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The Reaction between Dimethyl 2-Bromo-1-phenylpropylidenemalonate and Sodium Methoxide in Methanol; Formation of a Cyclopropene by an Addition—Elimination Reaction

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The reaction between dimethyl 2-bromo-1-phenylpropylidenemalonate and sodium methoxide in methanol has been investigated. If the reaction is run at room temperature for 25 h, dimethyl 2-methyl-3-phenyl-2-cyclopropene-1,1-dicarboxylate is formed in 19 % yield in addition to dimethyl 2,2-dimethoxy-1-methyl-2-phenylethylmalonate (<4 %), dimethyl 2-methoxy-1-phenylpropylidenemalonate (11 %), dimethyl (*E*)-2-bromo-1-phenyl-1-propenylmalonate (10 %), dimethyl (*Z*)-2-bromo-1-phenyl-1-propenylmalonate (13 %) and dimethyl 1,2-dimethoxy-1-phenylpropylmalonate (33 %). The reaction mechanism for the formation of the cyclopropene is discussed in some detail.

The reaction of dimethyl 2-bromo-2-methylpropylidenemalonate[1] and dimethyl (1-bromocyclohexyl)-methylidenemalonate[2] with sodium methoxide in methanol gave cyclopropane derivatives in high yields. In the course of an investigation intended to give a general view of the reaction between nucleophiles and allylic halides carrying electron-withdrawing substituents in the γ position, dimethyl 2-bromo-1-phenylpropylidenemalonate (*1*) was treated with an equivalent amount of sodium methoxide in methanol at room temperature. A mixture of compounds was formed (Scheme 1).

Identification of products. When the crude product from this reaction was dissolved in methanol or light petroleum, pure dimethyl 2-methyl-3-phenyl-2-cyclopropene-1,1-dicarboxylate (*2*) precipitated on cooling. The assignment of the structure of this product is based on the following data.

The ^{1}H NMR spectrum ($CDCl_3$) showed the presence of five aromatic protons, a six proton singlet (δ 3.70) expected for two identical methoxycarbonyl groups and a three proton singlet (δ 2.37) within the range of shifts found for a methyl group attached to the double bond of a cyclopropene ring.[3] The presence of only one type of methoxycarbonyl group was confirmed by ^{13}C NMR, showing only one line (δ 171.4) in the ester carbonyl region. Further, the peaks at δ 105.3 and δ 104.9 are reasonable shifts for the two double-bonded carbon atoms.

High resolution MS gave a peak at *m/e* 246 (M^+, 53) with the composition $C_{14}H_{14}O_4$. The base peak at *m/e* 187 ($C_{12}H_{11}O_2$) is easily explained by the loss of one methoxycarbonyl group from the molecular ion of the cyclopropene. Thus, a stable cyclopropenyl cation is formed.

The low-intensity band at 1900 cm^{-1} in the IR spectrum (KBr) may be due to the skeletal vibration of the cyclopropene ring.[4] In comparison, the corresponding band in cyclopropene *3* is recorded at 1890 cm^{-1}.[5] Strong absorptions at 1740 and 1710 cm^{-1} for the two identical methoxycarbonyl groups are not unreasonable since β-diesters such as diethyl malonate also show two carbonyl bands.[6]

All spectroscopic data agreed with the cyclopropene structure. However, the isolation of a cyclopropene under these conditions was somewhat unexpected and the compound was further investigated by X-ray crystallographic methods which confirmed the molecular structure.[7]

The dibromide *4* was obtained in 32 % yield by

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adding bromine in carbon tetrachloride to the cyclopropene in diffuse light. Only a single isomer was formed (^{1}H NMR). As bromination of methyl 2,3-diphenyl-2-cyclopropenecarboxylate in chloroform in the dark or in diffuse light gave exclusively the *trans* dibromide in 39 % yield,[8] *4* most probably also has the *trans* configuration.

Column chromatography of the residue left after filtration of *2* gave, mentioned in the order of elution from the column, a mixture of dimethyl (*E*)-2-bromo-1-phenyl-1-propenylmalonate (*5a*) and the *Z* isomer (*5b*), pure dimethyl 1-benzoylethylmalonate (*6*) and pure dimethyl 1,2-dimethoxy-1-phenylpropylmalonate (*7*). Compound *6* is not present in the reaction mixture as seen from the ^{1}H NMR spectrum and is most likely formed from dimethyl 2,2-dimethoxy-1-methyl-2-phenylethylmalonate (*8*) during chromatography on the silica gel column.

