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PHOTOCHEMICAL FORMATION OF CHRYSANTHEMIC ACID AND CYCLOPROPYLACRYLIC ACID DERIVATIVES

A CASE OF MULTIPLICITY-DEPENDENT REGIOSPECIFICITY IN THE DI-π-METHANE REARRANGEMENT†

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Abstract—Photochemical transformations of methyl E- and Z - 4,4,6 - trimethyl - 2,5 - dienoate (**5a**) and of the corresponding acids (**5b**) have been investigated. In contrast to similar pure hydrocarbon di-π-methanes, these aliphatic α,β-unsaturated carboxylic acid derivatives react from both the singlet and the triplet excited states and form different types of vinylcyclopropanes depending on multiplicity. When irradiated in acetone, both **5aE** and **5aZ** give methyl E - 3(2,2,3,3 - tetramethylcyclopropyl)prop - 2 - enoate (**8aE**). The same is observed for the corresponding acids. Direct irradiation of **5aE**, but not of **5aZ**, readily gives methyl E-chrysanthemate (**4aE**). Only singlet excited **5Z** reacts by internal hydrogen abstraction to cyclopropylacetic acid derivatives (**7**). Procedures for independent synthesis of **7** and **8** are described.

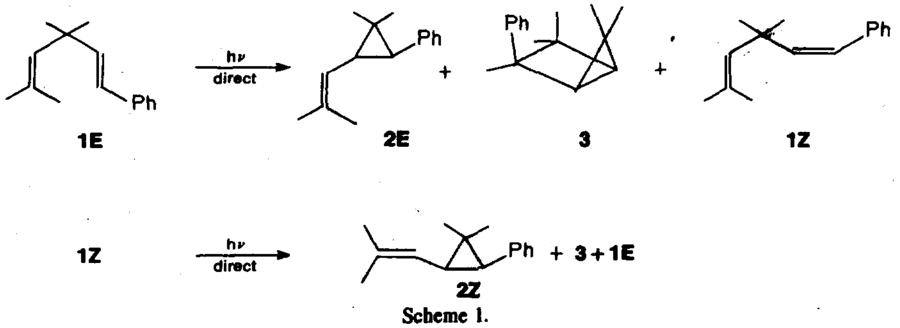
The generality of the di-π-methane rearrangement was first recognized by Zimmerman.[2] In his laboratories many examples of this reaction have been studied in great detail, among which are those[3] presented in Scheme 1. It was found that direct irradiation of compound **1E** leads to **2E** as the major product together with **3** and **1Z** while **1Z** under the same conditions leads to **2Z**, **3** and **1E**. Thus reactions (1) and (2) were found to be both regiospecific and stereospecific with regard to vinylcyclopropane formation. Triplet sensitized excitation in this case leads only to isomerization between **1E** and **1Z**, a common but not exclusive behaviour of acyclic di-π-methanes, explained by the free rotor effect.[2,4]

The similarity between **2** and 3,3 - dimethyl - 2 - (2 - methylpropenyl)cyclopropanecarboxylic acid (chrysanthemic acid) (**4b**) inspired the investigation of the photochemical behaviour of compounds **5E** and **5Z** reported in this paper.‡

The starting ester[5] **5aE** was made by condensation of methyl di - O - ethylphosphonoacetate[6] with 2,2,4 - trimethylpent-3-enal[5,7] obtained from commercially available 2,2,4,4-tetramethylcyclopropanediol. Acetone sensitized photoisomerization of **5aE** and chromatographic separation gave **5aZ**.

The results of the exploratory investigations are summarized in Scheme 2. Direct irradiation of **5aE** with 254 nm light in various solvents gave a mixture of isomeric products. However, the disappearance of large amounts of starting material could not be accounted for. The best results were obtained in non-polar solvents and preparative runs were made in hexane using a Vycor filtered 450 W Hanovia mercury lamp. Structural assignments were based on combined GC and MS, IR, UV and NMR spectra (Experimental). Using preparative GC with a Carbowax column the reaction mixture separated into four peaks, the first and the fourth of which contained E and Z starting material. The second peak consisted mainly of methyl E-chrysanthemate which was compared with an authentic sample. The third peak contained a mixture of at least two components, one of which was **7aE**, formed from **5aZ** by hydrogen abstraction and ring closure.[8]

The separate isomers of **7a** were independently prepared by addition of ethyl diazoacetate to diene **9** followed by Arndt Eistert homologization according to Scheme 3. When the Wolff rearrangement was attempted in methanol following standard procedures[9] the desired esters were obtained in very low yields. Considerable improvement was achieved by the addition of a one molar equivalent of sodium methoxide prior to silver oxide. The isomers of **7a** could be separated by preparative GC after the final step. However, separation of the diazoketone isomers (**11**) with chromatography on



Scheme 1.

