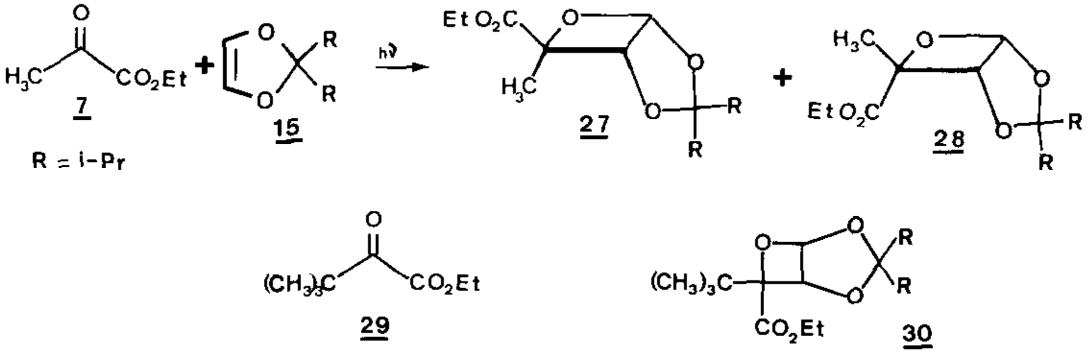
Table 2: Optimization of 21-preparation

Catalyst	Reaction Time	Reaction Temp. [°C]	Conc. Catalyst [mol %]	By-Products b) [%]	Oxetane 21 [%]
$ZnCl_2$	10 d	0	4	5	8
	5 d	20	4	8	20
	10 d	-10	4	0	0
	4 d, 9 h	80	4	2	84
	4 d	80	10	15	62
$TiCl_4$	5 d	0	0,5-1	14	25
	46 h	20	3-5	13	28
$BF_3 \cdot O(Et)_2$ c)	3 d	-20	0,5-1	5	15

a) Mol. ratio with regard to 14. b) 1-3 by products. c) The thin layer control experiments show a large amount of polmer products.

with ethyl pyruvate 7 and trimethylpyruvic acid ethyl ester 29 under photochemical conditions. Alone the reaction with 1,1-diethoxyethene 2 appears to be an exception, since here both methods are operative, however, with diverse regioselectivity (Scheme 1 and 2). The strongest acceptor 14, however, does not show any product formation upon irradiation with 2. Again, if the CT-character decreases, cycloadducts are formed photochemically even with 14; e.g. the oxetane 23 from cyclopentene beside the ene-type adduct 24 (Scheme 3) and corresponding products from norbornene or isoprene[26]. Other Paterno-Büchi reactions with various pyruvic acid esters have been reported by Scharf and coworkers[27].

Scheme 4



EXPERIMENTAL

GENERAL

The keto esters were synthezized according to methods described in the literature: Diethyl mesoxalate (14)[28], trimethylpyruvic acid ethyl ester (29)[29]. The donor olefins were prepared as described in the literature: 2,2-diisopropyl-1,3-dioxole (15)[30], ketene diethyl acetal (2)[31], 1,1-dimethoxy-2-methylpropene (26)[32]. The solvents were purified by standard methods[33]. - GC : Carlo Erba Fractovap 2101 using the OV 101 column (5% on chromosorb WAW DMCS 80/100 mesh.) - HPLC : Gilson-303 chromatograph and Chromosorb Si 60 columns, mixtures of AcOEt in cyclohexane as eluent. - Flash-Chromatography: Silicagel 60 (0.04-0.063 mm) from Machery & Nagel. - ^{1}H-nmr and ^{13}C-nmr spectra: Varian EM 390 (90 MHz), Varian VXR 300 (300 MHz), Varian CFT 20 (20 MHz), Varian VXR 300 (75 MHz). - ir spectra : Perkin-Elmer 377, Perkin-Elmer 1700. - GC-MS spectra : Varian MAT 212. - All glass apparatus were immersed over night in an aqueous sodium hydroxide solution to prevent acid-catalyzed side reactions.