On treatment of *1* with a large excess of sodium methoxide at a high concentration (see experimental), the yield of *2* was strongly reduced due to a further reaction of *2* with sodium methoxide* while the yield of *8* was increased. Ketal *8* could now be crystallized by addition of light petroleum to the crude product. The presence of *8* in the equimolar reaction was shown by GLC. Ketal *8* was transformed into ketone *6* by addition of trifluoroacetic acid – water to a solution of *8* in carbon tetrachloride. The reactions that occurred when *1* and *2* were treated with an excess of sodium methoxide at a high concentration were not further investigated.

The ^{1}H NMR spectrum of the last fractions obtained by chromatography of the reaction mixture indicated that dimethyl 2-methoxy-1-phenylpropylidenemalonate (*9*) was present. This was confirmed by GLC on comparison with an authentic sample synthesized by treating *1* with a solution of silver perchlorate in methanol.

The reaction mixture obtained after treatment of *1* with one equivalent 0.43 M sodium methoxide in methanol (bromide concentration 0.3 M) for 25 h at room temperature was analyzed by GLC and contained: *1* and *8* (4 %), *2* (19 %), *5a* (10 %), *5b* (13 %), *7* (33 %) and *9* (11 %). In addition, GLC showed the presence of another compound in about 8 % yield which has not been identified.

* When *2* was treated with sodium methoxide under the same conditions that were used for *1*, a reaction occurred. However, *8* was not formed (^{1}H NMR).

When *1* was treated with sodium methoxide using a longer reaction time, 93 h in one experiment, ^{1}H NMR (CCl_4) of the crude product showed the presence of only one of the isomers *5a* and *5b*. This isomer gave a singlet at δ 2.20 for the methyl group at the carbon – carbon double bond compared to δ 2.43 for the other isomer. The chemical shift at δ 2.20 is assigned to the *E* isomer *5a* on the basis of the assignment of resonances made for the methyl groups in the ^{1}H NMR spectra of *cis*- and *trans*-β-methylstyrenes and β,β-dimethylstyrenes.[9]

Discussion of reaction pathways for the formation of compounds 7 and 8. The formation of *8* is best explained by a nucleophilic attack on carbon 2 in an initially formed cyclopropane *10* (Scheme 2). Reactions analogous to the conversion of *10* into *8* have been reported on cyclopropanes having strongly electron withdrawing geminal substituents.[10,11]

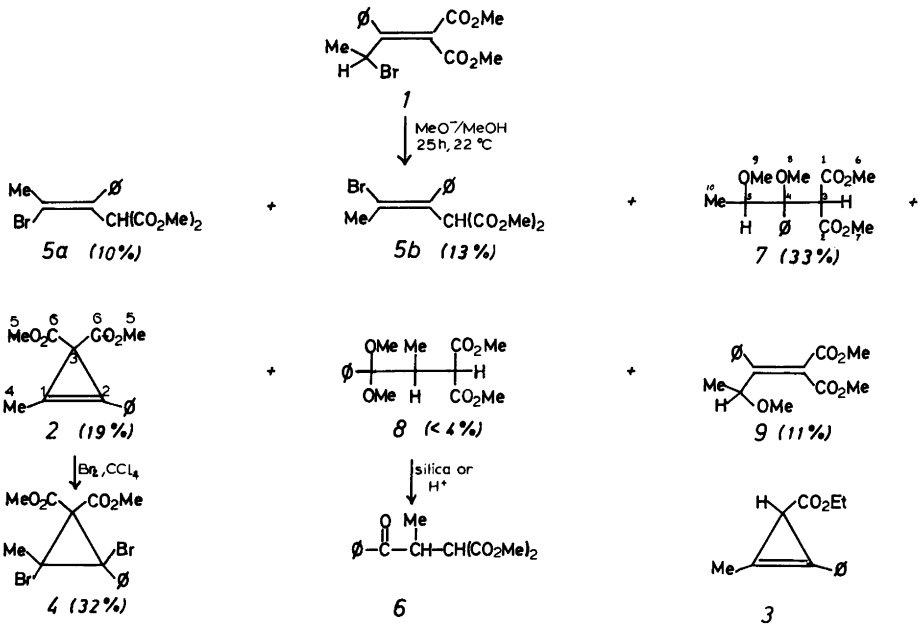
When *2* was treated with sodium methoxide under the same conditions as *1*, no reaction occurred. Thus, any *10* initially present is not formed by nucleophilic attack of methoxide on the carbon-carbon double bond in *2*, but by attack on the β-carbon of *1* followed by cyclization[1,2] (Scheme 2).