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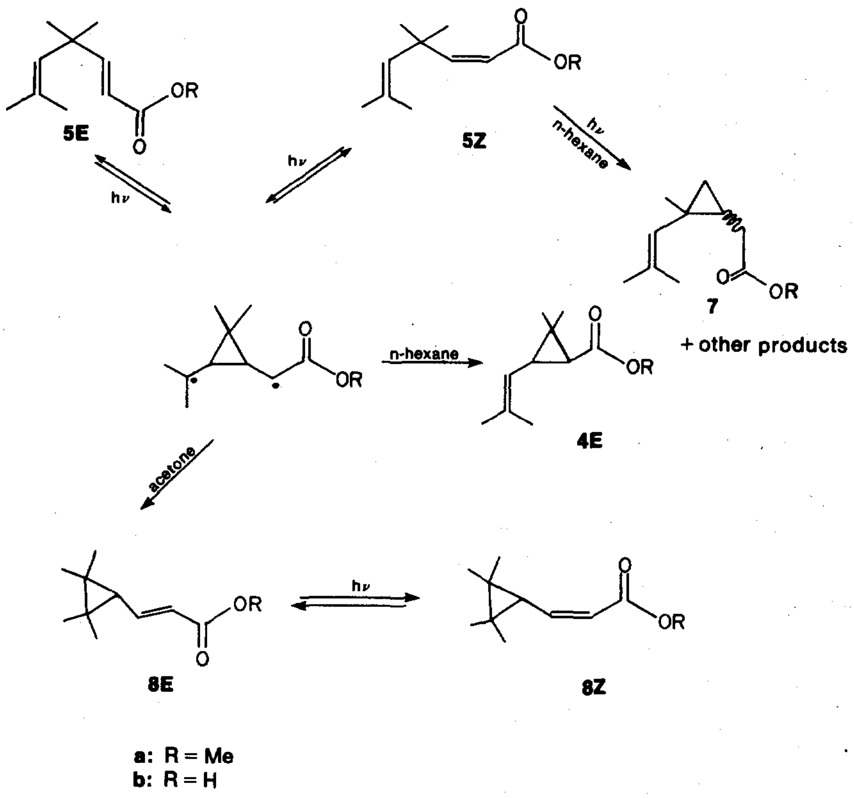
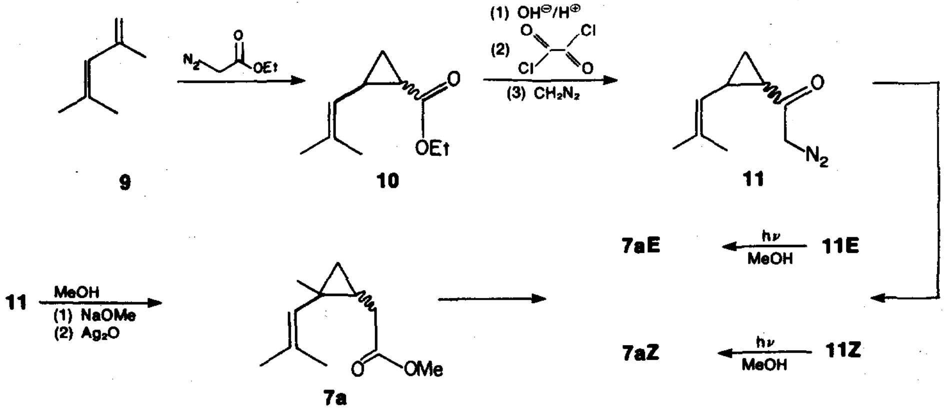
†A preliminary report of part of these studies has appeared.[1]

‡The photochemistry of **5a** has also been studied by Bullivant and Pattenden.[5]



Scheme 2.