PHOTOCHEMICAL REACTIONS. (GENERAL PROCEDURE)

The preparative irradiations were carried out in standard photoreactors (125 W high-pressure Hg lamp, pyrex) containing 100 ml of benzene solution of 0.03 mol olefin and 0.03 mol carbonyl compound under N_2. The reaction mixture was checked by anal. GC and the products were isolated by means of HPLC. Analytic irradiations were performed in a "merry-go-round" apparatus (from H. Mangels, Bornheim-Roisdorf).

THERMAL AND CATALYZED REACTIONS. (GENERAL PROCEDURE)

For preparations of the products 1:1 mixtures of the keto esters and alkenes (0,03 mol in 80 ml solvent) were stirred in the dark. The reaction temperatures and times are listed in Table 1. The catalyzed reactions were terminated by the addition of triethyl amine (2 ml). After evaporation of the solvents (acetonitrile or benzene) a 1:1 mixture of THF/ether (ca. 30 ml) was added until a light precipitate was formed. For work up (photochemical/and thermal reactions) the mixtures were first filtered over Al_2O_3 in order to remove polymeric materials and than separated by means of HPLC. The elution solvent mixtures are described in the following product part.

PRODUCTS OF 7 WITH 2 (THERMAL REACTION). - HPLC: AcoEt/C_6H_{12} 25:75.

i) Diethyl 2-methyl-4-ethoxymuconate 11. - Yield 45%. Colourless oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz): 1.15-1.45 (m, 3 CH_3 ester, ether), 2.05 (d, J= 1.5 Hz, CH_3-C(2)), 3.88 (q, J= 7.2 Hz, O-CH_2 ether), 4 11, 4.18 (2 q, J= 7.2 Hz, O-CH_2 ester), 5.00 (s, CH=), 7.15 (d, J= 1.5 Hz, C(4)=CH). - ir ($CDCl_3$): 3040 (-CH=), 1725, 1710 cm^{-1}(C=O). - ^{13}C-nmr (C_6D_6, 20 MHz): 13.8, 14.1, 14.5 (3 CH_3, ester, ether), 21.3 ($\underline{C}H_3$-C=), 59.4, 60.2, 64.0 (3 CH_2, ester, ether), 93.3 (H-C(5)-), 123.2 (H-C(3)-), 136.8 (=C(2)-), 165.0 (-C(4)-O), 166.5, 169.3 (2 CO_2). - ms: 256 (2.6 , $M^{+\cdot}$), 211 (12.5), 184 (10.1), 183 (100), 155 (55.6), 137 (42.2), 127 (38.3), 69 (20.7), 43 (9.2).

(ii) Diethyl 2-methyl-4-ethoxymuconate 12 - Yield 32%. White solid, mp 35 ^oC. - ^{1}H-nmr (CCl_4, 90 MHz): 1.32, 1.35, 1.40, (3t, J=7.2 Hz, CH_3 ester, ether); 2.09 (d, J=1.5 Hz, H_3C-C(2)), 3.92 (q, J=7.2 Hz, CH_2 ether), 4.10, 4.22 (q, J=7.2 Hz CH_2 ester), 5.21 (s, H-C(5)-), 8.00 (d, J=1.5 Hz, H-C(3)-). - ^{13}C-nmr (C_6D_6, 20 MHz): 13.9, 14.2, 14.5, (3 CH_3, ester, ether), 15.2, (CH_3), 59.7, 61.0, 64.0, (CH_2 ester, ether), 96.7 (H-C(5)=), 134.7 (H-C(3)=), 166.3, 168.0 (2 CO_2). - ms: 256 (1.1, $M^{+\cdot}$), 211 (12.4), 184 (12.2), 183 (100), 155 (55.6) 137 (33), 127 (38.3), 69 (17.9), 43 (9.4).

(iii) **Diethyl 2-hydroxy 2-methylsuccinate** 13 - Yield 8%. Yellowish oil - ^{1}H-nmr (CCl_4, 90 MHz): 1.22, 1.30 (2t, J=7.2 Hz, CH_3 ester), 1.40 (s, H_3C-C(2)-), 2.58, 2.90, (2d, J=15.5 Hz -CH_2), 3.72 (s, OH), 4.12, 4.25 (2q, J= 7.2 Hz, CH_2 ester). - ir (CCl_4): 3510 (OH), 1735 cm^{-1} (C=O). - ^{13}C- nmr: (C_6D_6, 20 MHz) 14.1 (2 CH_3 ester), 26.5 (CH_3), 44.7 (CH_2), 60.5, 61.6 (2 CH_2, ester), 72.6 (-C(2)-O), 170.5 (2 CO_2). - ms: 205 (0.5, $M^{+\cdot}$), 132 (5.7), 131 (84.9), 103 (20.5), 85 (79), 43 (100).