Two different reaction routes exist for the formation of *7*: attack of methoxide on carbon 3 in *10* or on the β-carbon in *9* (Scheme 2). When *9* was treated with two equivalents of sodium methoxide in methanol (0.43 M) for 45 h, no *7* was formed. Instead, migration of the carbon-carbon double bond had occurred, yielding enol ether *11* (10 %, ^{1}H NMR). One single isomer was formed, but configuration assignments have not been made. By using a large excess of sodium methoxide (12 equivalents) at a high concentration and a longer reaction time (93 h), *9* was completely transformed into *11* (only small quantities of other compounds were present). Treatment of *11* with trifluoroacetic acid – water gave ketone *12*.

The ability of allyl ethers to isomerize by treatment of bases into vinyl ethers, which are readily hydrolyzed to give aldehydes and ketones, is well known.[12]

However, *11* could not be detected in the ^{1}H NMR spectrum of the crude product from the *equimolar* reaction of *1* with sodium methoxide. Thus, if present at all, the yield of *11* should be increased at the expense of *9* by use of excess base and a long reaction time.

Furthermore, the stability of *11* during this

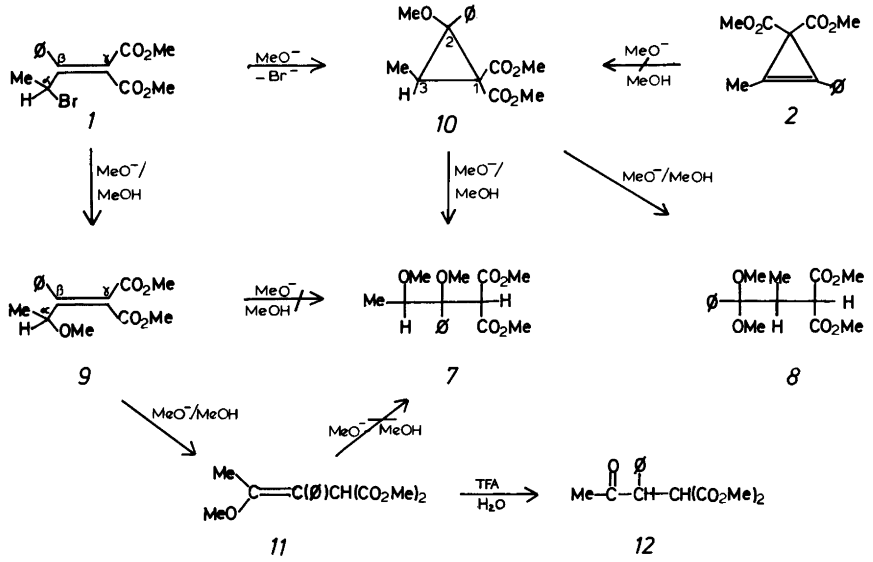


Scheme 1.

prolonged treatment with excess base, also precludes that *11* can be the precursor for *7*. Thus, the origin of *7* is best explained by a nucleophilic attack of methoxide on carbon 3 in cyclopropane *10*.

Both *7* and *8* turned out to be fairly stable in a sodium methoxide solution. One may therefore conclude that *7* and *8* are not precursors for any of the other compounds present in the reaction mixture.

A preferred attack of methoxide at the 3-position



Scheme 2. Reaction pathways for the formation of compounds *7* and *8*.

in *10* may explain the low yield of *8* (<4 %) compared to 7 (33 %).

Discussion of reaction pathways for the formation of cyclopropene 2. Cyclopropene derivatives have been made by addition of carbenes to alkynes, photolysis of 3H-pyrazoles, β-elimination on cyclopropanes and ring closure of alkenyl carbenes.[13]

The different reaction routes capable of describing the formation of *2* from *1* are given in Schemes 3 and 4.