Scheme 3.

silica gel, followed by photochemical Wolff rearrangement in methanol turned out to be the most convenient method of preparation.

The stereochemical assignments of **7aE** and **7aZ** were based on 200 MHz NMR data. Although the spectra were quite similar the non-equivalence of the side chain methylene protons adjacent to a chiral center were significantly different in the two isomers. The Z structure was assigned to the compound with the larger anisotropy effect caused by additional interaction with the 2-methylpropenyl group. With both isomers at hand it became apparent that **7aZ** had the same retention time as methyl E-chrysanthemate on all the tested GC columns. Material collected from peak two of the preparative GC showed a minor spot on TLC with the same R_f value as **7a** (*vide infra*).

A brief investigation of acid **5bE** was also made by direct irradiation in hexane with 254 nm light. The product mixtures were analysed by GC after esterification under mild conditions. The behaviour of the acid was essentially the same as that of the ester but erratic results were obtained with the appearance of varying amounts of additional unidentified products.

In contrast to the complex mixtures obtained by direct irradiation of **5a** and **5b**, irradiation of these compounds in acetone at 300 nm caused the clean formation of two products, except for Z isomerized starting material, when carried to moderate conversions. The irradiated acids were analysed and separated as esters. The four components could easily be separated by preparative GLC. Spectra of the compounds collected from peak two, which gave needle-formed crystals in the trap, and from peak four indicated that these were tetramethylvinylcyclopropanes **8aZ** and **8aE**, respectively. This was verified by independent synthesis of **8E** and photochemical interconversion starting with either **8aE** or **8aZ**. As can be seen from Table 1, yields slightly over 40% could be achieved both in the ester and in the acid cases. The appearance of secondary products makes separation more difficult at high conversions, however.

The independent synthesis of **8E** is outlined in Scheme 4. The acid **12** was prepared according to described procedures.[10] Reduction with LAH in THF using the convenient work-up method of adding an excess of a 1:1 mixture (by volume) of sodium sulfate decahydrate and Celite gave the known alcohol[11] **13** in 93% yield. A one molar solution of the chromium trioxide-dipyridine complex dissolved in acetic acid, easily prepared according to Stensiö and Wachtmeister,[12] was used in the oxidation step. The aldehyde, which proved to be remarkably unstable towards air oxidation, was obtained in 83% yield and was used immediately in the following condensation step or was stored under nitrogen. Condensation of **14** with an excess of methyl di - O - ethylphosphonoacetate gave **8a** in 90% yield with an E:Z ratio of 19:1. Pure **8bE** was prepared by hydrolysis and recrystallization.

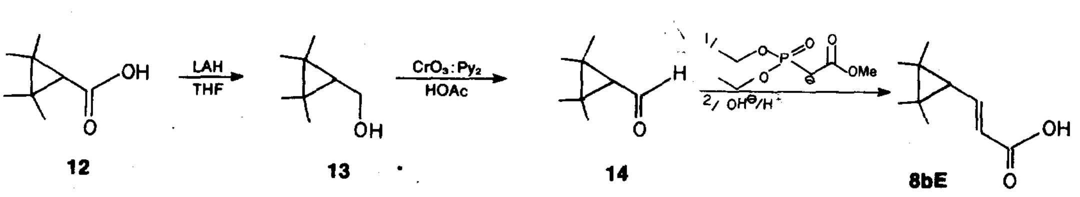
The change of the styryl moiety of compounds **1** to α,β-unsaturated carboxylic acids and esters of compounds **5** did lead to the expected chrysanthemic acid derivatives as a result of direct irradiation, albeit in low chemical yeilds. The most interesting result of the exploratory investigation with regard to the di-π-methane rearrangement was, however, the unexpected change of regiospecificity with multiplicity[13] which encouraged more detailed investigations.

Low conversion runs starting with either **5aE** or **5aZ** in acetone revealed that **8aE** was the predominant primary product in both cases. At 4.5% conversion of **5aZ** the **8aE**:**8aZ** ratio was 20:1. Continued irradiation lowered the ratio to the photostationary state of 2:1.