PRODUCT OF 7 AND 2 (PHOTOCHEMICAL REACTION)

Ethyl 2-methyl-3,3-diethoxyoxet-2-yl carboxylate 10. - Yield 79%. Colourless oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz): 1.20, 1.29, 1.32 (3t, J=7.2 Hz, -CH_3 ester, acetal), 1.61 (s, CH_3), 3.51, 3.61 (2q, J=7.2 Hz, CH_2 acetal), 4.12-4.65 (m, CH_2 ester, oxetane). - ir ($CDCl_3$): 1745 cm^{-1} (C=O). - ^{13}C-nmr ($CDCl_3$, 75 MHz): 13.07, 13.6, 13.8 (3 CH_3, OEt), 56.9, 57.2, 59.7 (3 CH_2-O), 74.8 (CH_2-O, oxetane), 91.9 (-C(quat)-O), 100.4 (O-C(quat)-O), 169.6 (CO_2). - ms: 202 (0.3, $M^{+\cdot}$-30), 161 (8.5), 128 (6), 116 (25), 100 (11.5), 89 (42.5), 87 (17), 72 (9.2), 70 (11.4), 61 (28.8), 60 (27.3), 45 (18.8), 43 (100), 42 (8.4).

PRODUCTS OF 7 AND 15. - Flash chromatography: AcOEt/C_6H_{12} 10:90.

(i) **Ethyl 7-endo-methyl-3,3-diiso-propyl-2,4,6,trioxabicyclo[3.2.0]hept-7-exo-yl-carboxylate** 27 - Yield 80%. Colourless oil, Rf 0.45. - ^{1} H-nmr (CCl_4, 90 MHz): 0.78, 0.87, 1.07 ,1.17 (4 d, J=7 Hz, -CH_3 iPr), 1.30 (t, J=7.5 Hz, CH_3 ester), 1.40 (s, H_3C-C(7)), 1.83-2.57 (m, CH-iPr), 4.17 (q, J=7.5 Hz, CH_2 ester) 4.77 (d, J=2.7 Hz, -H-C(1)-), 5.90 (d, J=2.7 Hz, -H-C(5)). - ir (CCl_4): 1735 (C=O), 1380 cm^{-1}d (iPr). - ^{13}C-nmr (C_6D_6, 20 MHz): 14.1 (CH_3 ester), 16.8 (H_3C-C(7)), 17.6, 17.9 18.26, 18.34 (CH_3, iPr), 34.4, 36.0 (2-CH-, iPr), 61.1 (CH_2 ester), 81.5 (-C(7)-O), 83.6 (-C(1)-), 102.5 (-H-C(5)-O), 124.1 (O-C(3)-O), 172 (CO_2). - ms: 273 (0.17, $M^{+\cdot}$+1), 246 (12.4), 245 (100), 171 (9.4), 131 (7.4) 115 (23.1), 111 (17.6), 97 (10.3), 73 (17.4), 71 (75.2), 69 (12.1), 43 (57.5), 41 (10.7). - $C_{14}H_{24}O_5$ (272.3) calcd C 61.74, H 8.88; found: C 61.48, H 9.06.

(ii) **Ethyl 7-exo-methyl-3,3-diisopropyl-2,4,6-trioxabicyclo[3.2.0]hept-7-endo-yl-carboxylate** 28. - Yield 20%. Colourless oil, Rf=0.35. - ^{1}H-nmr (CCl_4, 90 MHz): 0.80, 0.87, 0.97, 1.05 (4d, J=7 Hz, CH_3, iPr), 1.30 (t, J=7.5 Hz, CH_3 ester), 1.53 (s, H_3C-C(7)), 1.87-2.50 (m, CH-iPr),4.13 (q, 7.5 Hz, CH_2 ester), 4.77 (d, J=2.7 Hz, O-C(1)H-O), 5.87 (d, J=2.7 Hz, -C(5)H). - ^{13}C-nmr(C_6D_6, 20 MHz): 14.1 (CH_3 ester), 17.4, 17.7, 17.9 (4 CH_3, iPr), 23.1 ($H_3\underline{C}$-C(7)-), 33.9 35.5 (2CH-iPr), 60.3 (-CH_2-ester), 80.9 (O-C(7)-), 85.5 (O-C(1)H-), 100.5 (O-C(5)H-O), 124.3 (O-C(3)-O), 169.3 (CO_2). - ms: 245 (2, $M^{+\cdot}$-28), 199 (36), 111 (11), 71 (55), 69 (15), 55 (7), 44 (7), 43 (100), 41 (26).