Route 1. Elimination of methanol from cyclopropane intermediate 10. Using *methoxide* as a base, β-elimination of nitrous acid occurs in systems where the elimination is facilitated by *activation* provided by aromatic groups.[14] Dimethyl 2,3-diaryl-2-cyclopropene-1,1-dicarboxylate has been synthesized by this method.[15] In *non-acticated* systems like 1-*t*-butyl-2-chloro-3,3-dimethylcyclopropane[16] and a series of monobromocyclopropanes[17] a stronger base like *potassium* t-*butoxide* in dimethyl sulfoxide is used for elimination.

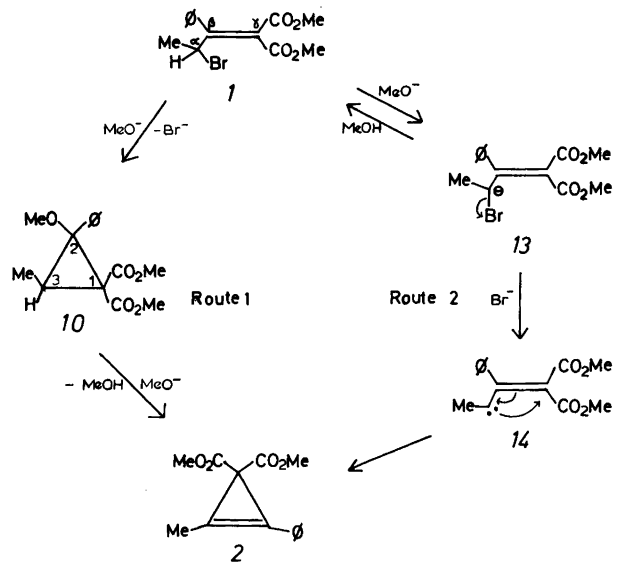
As shown, isolation of compounds 7 and *8* in the equimolar reaction indicates that *10* is initially present. However, methoxide being the base, the low acidity of the proton at carbon 3 in *10* and the necessity of expelling a methoxide ion on formation of *2*, makes *10* a less plausible precursor for a cyclopropene than the cyclopropanes mentioned above[15-17] (Scheme 3, Route 1).

One should, however, recall that the effect of the leaving group on elimination is hard to predict without knowing the mechanism by which elimination occurs.[18] The use of *strong bases* like alkylsodium or alkyllithium are reported to give β-elimination of alkoxide from *non-activated* ethers as in the case of 2-methoxyoctane.[19] This elimination is facilitated when the alkoxy group is situated in the β-position to an electron-withdrawing group (*E*1c*B*-mechanism).[20]

Route 2. Ring closure of an alkenyl carbene. Alkenyl carbenes or alkenyl carbene-like intermediates are known to yield cyclopropenes.[21] Several methods have been described to generate the hypothetical alkenyl carbenes, one of them being the α-elimination of hydrogen halide with strong bases from an allylic halide. Examples are the reaction of 1-chloro-2,3-dimethyl-2-butene with butyllithium which gave a low yield of 1,3,3-trimethylcyclopropene[22,23] and the treatment of α-methallyl chloride with sodium amide to give methylcyclopropene in approximately 50 % yield.[24]

The formation of *5a* and *5b* is easily explained by invoking abstraction of the α-hydrogen in *1* by methoxide followed by isomerization.* Formation

* In comparison, the formation of small amounts of dimethyl 2,4,6-octatrienedioate from methyl 4-bromo-2-butenoate with sodium methoxide in benzene is also explained by a mechanism involving abstraction of an α-hydrogen.[25]



Scheme 3. Reaction pathways for the formation of cyclopropene *2*. Route 1 and 2.

of alkenyl carbene *14* from anion *13* by loss of bromide ion followed by ring closure would explain the formation of *2* (Scheme 3, Route 2). However, alkenyl carbenes are usually generated in inert solvents with strong bases like butyllithium,[22,23] sodium amide[24] or potassium *t*-butoxide.[26] The formation of an alkenyl carbene in a protic solvent like methanol is less plausible. Most carbenes react readily with heteroatoms carrying lone pair electrons.[27] Formation of *9* is, however, easier explained by a straightforward substitution on *1* than by attack of methanol on *14*.