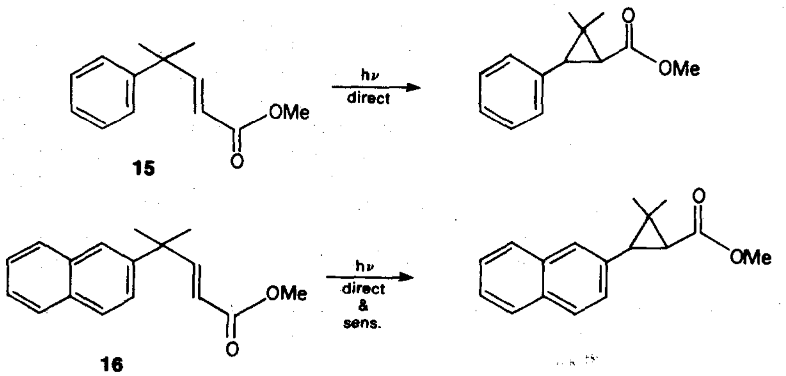
Efforts were also made to determine the stereochemistry of the singlet rearrangement of **5a** to **4a**. Regardless of starting material, only the E isomer of **4a** was detected in the reaction mixtures, which reduced the problem to specify if **5aZ** was contributing to the formation of **4aE**, thus contrasting to the behaviour of **1Z**. An irradiated sample of **5aZ** in which 7% had been converted to **5aE**, 0.6% to **7aE** and $\simeq 0.5\%$ to **7aZ**, was analysed by GC–MS. In this sample the presence of **4aE** but not **4aZ** could be established (Experimental). Due to unsatisfactory separation of **4aE** and **7aZ**, the amount of **4aE** could not be determined and could possibly be small enough to originate from **5aE**. For this reason no definite conclusions could be drawn except that **5aZ** reacts very inefficiently *via* the di-π-methane route.

During these investigations it was noted that direct irradiation of **5aE** gave rise to a minor component with the same GC retention time as **8aE**, which earlier was considered only to appear in the triplet reactions.[1] Combined GC and MS verified that **8aE** in fact is formed even as a result of direct irradiation of air saturated solutions of **5aE**. This suggests that **8aE** can be formed also via the singlet excited state.† The alternative explanation involves partial intersystem crossing followed by a triplet reaction too rapid to be quenched.

Two other di-π-methane rearrangements involving acyclic α,β-unsaturated esters have been described in the literature. The reactions are shown in Scheme 5. When the other moiety is phenyl,[8b] the reaction takes place via the singlet state only. With a naphthyl moiety,[15] both direct and sensitized excitation causes rearrangement. The different behaviour between **15** and **16** has been explained in terms of excitation energy being localized to the chromophore with the lower triplet energy. Consequently rotational deactivation would be prevented in **16** but not in **15**. The situation in **15** resembles that of the isomers of **5**, from which vinylcyclopropane formation, however, does take place from the triplet state. The reason for this remains unclear.



Scheme 4.



Scheme 5.

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†A bidirectional di-π-methane rearrangement from the triplet state of an α,β-unsaturated ester as part of a substituted norbornadiene system, has been reported.[14]

Table 1. Distribution of compounds after irradiation in acetone expressed as per cent of starting amount of **5E**

Starting material	5 converted (100-Σ5)	5E	5Z	8E	8Z	Σ8
5aE	36.6	37.3	26.1	18.7	10.1	28.8
"	51.6	27.9	20.5	25.0	12.9	37.9
"	70.2	17.4	12.4	26.7	14.0	40.7
5bE	58.2	26.5	15.3	24.3	12.2	36.5
"	71.9	17.6	10.5	27.4	13.9	41.3
"	79.1	12.8	8.1	24.2	12.2	36.4

