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THE REACTION OF OZONIDES DERIVED FROM CYCLOALKENES WITH STABILIZED PHOSPHORUS YLIDES

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Abstract: Ozonides derived from cycloalkenes reacted with 2.2 equivalents of methyl (triphenylphosphoranylidene)acetate or (triphenylphosphoranylidene)acetophenone to form *trans,trans*-α,β,χ,φ-unsaturated dioates or diones, respectively. The trapping experiments have ruled out the possibility that the reaction involved the carbonyl oxide intermediate.

Ozonolysis is an important reaction for the cleavage of carbon-carbon double bonds[1,2]. Recently, we reported that the ozonides derived from a terminal double bond reacted directly with stabilized phosphorus ylides in a one-pot sequence to give corresponding α,β-unsaturated esters or ketones in high yield[3].(Scheme 1) Apparently,

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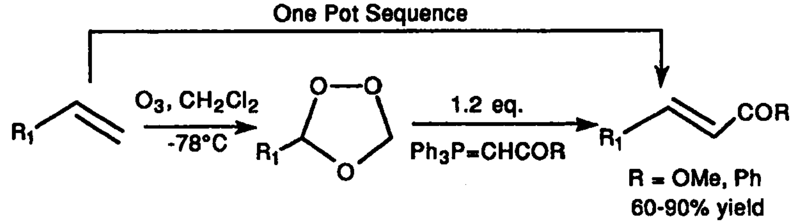
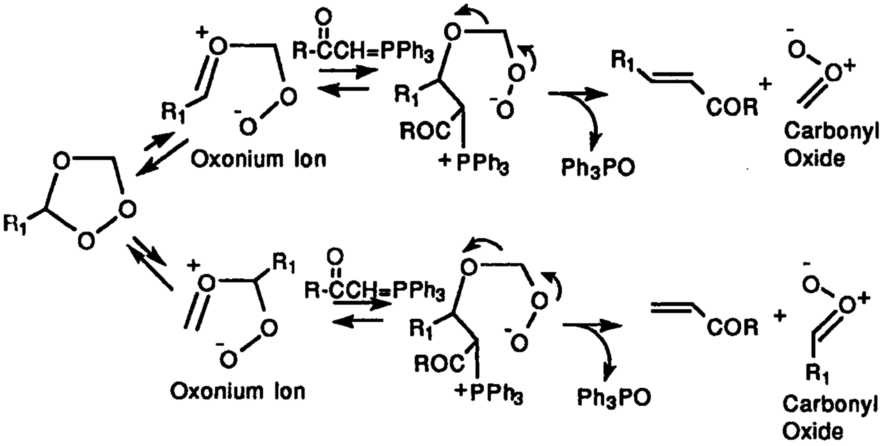
Scheme 1

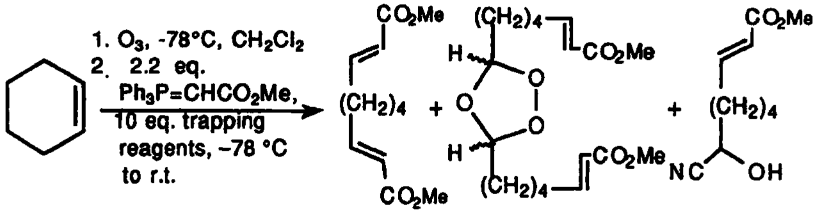


Scheme 2



this reaction did not involve the oxidation-reduction processes since only 1.2 equivalents of ylide are needed to consume all the ozonide and form olefinic adducts. Moreover, only very small amount of methyl acrylate (or phenyl vinyl ketone) was formed from each reaction. In other words, the regioselectivity of this type reaction is very high. It was assumed that the oxonium ion and carbonyl oxide intermediates might be formed in the reaction. (i. e. retro-1,2,4-trioxolane formation). Since the secondary oxonium ion is more stable than that of the primary one, the high regioselectivity was achieved.(Scheme 2) In order to

Scheme 3



1 2 3

understand the reaction mechanism and the scope of this type reaction, the cycloalkenes were subjected to the ozonolysis, followed by reaction with stabilized phosphorus ylide in the presence of nucleophiles or 1,3-dipolarophiles[4]. Hopefully, we could trap the reaction intermediate and understand the reaction mechanism. In this report, we would like to describe the results of our research in this direction.