PRODUCTS OF 14 AND 2 IN CH_3CN. - HPLC: AcOEt/C_6H_{12} 20:80.

(i) **Diethyl 2-ethyloxycarbonyl-2-hydroxysuccinate** 16. - Yield 53%. Colourless oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz): 1.20, 1.27 (2t, J=7.2 Hz, CH_3 ester); 3.10 (s, CH_2); 4.10 (q, J=7.2 Hz, CH_2 ester), 4.23 (q, J=7.2 Hz, CH_2 ester). - ^{13}C-nmr ($CDCl_3$, 20 MHz): 12.83 (CH_3 ester), 12.98 (CH_3 ester), 39.0 (CH_2); 59.9, 61.6 (2 CH_2 ester); 75.8 (-C(2)-O), 168.3 (CO_2). - ms: 263 (0.5, $M^{+\cdot}$), 217 (11), 190 (14), 189 (65), 144 (31), 143 (52), 116 (35), 115 (100), 88 (26), 43 (62). - ir ($CDCl_3$): 3500 (OH), 1740 cm^{-1} (C=O).

(ii) **Diethyl 4-ethoxy-2-ethyloxycarbonylmuconate** 17. - Yield 10%. Colourless oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz): 1.13-1.50 (m, CH_3 ester, ether) 3.87 (q, J=7.2 Hz, CH_2 ether); 4.03-4.47 (m, CH_2 ester), 5.27 (s, H-C(5)), 8.40 (s, H-C(3)-). - ms: 314 (15.4, $M^{+\cdot}$), 269 (28), 190 (12), 189 (59), 144 (28.5), 143 (48), 116 (36), 115 (100), 88 (27), 87 (20.5), 43 (48.5). - ir ($CDCl_3$): 3100, 1645, 1595 (=CH conj.), 1740 cm^{-1}(C=O).

(iii) **Ethyl 2-ethyloxycarbonyl-4-triethoxycrotonate** 18. Yield 6%. Colourless oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz): 1.20, 1.30, 1.33 (3 t, J=7.2 Hz, CH_3 ester, ether), 3.53 (q, J=7.2 Hz, CH_2 ether), 4.23, 4.27 (2q, J=7.2 Hz, CH_2 ester), 6.60 (s, -CH=C). - ^{13}C-nmr ($CDCl_3$,20 MHz): 14.0 (CH_3 ester), 14.9 (CH_3 ether), 58.1 (CH_2 ether), 61.1, 61.9 (2CH_2 ester); 111.5 (-C- quat.), 132.6 (-C=), 139.4 (-CH=), 163.2 (CO_2), 165.20 (CO_2). - ir ($CDCl_3$): 1760 (C=O), 1660 cm^{-1} (CH=C).

(iv) **Diethyl 2-ethyloxycarbonylfumarate** 19. - Yield 25%. Colourless oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz): 1.07-1.47 (m, CH_3 ester), 4.21, 4.23, 4.27 (3q, J=7.1 Hz, CH_2 ester), 6.83 (s, =CH-). - ms: 244 (0.1, $M^{+\cdot}$); 199 (32), 171 (90.5), 154 (27.5), 143 (100), 126 (31.2), 125 (41.9), 53 (21.8). - ir (neat): 3040, 1650 (-CH=), 1740 cm^{-1}(C=O).

PRODUCTS OF 14 AND 2 IN BENZENE. - HPLC: AcOEt/C_6H_{12} 20:80.

(i) Succinic acid derivative 16. - Yield 42%.