EXPERIMENTAL

UV measurements were obtained using a Beckman DK-2 instrument and a Beckman DU connected to Optilab Multiblank 171 and Optilab Multilog 802 units. IR spectra were recorded on Perkin-Elmer model 257 and model 421 instruments. Varian model A-60A or model EM 360 instruments were used for 60 MHz and a Brucker WP 200 for 200 MHz NMR spectra, recorded with TMS as internal standard. Analytical GC was performed on a PYE GCV instrument connected to a Spectra Physics Minigrator integrator. For preparative GC a PYE 104 instrument was used. A split with a 100–1 ratio was used and fractions were collected manually. Both GC instruments were equipped with flame ionization detectors. A Hewlett-Packard model 5750 oven unit connected to an LKB model 9000 instrument was used to record GC–MS spectra unless otherwise stated. A Büchi kugelrohr apparatus was used for bulb-to-bulb distillations. M.Ps and b.ps are uncorrected. Petroleum of b.p. 68° and Merck 60 silica gel were used for column chromatography. Micro analyses were performed by Centrala Analys-laboratoriet, Uppsala.

Photochemical and analytical procedures. Small scale investigations were made in 0.7 × 15 cm quartz tubes placed in a merry-go-round inside a Rayonet reactor fitted with 16 RPR 254 or 300 nm lamps. Samples dissolved in n-hexane or acetone (typical 0.01 M) with tetradecane added as internal standard, were purged with nitrogen and were sealed with rubber septa prior to irradiation. The nitrogen was passed through a train of two washbottles of V^{2+} to remove oxygen,[16] a cold-trap for drying, and a washbottle with solvent to counteract evaporation during de-aeration. Irradiation times were varied from 0.5 to 240 min. The irradiated acids were esterified with anh. K_2CO_3 and excess MeI in acetone with stirring >5 hr at room temp. Analyses were made by GC and electronic integration. A glass column was used for quantitative work (4 mm id × 2 m, 10% PEG 20 M, Chrom. W 80–100, 120°, 30 ml/min) and a stainless steel column (1/8 inch × 2 m) of the same kind was used for GC–MS. Separate tests showed that neither this column nor any of the numerous tested packed columns separated compounds **4aE**, **4aZ** and **7aZ**. A 25 m SP 1000 capillary column did give a baseline separation of **4aE** and **4aZ** but **4aE** and **7aZ** still eluted together in a somewhat broadened peak. The irradiated sample of **5aZ** discussed in the preceding text, was analysed on this column when fitted to a Finnigan 4000 GC–MS instrument. MS spectra were recorded during the upward and the downward slope of the peak with the retention time of **4aE** and **7aZ**. The former spectrum matched a spectrum of pure **7aZ**. The latter spectrum was consistent with a 3 : 1 mixture of **4aE** and **7aZ**.

Preparative runs were made with 1 g of **5aE** and **5bE** dissolved in 350 ml n-hexane or acetone and irradiated with a Hanovia 450 W mercury arc placed in a water-cooled quartz immersion well. A Vycor filter was used for hexane and Pyrex for acetone runs. The acids were esterified by the method mentioned above. The esters were distilled bulb-to-bulb before using prep. GC (9 mm o.d. × 2 m, 20% Carbowax 4000, Chrom. W 60–80. 140°, 180 ml/min). The contents of the different peaks are described in the previous text. When product mixtures obtained from acetone runs were subjected to chromatography on silica gel with 5% ether in petroleum as eluent, **5aZ** and **8aZ** eluted together followed by separated **5aE** and **8aE**.

Methyl E - 4,4,6 - trimethyl - 2,5 - heptadien - 1 - oate (**5aE**) *and E - 4,4,6 - trimethyl - 2,5 - heptadiene - 1 - carboxylic acid* (**5bE**). A soln of 18.018 g (0.0858 mol) methyl di - O - ethylphosphonoacetate[6] in 100 ml DMF added to dry NaOMe (from 1.973 g Na) was stirred for 15 min. After addition of 9.009 g (0.0715 mol) 2,2,4 - trimethylpent - 3 - enal[7b] in 10 ml DMF the mixture was left at room temp for 15 hr, poured into 100 ml water and extracted with light petroleum. Drying ($MgSO_4$) and solvent removal gave 11.71 g (90%) colorless oil. Chromatography on 300 g silica gel, eluting with 5% ether in petroleum and distillation, b.p.$_{10}$ 92–93°, gave 9.760 g (75%) pure E isomer. Hydrolysis and recrystallization from water, MeOH, 1:1, and drying over P_2O_5 gave **5bE**, m.p. 79–80°. Spectral data **5aE**: UV: λ_{max}^{EtOH} 213 nm (ϵ 11,200), lit.[5] λ_{max} 220 nm (ϵ 6300). For IR and NMR see Ref. 5: MS: *m/e* (rel. int.) 182 $M^{\cdot+}$ (5), 167 (17), 151 (10), 139 (16), 135 (7), 125 (52), 123 (68), 107 (100). Data **5bE**: (Found: C, 71.22; H, 9.48. Calc. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%). UV: λ_{max}^{EtOH} 213 nm (ϵ 10,200). NMR ($CDCl_3$): 12.24, variable (1H, s, OH), 7.25, 5.87 (2H, AB, J = 16 Hz, CH=CH), 5.22 (1H, m, =CH), 1.71 (3H, d, J = 1.5 Hz, =C–CH_3), 1.60 (3H, d, J = 1.5 Hz, =C–CH_3), 1.22 (6H, s, gem. CH_3). IR (KBr): 1720 cm^{-1}.