Attempts to increase the yield of *2* by adding solid sodium methoxide to a solution of *1* in nonprotic solvents like ether, 1,2-dimethoxyethane and benzene were unsuccessful. No cyclopropene was formed (^{1}H NMR). The major product in all reactions was vinyl bromide *5a*. Specifically, the reaction of *1* in boiling benzene gave pure *5* (^{1}H NMR). The isomer ratio *5a*/*5b* was 8.2 after 4.5 h reflux. These experiments indicate that *14* is no intermediate in the formation of *2*.

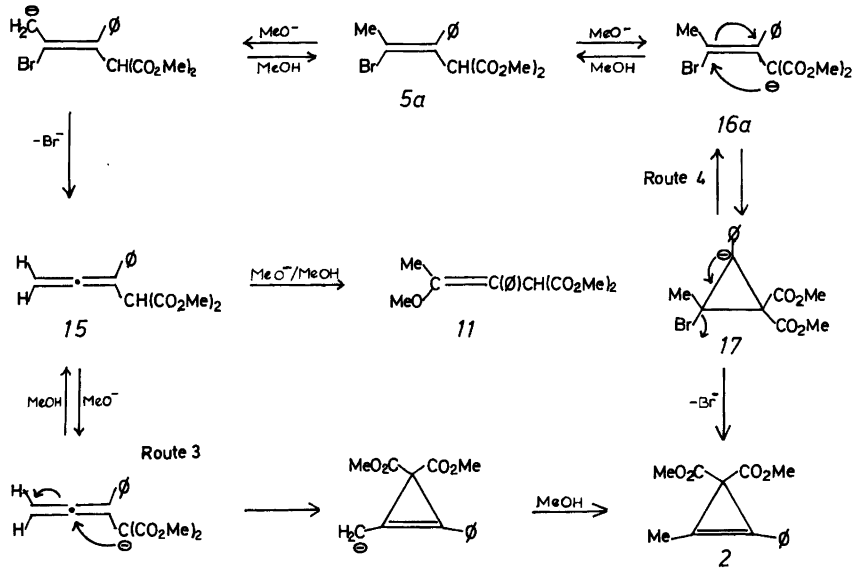
Route 3. Formation of 2 *via an allene intermediate.* Because of (i) the ability of vinylic halides to form allenes by base-promoted elimination of hydrogen halide[28,29] and (ii) the susceptibility of nucleophilic attack on the central carbon atom of suitably substituted allenes in either intermolecular[30] or intramolecular[31] reactions, route 3 is *a priori* a possible pathway to cyclopropene *2* (Scheme 4).

If *2* is formed *via* allene derivative *15*, one would expect *11* to be formed as a byproduct. However, *11* has not been detected in the reaction mixture.

In the last step of route 3, a proton is abstracted from the solvent. Thus, use of CH_3OD as the solvent should give a deuterated cyclopropene. Bromide *1* was treated with sodium methoxide in in CH_3OD under the same conditions as earlier. ^{1}H NMR and MS of the crystallized cyclopropene showed that no incorporation of deuterium had occurred. Accordingly, *2* is not formed by route 3.

Route 4. Formation from vinyl bromide 5. When *5a* was treated with a solution of sodium methoxide in methanol, *2* was formed (see Experimental). This may be explained by a reaction pathway involving abstraction of the acidic proton (α to the methoxycarbonyl groups) in *5a* by methoxide, formation of cyclopropane anion *17* by attack of the negative charge created on the carbon-carbon double bond in *16a*, followed by elimination of bromide ion (Scheme 4, Route 4). Route 4 is an addition-elimination reaction analogous to the substitution taking place on vinylic halides activated by electron-withdrawing substituents.[32] The last step in the sequence, elimination of a halide ion, is a well-known synthetic pathway to cyclopropenes.[13]

Conversion of a cyclopropyl anion into an allyl anion is known to occur if the structural prerequisites are fulfilled.[33,34] The ring closure of *16a* into *17* is the reversed reaction. Even if *16a* is



Scheme 4. Reaction pathways for the formation of cyclopropene *2*. Route 3 and 4.

greatly favoured in the assumed equilibrium between *16a* and *17* (suggested by the empirical rule predicting a 3-*Endo-Trig* ring closure reaction to be disfavoured [35]), elimination of bromide ion from *17* is suggested to be irreversible and would explain the formation of *2*.