The cyclohexene was subjected to ozonolysis in dichloromethane at −78 °C, followed by reaction with 2.2 equivalents of methyl (triphenylphosphoranylidene)acetate ($Ph_3P=CHCO_2Me$) and 10 equivalents of methanol (as nucleophile), ethyl vinyl ether or methyl acrylate (as 1,3-dipolarophiles) in a one-pot sequence. The reaction mixture was warmed up slowly to room temperature and stirred for 12 h. Dienedioate (**1**) and trioxolane (**2**) were formed in 38–40% and 4–5% yields, respectively.(Scheme 3 and Table 1) While the reaction appeared to be very clean (as judged by TLC), the yield tended to be low. The less amount of phosphorus ylide was used, the more of the trioxolane (**2**) was obtained. None of the trapped adducts, such as α-alkoxy hydroperoxide (i. e. nucleophilic addition product) or cyclic

Table 1: The products distribution of the reaction between the ozonide derived from cyclohexene, 2.2 eq. of $Ph_3P{=}CHCO_2Me$ and the trapping reagent in CH_2Cl_2.

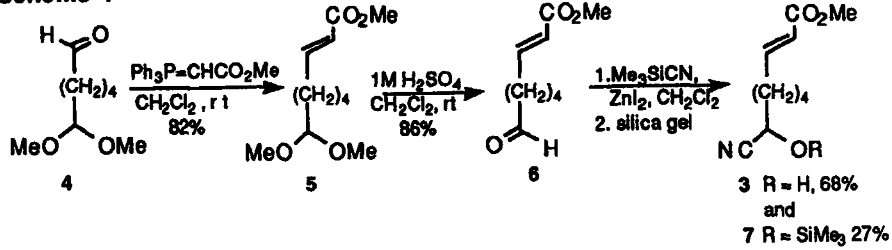
Trapping Reagents	Products Distribution (% yield) 1	2	3
10 eq. MeOH	40[a]	4[b]	—
10 eq. Methyl Acrylate	38[a]	4[b]	—
10 eq. Methyl Vinyl Ether	38[a]	4[b]	—
10 eq. TMSCN	39[a]	5[b]	5

[a] The *trans,trans/cis,trans* isomeric ratio are ranged from 8:1—10:1 estimated from GC integration.

[b] The *cis/trans* isomeric ratio is almost 1:1 in all cases which are estimated from ^{1}H NMR integration.

peroxide (i. e. 1,3-dipolar addition product), was isolated from the reaction mixtures. However, when trimethylsilyl cyanide (10 equivalents) was used as the trapping reagent[5], compounds (**1**), (**2**) and cyanohydrin (**3**) were formed in 39, 5 and 5% yields, respectively. The structure of compound (**3**) is a cyanohydrin but not a cyanohydroperoxide. Its structure was determined unambiguously by comparing with the synthetic product (**3**) from Scheme 4. 6,6-Dimethoxyhexanal (**4**)[6,7] was treated with 1.1 equivalents of $Ph_3P{=}CHCO_2Me$ to give the α,β-unsaturated ester (**5**). The acetal group was deprotected by aqueous acid and the resulted aldehyde was treated with trimethylsilyl cyanide in the presence of zinc iodide in dichloromethane[8], followed by silica gel column chromatography to

Scheme 4

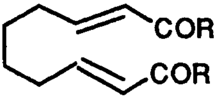
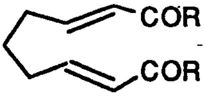
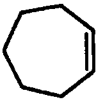
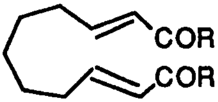
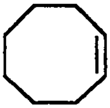
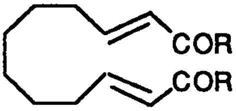
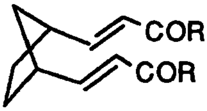


give the corresponding cyanohydrin (**3**) and trimethylsiloxy nitrile (**7**) in 68% and 27% yields, respectively. (Scheme 4)

Although mono-substituted ozonides could be isolated as the pure, monomeric products,[9] the ozonides derived from cycloalkenes were formed as the polymeric or oligomeric form[10,11]. Therefore, there is an ozonide moiety in structure (**1**). Among these three trapping experiments, none of their results supported that the carbonyl oxide species was formed as the intermediate during the reaction. The cyanohydrin formation indicated that the aldehyde is formed before the double bond formation. The rate of the cyanohydrin formation is much slower than that of the Wittig reaction under uncatalyzed condition[8]. Therefore, compound (**1**) was formed as the major product. (Scheme 3)

Since *trans,trans*-α,β,χ,φ-unsaturated dioates were useful starting materials to the natural product synthesis[12] and to the electrochemical[13-15], photochemical[16] cyclization studies, various cycloalkenes and bicycloalkene were tried and their results were listed in the Table 2. Similar reaction can also be applied to the *trans,trans*-di-enones (**8**, **10**, **12**, **14** and **16**) formations although the chemical yields were slightly lower. (Table 2)