Methyl Z - 4,4,6 - trimethyl - 2,5 - heptadien - 1 - oate (**5aZ**). Solns of 1.0 g **5aE** in 100 ml acetone were purged with N_2 and irradiated with 300 nm lamps in a Rayonet reactor until GC monitoring showed an E:Z ratio of ≃2:1. The isomers were separated with prep GC. UV: λ_{max}^{EtOH} 211 nm (ϵ 6500). For IR and NMR see Ref. 5. MS: *m/e* (rel. int.) 182 $M^{\cdot+}$ (13), 167 (27), 151 (27), 139 (9), 125 (60), 123 (100), 107 (96).

Ethyl 2 - methyl - 2 - (2 - methylpropenyl)-cyclopropanecarboxylate (**10**). A stirred suspension of 1 g copper bronze and 5 g **9**[17] was heated to 90° and a soln of 12 g (0.105 mol) ethyl diazoacetate in 20 g diene (0.298 mol in all) was added during 3.5 hr. The excess diene was distilled off and the residue filtered. Distillation b.p.$_{15}$ 90–105° and redistillation b.p.$_{13}$ 89–91° gave 10.04 g (52%) of an ≃1 : 1 mixture of E:Z of **10**. NMR, mixture (CCl_4): δ 5.28 (1H, m, =CH), 5.12 (1H, m, =CH), 4.07 (2H, q, J = 7 Hz, $C\underline{H}_2CH_3$), 4.00 (2H, q, J = 7 Hz, $C\underline{H}_2CH_3$), 1.63 (12H, m, =C–CH_3), 1.30 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 1.20 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 1.53–0.80 (6H, m, cyclopr. H).

2 - Methyl - 2 - (2 - methylpropenyl)-cyclopropyl(diazomethyl)ketone (**11**). To a soln of 5.89 g (0.083 mol) of the acids corresponding to esters **10** in 25 ml benzene, 9.65 g (0.076 mol) oxalyl chloride and 2 drops DMF were added. The evolved gas caused foaming. The mixture was distilled after 3 hr at room temp. which gave 4.82 g (73%) acid chloride, b.p.$_{14}$ 78–80°. IR neat: 1795 cm^{-1}. The acid chloride was added to ≃0.080 mol diazomethane in ether. After 3 hr, the excess diazomethane was removed by a stream of N_2. Concentration *in vacuo* gave the crude **11** showing two well separated spots on TLC (eluent, 10% ether in petroleum). IR neat: 2100, 1630 cm^{-1}. The two isomers of **11** could be separated on silica gel with the same eluent as above. NMR: first eluted isomer ($CDCl_3$), δ 5.37 (1H, s, $C\underline{H}N_2$), 5.32 (1H, m, =CH), 1.70 (3H, d, J = 2 Hz, =C–CH_3), 1.63 (3H, d, J = 2 Hz, =C–CH_3), 1.23 (3H, s, cyclopr. CH_3), 1.50–0.90 (3H, m, cyclopr. H); second eluted isomer ($CDCl_3$), δ 5.30 (1H, s, $C\underline{H}N_2$), 5.13 (1H, m, =CH), 1.67 (6H, d, J = 2 Hz, =C–CH_3), 1.23 (3H, s, cyclopr. CH_3), 1.57–0.93 (3H, m, cyclopr. H).