Conclusion. Four different reaction pathways to cyclopropene *2* have been discussed.

The probability of cyclopropene formation by way of route *1* is weakened mainly because of the low acidity of the proton at carbon 3 in the cyclopropane intermediate. Route 2 has been excluded since (i) formation of alkenyl carbenes in a protic solvent like methanol is less probable and (ii) when nonprotic solvents like ether, 1,2-dimethoxyethane or benzene were used, no cyclopropene was formed.

Route 3 has been excluded since *2* did not incorporate deuterium when *1* was treated with methoxide in CH_3OD.

The fact that *5a* yields *2* on treatment with methoxide and the support found in the literature for the probability of the reaction sequence *16a* ⇄ *17* → *2*, make route 4 the most plausible way to explain the formation of *2* from *1*.

EXPERIMENTAL

General. Melting points (uncorrected) were determined on a micro hot-stage. IR spectra were recorded on a Perkin-Elmer 457 Grating Infrared Spectrophotometer, ^{1}H NMR spectra on a Varian A-60A Spectrometer, ^{13}C NMR spectra on an FT NMR Spectrometer JEOL FX-60, the mass spectra on an AEI MS 902 instrument and the UV spectra on a Cary 14 spectrophotometer. Elemental analysis were performed by I. Beetz, West-Germany.

Reaction of dimethyl 2-bromo-1-phenylpropylidenemalonate (1) *with sodium methoxide in methanol.* An equivalent amount of 0.43 M NaOMe in MeOH was added dropwise at 25 °C to a solution of bromide *1* (6.5 g, 19.9 mmol)[36] in MeOH (25 ml). The solution was stirred for 93 h. Water was added and the mixture was extracted several times with ether. The combined ether extracts were washed with water until neutral reaction and dried over $MgSO_4$. The solvent was removed and the crude product dissolved in light petroleum 40–60 °C or MeOH. On cooling *dimethyl 2-methyl-3-phenyl-2-cyclopropene-1,1-dicarboxylate* (*2*) precipitated, yield 0.55 g (11 %), (55 % of the amount present in the reaction mixture), m.p. 92–93 °C (MeOH). Anal. $C_{14}H_{14}O_4$: C, H. MS: *m/e* 246 (M^+, 53), $C_{14}H_{14}O_4$, *m/e* 187 ($M-CO_2Me$, 100), $C_{12}H_{11}O_2$. ^{1}H NMR ($CDCl_3$): δ 7.2–7.7 (5 H, m), 3.70 (6 H, s), 2.37 (3 H, s). ^{13}C NMR (15.0 MHz, $CDCl_3$): δ 171.4 (C6), 129.6, 129.5, 128.8 and 125.1 (Ph), 105.3 and 104.9 (C1 and C2), 52.2 (C5), 35.1 (C3), 9.5 (C4). UV (MeOH): λ_{max} 258 nm, ε 19 100. IR (KBr): 1900, 1740 and 1710 cm^{-1}. One gram of the residue was dissolved in dichloromethane. Chromatography on a silica gel column (silica gel 60, 0.2–0.5 mm; column 2.5 cm × 25 cm) with dichloromethane as the eluent gave fraction 1 (200 mg) mainly consisting of *dimethyl* (E)*-2-bromo-1-phenyl-1-propenylmalonate* (*5a*) in addition to some unreacted *1*, fraction 2: pure *dimethyl 1-benzoylethylmalonate* (*6*), fraction 3: pure *dimethyl 1,2-dimethoxy-1-phenylpropylmalonate* (*7*) and fraction 4 containing mainly cyclopropene *2* in addition to some *dimethyl 2-methoxy-1-phenylpropylidenemalonate* (*9*).

By chromatography of fraction 1 on a silica gel column using cyclohexane/isopropyl ether 3:1 as the eluent, a pure sample of vinylbromide *5a* was obtained. Anal. $C_{14}H_{15}O_4Br$: C, H. MS: *m/e* 247 ($M-Br$, 100) $C_{14}H_{15}O_4$. ^{1}H NMR (CCl_4): δ 7.25 (5 H, s), 4.88 (1 H, s), 3.53 (6 H, s), 2.20 (3 H, s). On addition of D_2O/DO^- the one proton singlet at δ 4.88 disappeared. IR (film): 1760, 1740 and 1635 cm^{-1}. The other isomer *5b* was not purified, but its NMR spectrum could be assigned from the isomer mixture, ^{1}H NMR (CCl_4): δ 7.20 (5 H, s), 4.52 (1 H, s), 3.60 (6 H, s), 2.43 (3 H, s).