Table 2. Yields of Di- α,β -Unsaturated Esters and Ketones Formation

entry	Substrate	product	Yield^a
1		 **1** R = OMe **8** R = Ph	40% 23%
2		 **9** R = OMe **10** R = Ph	30% 27%
3		 **11** R = OMe **12** R = Ph	31% 26%
4		 **13** R = OMe **14** R = Ph	42% 26%
5		 **15** R = OMe **16** R = Ph	42% 26%

[a] The *trans, trans/cis, trans* isomer ratio are ranged from 8:1—10:1 estimated by GC integration. The yield were not optimized.

In summary, the primary product of the reaction between ozonide and phosphorus ylide was the corresponding aldehyde, which subsequently reacted with phosphorus ylide to form the Wittig reaction adduct. This reaction did not involve the carbonyl oxide intermediate. Although the exact mechanism of this type reaction is not clear now, the further work in the mechanistic studies is under investigation. However, the ozonides derived from cycloalkenes could reacted directly with the phosphorus ylides represents an alternative way to form the α,β,χ,φ-unsaturated dioates and diones.

EXPERIMENTAL

All reactions were carried out under nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Melting points were determined using a Yanaco micro melting point apparatus and were uncorrected. The ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AC 200 spectrometer, and chemical shifts were given in ppm downfield from tetramethylsilane (TMS). IR spectra were taken with a Perkin Elmer 882 spectrophotometer and only noteworthy absorptions were listed. Mass spectra were measured on a VG 70-250S mass spectrometer by electronic impact at 70 eV (unless otherwise indicated).

General Procedure for the Trapping Experiment

Ozone was introduced into a flask containing a cyclohexene in dichloromethane at –78 °C until the solution turned blue. The excess ozone was then excluded by nitrogen gas stream. A solution of $Ph_3P{=}CHCO_2Me$ (2.2 equivalents) and ethyl vinyl ether (methyl acrylate, or trimethylsilyl cyanide) (10 equivalents) in dichloromethane was added to the solution and the resulting solution was warmed up slowly to room temperature. The reaction was completed within 10–12 h. The reaction mixture was concentrated and purified by silica gel chromatography (hexane/ethyl acetate = 15:1) to isolate each product.

Dimethyl *trans, trans* - 2,8-decadienedioate (1).

Colorless oil, 40% from cyclohexene. ^{1}H-NMR ($CDCl_3$) δ 6.95 (dt, J= 15.7 and 6.9 Hz, 2H), 5.82 (dt, J= 15.7 and 0.7 Hz, 2H), 3.72 (s, 6H), 2.20 (m, 4H), 1.50 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 166.92 (s), 148.82 (d), 121.17 (d), 51.30 (q), 31.79 (t), 27.38 (t); IR (neat) (v, cm^{-1}): 1721 (C=O), 1653 (C=C); MS (m/z): 226 (M$^+$), 166, 134, 107 (base peak), 81; HRMS (m/z): 226.1205 (M$^+$, $C_{12}H_{18}O_4$, calcd 226.1205).

3,5-Di-[7-(*trans* -1-carbomethoxy-1-hexyl)]-1,2,4-trioxolane (2).

Pale yellow oil; ^{1}H-NMR ($CDCl_3$) δ 6.95 (dt, J= 15.6 and 6.9 Hz, 2H), 5.83 (dt, J= 15.6 and 1.3 Hz, 2H), 5.18 (t, J= 5.0 Hz, trioxolane ring proton), 5.14 (t, J= 4.7 Hz, trioxolane ring proton), 3.72 (s, 6H), 2.17–2.27 (m, 4H), 1.65–1.75 (m, 4H), 1.44–1.58 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 166.93 (s), 148.84 (d), 121.13 (d), 103.87 (d), 51.31 (q), 31.98 (t), 31.85 (t), 30.37 (t), 27.72 (t), 27.61 (t), 23.31(t), 23.12(t); IR (neat) (v, cm^{-1}) 1713, 1654, 1270, 1197, 1118. The chemical shifts underlined are from the other isomer. The ratio of these two isomers is about 1 : 1.