Methyl 2 - methyl - 2 - (2 - methylpropenyl)-cyclopropaneacetate (**7a**). *Method A*. A soln of 1.00 g (0.060 mol) crude **11** and 0.301 g (0.060 mol) NaOMe in 20 ml dry MeOH was heated to 60° and 1.50 g (0.064 mol) Ag_2O was added in portions with stirring. After the last addition the mixture was kept at 60° for 30 min, filtered through Celite, concentrated and subjected to bulb-to-bulb distillation. The resulting products consisted of two major components which were separated with prep GC (Carbowax 4000, 140°). *Method B*. The separated diazoketones were irradiated in MeOH with 300 nm lamps in the Rayonet reactor until TLC monitoring no longer showed the presence of starting material. The diazoketone with the shorter retention time on the silica gel column gave rise to the ester with the longer retention time on GC, namely **7aE**. The yield of ester was 64% in both cases, as determined by GC. NMR, 200 Mc ($CDCl_3$): **7aE**, δ 5.31 (1H, m, =CH), 3.70 (3H, s, OMe), 2.44, 2.31 (2H, AB of ABX, J_{AB} = 16.11, J_{AX} = 6.79, J_{BX} = 7.37 Hz, $C\underline{H}_2CO$), 1.68 (3H, d, J = 0.99 Hz, =C–CH_3), 1.63 (3H, d, J = 0.93 Hz, =C–CH_3), 1.09 (3H, s, cyclopr. CH_3), ≃1.07 (1H, m, partially obscured, cyclopr. H), 0.71 (1H, dd, J = 4.40 and 8.80 Hz, cyclopr. CH_2), 0.21 (1H, dd, apparent triplet, J = 4.40 and ≃5, cyclopr. CH_2); **7aZ**, δ 5.20 (1H, m, =CH), 3.69 (3H, s, OCH_3), 2.38, 2.11 (2H, AB of ABX, J_{AB} = 16.11, J_{AX} = 6.48, J_{BX} = 7.69 Hz, CH_2CO), 1.70 (3H, d, J = 1.47, =C–CH_3), 1.67 (3H, d, J = 1.46 Hz, =C–CH_3), 1.11 (3H, s, cyclopr. CH_3), 0.96 (1H, m, cyclopr. H), 0.74 (1H, dd, J = 4.40 and 8.30, cyclopr. CH_2), 0.26 (1H, dd, apparent triplet, J = 4.40 and ≃4.4, cyclopr. CH_2).

2,2,3,3 - *Tetramethyl* - 1 - *hydroxymethylcyclopropane* (**13**).[11] A slurry of 2.050 (0.054 mol) LAH in 15 ml THF, distilled from potassium and benzophenone, was cooled in an ice-bath, and a soln of 6.00 g (0.042 mol) **12**, prepared according to Ref. 10*b*, in 15 ml THF was added during 1.5 hr with stirring. The mixture was then stirred at room temp. for 2 hr and heated to reflux for 1 hr. An excess of $Na_2SO_4 \cdot 10H_2O$ and celite (1 : 1 by volume) was added to the cooled mixture. After 3 hr stirring the solid was filtered with ease and washed with ether. The filtrate was washed once with 2 M NaOH and dried ($MgSO_4$). Solvent removal and bulb-to-bulb distillation gave 4.95 g (93%) of the alcohol. For NMR data see Ref. 11.

2,2,3,3 - *Tetramethylcyclopropanecarboxaldehyde* (**14**). Chromium trioide-dipyridine (0.300 mol) in 300 ml AcOH[12] was cooled to 5° and a soln of 4.490 g (0.350 mol) of **13** in 50 ml ether was added with stirring during 6 min. After 10 min additional stirring the mixture was poured into 750 ml ice-water and extracted with three portions of ether. The combined ether layers were washed with water three times, neutralized with solid K_2CO_3 and dried over $MgSO_4$. Solvent removal gave 3.647 g (83%) of the aldehyde which was used immediately in the following condensation step or was stored under N_2. Due to extreme sensitivity towards air oxidation a correct elemental analysis was not obtained. NMR (CCl_4), δ 9.51 (1H, d, J = 5.5 Hz, $C\underline{H}O$), 1.27 (1H, d, J = 5.5 Hz, cyclopr. H), 1.25 (6H, s, cyclopr. CH_3).