(ii) Diethyl 2,2-Diethyoxy-4,4-oxet-4,4-diyl-dicarboxylate 25. - Yield (58%). Colourless oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz) 1.12, 1.23 (2t, J=7.3 Hz, CH_3 ester/ether); 2.80 (s,CH_2); 3.52 (q, J=7.3 Hz, -CH_2-O-ether); 4.13 (q, J=7.3 Hz, ester). - ir ($CDCl_3$): 1740 cm^{-1} (C=O). - ms: 291 (17, $M^{+\cdot}$+1); 273 (12), 245 (6), 218 (12.6), 217 (100), 203 (14.4), 199 (19), 189 (17.9), 171 (24.1), 154 (8.1), 143 (64), 127 (16.9), 125 (11.4), 115 (40.2), 99 (11.7), 87 (11.2), 43 (18.8).

PRODUCT OF 15 AND 26. - HPLC: AcOEt/C_6H_{12} 10:90.

Diethyl 2,2-dimethyoxy-3,3-dimethyl-oxet-4,4-diyl-dicarboxylate 20. Colourless oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz)· 1.27 (s, CH_3), 1.30 (t, J=7.5 Hz, CH_3 ester), 3.33 (s, -O-CH_3), 4.23 (q, J=7.5 Hz, CH_2 ester). - ir (neat): 2870, 2860 (-O-CH_3), 1750 cm^{-1} (C=O). - ^{13}C-nmr ($CDCl_3$, 20 MHz): 14.2 (CH_3 ester), 20.0 (CH_3), 50.1 (O-CH_3), 54.3 (-C(3)-), 61.8 (CH_2, ester), 83.0 (-C(4)-O), 136.4 (O-C(2)-O), 166.6 (CO_2).

Acid hydrolysis of 20. - Ethyl 2-Ethyloxycarbonyl-2-hydroxy-3-methyl-3-methyloxycarbonyl-butyrate 22:

The cation exchange resins Lewatit SC 104 was added to a solution of 20 in methanol/water (1:1) and stirred for 3h (25°C).After filtration and evaporation the product was pure and satisfactory microanalytical data were obtained. Colourless oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz): 1.33 (s, CH_3), 1.47 (t, J=7 Hz, CH_3 ester), 3.70 (s, O-CH_3), 4.30 (q, J=7 Hz, CH_2 ester). - ir (neat): 3490 (OH), 1740 cm^{-1} (C=O). - $C_{12}H_{20}O_4$ (276.29): calcd C 52.17 H 7.30; found C 51 87 H 7.12.

PRODUCT OF 14 AND 15. - Flash chromatography: AcOEt/C_6H_{12} 25:75. Diethyl 3,3-diisopropyl-2,4,6-trioxabicyclo[3.2.0]hept-7,7-diyl-dicarboxylate 21. Yellowish oil. - ^{1}H-nmr ($CDCl_3$, 90 MHz): 0.80 0.87, 1.00, 1.07 (4d, J=7 Hz, CH_3iPr); 1.31(t, J=7.3 Hz, CH_3 ester), 1.98-2.51(m, CH iPr), 4.29 (q, J=7.3 Hz, CH_2 ester), 5.26 (d, J=3 Hz H-C(1)-), 6.12 (d, J=3 Hz, H-C(5)-). - ^{13}C-nmr ($CDCl_3$, 20 MHz): 13.9, 14.1 (2 CH_3 ester), 17.4, 17.6 (2 CH_3 iPr), 17.8 (2 CH_3 iPr), 34.0, 35.5 (2CH- iPr), 61.8, 62.7 (2CH_2 ester, 82.1 (-C(7)-O), 83.5 (HC(1)-O), 102.8 (O-H-C(5)-O); 125.7 (O-C(3)-O), 165.0, 167.5 (2 CO_2). - ir ($CDCl_3$): 1735 (C=O), 1380 cm^{-1} d (iPr). - ms: 330 (0.07 $M^{+\cdot}$); 288 (10.2), 287 (70.7), 257 (12.3), 187 (7.5), 159 (10.7), 143 (16.8), 113 (36.6), 97 (23.3), 71 (81.4), 55 (16.1), 43 (100), 41 (12 1).

PRODUCTS OF 14 AND CYCLOPENTENE -. HPLC: AcOEt/ C_6H_{12} 15:85.