Dimethyl 2-bromo-1-phenyl-1-propenylmalonate (5). Bromide *1* (1.0 g, 3.1 mmol) was dissolved in benzene (10 ml). Sodium methoxide (0.65 g, 12.2 mmol) was added and the mixture refluxed for 4.5 h. After cooling, the suspension was poured into sodium chloride solution and extracted several times with benzene. The organic layer was washed with ammonium chloride solution and water and dried over $MgSO_4$ to give *5a*/*5b* (8.2/1), yield 60 %.

Dimethyl 1-benzoylethylmalonate (6), m.p. 51–53 °C (Ether/pentane). Anal. $C_{14}H_{16}O_5$: C, H. MS: *m/e* 264 (M^+, 0.2), *m/e* 105 ($Ø-CO^+$, 100). ^{1}H NMR (CCl_4): δ 7.2–8.1 (5 H, m), 3.8–4.3 (2 H, m), 3.75 (3 H, s), 3.62 (3 H, s), 1.14 (3 H, d, *J* 6.5 Hz). IR (KBr): 1755, 1740 and 1685 cm^{-1}.

Dimethyl 1,2-dimethoxy-1-phenylpropylmalonate (7). MS: *m/e* 279 ($M-OMe$, 5), *m/e* 151 ($\phi-C^+(OMe)_2$, 100), *m/e* 105 ($\phi-CO^+$, 39). ^{1}H NMR (CCl_4): δ 7.1–7.6 (5 H, m), 3.70 (3 H, s), 3.47 (3 H, s), 3.22 (3 H, s), 3.08 (3 H, s), 2.8–3.4 (2 H, $-CH(CO_2Me)_2$ and $MeO-\underset{|}{\overset{|}{C}}-H$), 0.77 (3 H, d, *J* 6.5 Hz). ^{13}C NMR (15.0 MHz, $CDCl_3$): δ 169.6 and 169.0 (C1 and C2), 137.2, 128.3, 128.1 and 127.8 (Ph), 104.9 (C4), 53.8 and 39.3 (C3 and C5), 52.4, 52.2, 49.8 and 48.5 (C6, C7, C8 and C9), 12.5 (C10). IR (film): 1750 cm^{-1}.

Reaction of bromide 1 with silver perchlorate in

methanol. Synthesis of dimethyl 2-methoxy-1-phenylpropylidenemalonate (9). A solution of silver perchlorate (3.2 g, 14.2 mmol) in methanol (15 ml) was added to a solution of *1* (4.0 g, 12.2 mmol) in methanol (35 ml) at room temperature. Silver bromide precipitated. The mixture was stirred for 30 min, filtrated and the solvent removed. Chloroform was added and the organic layer was washed with water and dried over $MgSO_4$ to give *9*, yield 68 % (NMR), b.p. 100–102 °C/0.05 mmHg. MS: *m/e* 246 (M–MeOH, 52). ^{1}H NMR ($CDCl_3$): δ 7.0–7.5 (5 H, m), 4.53 (1 H, q, *J* 6.5 Hz), 3.82 (3 H, s), 3.48 (3 H, s), 3.37 (3 H, s), 1.27 (3 H, d, *J* 6.5 Hz). IR (film): 1730 and 1635 cm^{-1}.