Methyl E - 3 - (2,2,3,3 - tetramethylcyclopropyl)prop - 2 - enoate (**8aE**) *and E-3-(2,2,3,3-tetramethylcyclopropyl)prop-2 - enecarboxylic acid* (**8bE**). Methyl di - O - ethylphosphonoacetate was made by the gradual heating of 6.73 g (0.044 mol) methyl bromoacetate and 7.47 g (0.045 mol) triethyl phosphite to 180° with simultaneous distillation of the formed EtBr. After cooling in an ice-bath, 40 ml DMF and 2.73 g (0.051 mol) NaOMe was added and the mixture was stirred for 15 min. After addition of 0.567 g (0.005 mol) aldehyde **14** the reaction mixture was left at room temp. for 12 hr, poured into 80 ml water and extracted with three portions of petroleum. Washing with water, drying ($MgSO_4$) and removal of the solvent gave 0.801 g (88%), which was a 19 : 1 mixture of the E and Z isomers of **8a**. Material made in this way was either chromatographed on silica gel using 5% ether in petroleum as the eluent or hydrolyzed and recrystallized from MeOH–water, 1 : 1, m.p. 130–131°. The over-all yield to the acid was 80%.

Spectral data, **8aE**: UV: λ_{max}^{EtOH} 245 nm (ϵ 14,500). IR ($CHCl_3$): 1700, 1630 cm^{-1}. NMR, 200 MHz ($CDCl_3$): 6.81, 5.89 (2H, AB of ABX, J_{AB} = 15.38, J_{AX} = 11.14, J_{BX} = 0 Hz, $C\underline{H}$=$C\underline{H}$–CH), 3.71 (3H, s, OCH_3), 1.16 (6H, s, cyclopr. CH_3), 1.13 (6H, s, cyclpr. CH_3), 1.13 (1H, X of ABX, partially obscurred d, J = 11.14 Hz, cyclopr. H). MS: *m/e*: (rel. int.) 182 $M^{\cdot +}$ (7), 167 (19), 151 (10), 139 (11), 135 (6), 125 (100), 123 (37), 107 (56). Data **8bE**: UV: λ_{max}^{EtOH} 245 nm (ϵ 16,000). IR (KBr): 1675, 1620 cm^{-1}. NMR ($CDCl_3$): 11.3 variable (1H, s, COOH), 6.93, 5.89 (2H, AB of ABX, J_{AB} = 15, J_{AX} = 11, J_{BX} = 0 Hz, $C\underline{H}$=$C\underline{H}$–CH), 1.17 (6H, s, cyclopr. CH_3), 1.12 (6H, s, cyclopr. CH_3), 1.13 (1H, X of ABX, d, J = 11 Hz, cyclopr. H). (Found: C, 71.50; H, 9.40. Calc. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%).

Methyl Z - 3 -(2,2,3,3 - tetramethylcyclopropyl)prop - 2 - enoate (**8aZ**). A soln of 0.5 g **8aE** in 90 ml acetone was purged with N_2 and irradiated in the Rayonet reactor until GC monitoring showed an E : Z ratio of ≃7 : 3. The isomers were separated by prep GC. Data: m.p. 56–57°. UV: λ_{max}^{EtOH} 253 nm (ϵ 11,300). IR ($CHCl_3$): 1710, 1620 cm^{-1}. NMR 200 MHz ($CDCl_3$): 6.03, 5.82 (2H, AB of ABX, J_{AB} = 11.5, J_{AX} = 10.9, J_{BX} = 0.5 Hz, $C\underline{H}$=$C\underline{H}$–CH), 3.71 (3H, s, OCH_3), 2.40 (1H, X of ABX apparent d, J = 10.99 Hz, CH=CH–$C\underline{H}$), 1.20 (6H, s, cyclopr. CH_3), 1.09 (6H, s, cyclopr. CH_3). MS: *m/e* (rel. int.), 182 $M^{\cdot +}$ (5), 167 (8), 151 (5), 139 (6), 135 (6), 125 (100), 123 (14), 107 (54), 98 (53).

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