(i) Diethyl 6-oxabicyclo[3.2.0]-7,7-diyl-dicarboxylate 23. - Yield 37%. Colourless oil . - ^{1}H-nmr (CCl_4, 90 MHz): 1.25 (t, J=7.5 Hz, CH_3 ester), 1.35-2.10 (m, CH_2 cyclopentane), 3.35-3.60 (m, H-C(3)-), 4.18 (q, J=7.5 Hz, CH_2 ester), 5.03-5.17 (m, H-C(7)-O). - ir (CCl_4): 1740 cm^{-1} (C=O). - ^{13}C-nmr (CCl_4, C_6D_6): 13.9, 14.1 (2 CH_3 ester), 24.2, 27.4, 33.7 (3 CH_2), 44.5 (H-C(3)), 60.4, 61.2 (2 CH_2 ester), 84.6 (H-C(7)-O), 166.5, 168.0 (2 CO_2). - ms: 242 (4.1, $M^{+\cdot}$), 176 (5.2), 170 (14), 169 (32.5), 152 (10.7), 151 (100), 141 (8.9), 123 (40.2), 105 (12.2), 96 (9.9), 95 (41.9), 67 (30), 41 (7.1).

(ii) Diethyl 2-cyclopenten-3'yl-2-hydroxymalonate 24. - Yield 54%. Colourless oil. - ^{1}H-nmr (CCl_4, 90 MHz): 1.3 (t, J=7.5 Hz, CH_3 ester), 1.6-2.5 (m, CH_2 *cyclopentene*), 3.4-3.6 (m, H-C(1')-), 3.51 (s, OH), 4.23 (q, J=7.5 Hz, O-CH_2 ester), 5.46, 5.79 (2 d/q, J=5.4/1.8 Hz, H-C(2',3')). - ir (CCl_4): 3500 (OH), 3030 (C=C), 1740 cm^{-1} (C=O). - ^{13}C-nmr (CCl_4/C_6D_6): 14.0 (CH_3 ester), 24.2, 32.3 (2 CH_2), 50.5 (H-C(1')), 61.5 (CH_2-O ester), 80.3 (-C-OH), 129.1, 133.7 (2 CH=), 169.74 (CO_2).

PRODUCT OF TRIMETHYLPYRUVIC ACID ETHYLESTER 29 and 15. - HPLC: AcOEt/C_6H_{12} 10:90.

7-t-Butyl-7-ethyloxycarbonyl-3,3-diisopropyl-2,4,6-trioxabicylo[3.2.0]heptane 30. - Yield 65%. Colourless oil. - ^{1}H-nmr ($CDCl_3$, 300 MHz): 0.81, 0.93, 1.11, (3d, J=7 Hz, CH_3 iPr), 1.11 (s, 3 CH_3 tBu), 1.15 (d, J=7 Hz, CH_3 iPr), 1.35 (t, J=7 Hz, CH_3 ester), 2.05, 2.50 (2 sept., J=7 Hz, CH- iPr), 4.28 (q, J=7 Hz, CH_2-O, ester), 4.99 (d, J=2.5 Hz, -C(1)H-O), 5.82 (d, J=2.5 Hz, -C(5)H-O). - ^{13}C-nmr ($CDCl_3$, 75 MHz): 14.3 (CH_3, ester), 18.2, 18.7, 18.8, 18.9 (4 CH_3, iPr), 26.6 (3 CH_3, tBu), 34.0 (-CH- iPr), 35.4 (-C(quat), tBu), 37.6 (-CH- iPr), 61.3 (O-CH_2- ester), 86.9 (-C(1)H-O), 87.5 (C(7)-O), 101.1 (C-C(5)H-O), 125.0 (O-C(3)-O), 172.6 (CO_2). - ir ($CDCl_3$): 1720 (C=O), 1375 cm^{-1} d (iPr). - ms: 314 (0.12, $M^{+\cdot}$), 271 (12), 156 (9), 127 (12), 114 (7), 113 (100), 97 (13), 85 (23), 71 (70), 57 (49), 55 (17), 43 (70), 41 (23). - $C_{17}H_{30}O_5$ (314.4) calcd C 64.94, H 9.62; found C 64.85, H 9.79.

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