Reaction of bromide 1 *with ten equivalents of 4.3 M sodium methoxide. Isolation of dimethyl 2,2-dimethoxy-1-methyl-2-phenylethylmalonate* (8). Ten equivalents of sodium methoxide (70 ml, 4.3 M) was added to a solution of *1* (10.0 g, 30.6 mmol) in methanol (65 ml) at room temperature. The solution was stirred for 23 h, poured into ether–water and the product extracted into ether. The combined ether extracts were washed with water until neutral reaction, dried over $MgSO_4$ and the solvent removed. The precipitate (4.1 g) formed on addition of light petroleum 40–65 °C was recrystallized, yield 1.7 g (18 %), m.p. 90–92 °C (ether–pentane). Anal. $C_{16}H_{22}O_6$: C, H. MS: *m/e* 279 (M–OMe, 14), *m/e* 151 (Ø–$C^+(OMe)_2$, 8), *m/e* 115 (100), *m/e* 105 (Ø–CO^+, 22). ^{1}H NMR (CCl_4): δ 7.1–7.6 (5 H, m), 3.68 (3 H, s), 3.47 (3 H, s), 3.42 (3 H, s), 3.14 (3 H, s), 3.18 (1 H, d, *J* 12 Hz), 2.2–2.9 (1 H, m), 0.98 (3 H, d, *J* 6.5 Hz). IR (KBr): 1750 cm^{-1}. TFA/H_2O was added to a solution of *8* in CCl_4. The mixture was stirred overnight at 25 °C. The organic layer was separated, washed with water, dried over $MgSO_4$ and the solvent removed. The oil was crystallized from ether–pentane to give *6*.

Dimethyl 2,3-dibromo-2-methyl-3-phenylcyclopropane-1,1-dicarboxylate (4). Cyclopropene *2* (230 mg, 0.93 mmol) was dissolved in tetrachloromethane (15 ml). An equivalent amount of bromine in tetrachloromethane (2.5 % solution) was added and the solution stirred overnight. The solvent was removed and the oil was dissolved in ether. On cooling *4* crystallized, yield 120 mg (32 %), m.p. 52–55 °C (ether–pentane or MeOH). MS: *m/e* 327/325 (M–Br, 8/8), *m/e* 246 (M–Br_2, 71), *m/e* 187 (M–Br_2–CO_2Me, 100). ^{1}H NMR ($CDCl_3$): δ 7.2–7.7 (5 H, m), 3.86 (3 H, s), 3.67 (3 H, s), 2.50 (3 H, s). IR (KBr): 1755 and 1745 (shoulder) cm^{-1}.

Treatment of 9 with sodium methoxide in methanol. Formation of dimethyl 2-methoxy-1-phenyl-1-propenylmalonate (11). Two equivalents of sodium methoxide in methanol (0.43 M) were added to *9*. After 48 h at room temperature 10 % *11* was formed (^{1}H NMR). Ten equivalents solid sodium methoxide were added and the solution stirred for 45 h to give *11*, ^{1}H NMR ($CDCl_3$): δ 7.25 (5 H, s), 4.77 (1 H, s), 3.63 (9 H, s), 1.81 (3 H, s). On addition of benzene, the 9-H singlet at δ 3.63 split into a 6-H singlet and a 3-H singlet. On addition of D_2O/DO^-, the signal at δ 4.77 disappeared.

Dimethyl 1-phenyl-2-propionylmalonate (12). TFA/H_2O was added to a solution of enol ether *11* in tetrachloroethane. ^{1}H NMR showed that *11* was transformed into *12*. ^{1}H NMR (CCl_4): δ 7.22 (5 H, s (broad)), 4.34 (1 H, d, *J* 11.5 Hz), 4.09 (1 H, d, *J* 11.5 Hz), 3.71 (3 H, s), 3.35 (3 H, s), 2.20 (3 H, s).

Treatment of a 5a *with sodium methoxide in methanol. Formation of cyclopropene* 2. Sodium methoxide (0.6 mmol, 0.43 M) was added to a solution of *5a* (100 mg, 0.31 mmol) in methanol (1.0 ml). The solution was stirred at room temperature for 67 h, added water and extracted several times with ether. ^{1}H NMR of the crude product showed that 55 % of *5a* had been transformed into *2*. On addition of light petroleum 40–65 °C, pure *2* crystallized. The m.p., NMR and IR spectrum were identical to those recorded earlier.

Treatment of 1 *with sodium methoxide in CH_3OD.* Sodium methoxide (75 mg, 1.4 mmol) was added to a solution of *1* (400 mg, 1.4 mmol) in CH_3OD (4.2 ml). The solution was stirred at room temperature for 25 h. Ether was added and the mixture was washed with deuterium oxide until neutral reaction and dried over $MgSO_4$. The crude product was dissolved in light petroleum 40–60 °C. Cyclopropene *2* precipitated on cooling and was recrystallized from methanol. MS and ^{1}H NMR showed that no incorporation of deuterium had occurred.

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