***trans*-Methyl 8-cyano-8-hydroxy-2-octenoate (3).**

Colorless oil. ^{1}H-NMR ($CDCl_3$) δ 6.89 (dt, J= 15.7 and 7.0 Hz, 1H), 5.77 (dt, J= 15.7 and 1.5 Hz, 1H), 4.40 (t, J= 6.6 Hz, 1H), 3.67 (s, 3H), 2.16–2.20 (m, 2H), 1.77–1.80 (m, 2H), 1.43–1.50 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 167.45 (s), 149.11 (d), 121.10 (d), 120.00 (s), 60.79 (d), 51.53 (q), 34.73 (t), 31.73 (t), 27.17 (t), 23.97 (t); IR (neat) (v, cm^{-1}): 2241 (CN), 1720, 1710, 1700, 1169, 1647; MS (m/z): 197 (M$^+$), 187, 165, 154, 138, 136 (base peak), 108.

trans-Methyl 8,8-dimethoxy-2-octenoate (5).

To a mixture of 6,6-dimethoxyhexanal (4)[6,7] (664.3 mg, 4.14 mmol) in 40 mL of CH_2Cl_2 was added $Ph_3P{=}CHCO_2Me$ (1660mg, 4.97 mmol). The reaction was stirred at rt for 12 h and concentrated to give a crude residue, which was separated by the silica gel column chromatography to give 741 mg of product in 86% yield as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ 6.97 (dt, J=15.6 and 7.0 Hz, 1H), 5.83 (dt, J= 15.6 and 1.7 Hz, 1H), 4.36 (t, J=5.7 Hz, 1H, $(MeO)_2C\underline{H}$-), 3.73 (s, 3H, CO_2-$C\underline{H}_3$), 3.31 (s, 6H, $(C\underline{H}_3O)_2C$-), 2.17–2.24 (m, 2H), 1.37–1.66 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ 166.93 (s), 149.12 (d), 120.95 (d), 104.27 (d), 52.56 (q), 51.20 (q), 32.16 (t), 31.98 (t), 27.75 (t), 24.00 (t); IR (neat) (v, cm^{-1}): 1722, 1654; MS (m/z): 215 (M^+-1), 184, 152, 117, 113, 100, 93, 85, 75 (base peak), 71.

trans-Methyl 7-formyl-2-heptenoate (6).

To a mixture of compound (5) (529.2 mg, 2.44 mmol) in 10 mL of CH_2Cl_2 was added 10 mL of 1M aqueous H_2SO_4. The reaction was stirred at rt for 65 h. The reaction mixture was extracted with two 40 mL portions of CH_2Cl_2. The organic laayer was washed with water, dried with anhydrous Na_2SO_4, and evaporated to give crude mixture. The crude mixture was separated by silica gel column chromatography (hexane/ethyl acetate = 20:1) to give 361 mg of product (6) as a colorless oil in 86% yield. ^{1}H-NMR ($CDCl_3$) δ 9.77 (t, J= 1.5 Hz, 1H), 6.95 (dt, J= 15.7 and 6.9 Hz, 1H), 3.73 (s, 3H), 2.46 (td, J= 7.0 and 1.5 Hz, 2H), 2.24 (ddd, J= 8.6, 7.2 and 1.5 Hz, 2H), 1.40–1.80 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 202.00 (d), 166.93 (s), 148.56 (d), 121.33 (d), 51.35 (q), 43.49 (t), 31.80 (t), 27.41 (t), 21.43 (t); IR (neat) (ν, cm^{-1}): 1723, 1714, 1654; MS (m/z): 171 (M$^+$+1), 138 (base peak), 127, 113, 94, 82.

trans-Methyl 8-cyano-8-hydroxy-2-octenoate (3) and _trans_-Methyl 8-cyano-8-trimethylsiloxy-2-octenoate (7).

To a mixture of compound (6) (143.9 mg, 0.84 mmol) in 5 mL of CH_2Cl_2 was added Me_3SiCN (92.1 mg, 0.93 mmol) and ZnI_2 (2 mg) at 0°C. The solution was warmed slowly to rt and stirred for 18 h. The reaction mixture was concetrated and purified by silica gel chromatography (hexane/ethyl acetate = 10:1) to give 112.9 mg of compound (3) (68% yield) and 62.1 mg of compound (7) (27% yield). Both of compounds are colorless oils.

For compound (3): ^{1}H-NMR ($CDCl_3$) δ 6.89 (dt, J= 15.7 and 7.0 Hz, 1H), 5.77 (dt, J= 15.7 and 1.5 Hz, 1H), 4.40 (t, J= 6.6 Hz, 1H), 3.67 (s, 3H), 2.16–2.20 (m, 2H), 1.77–1.80 (m, 2H), 1.43–1.50 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 167.45 (s), 149.11 (d), 121.10 (d), 120.00 (s), 60.79 (d), 51.53 (q), 34.73 (t), 31.73 (t), 27.17 (t), 23.97 (t); IR (neat) (ν, cm^{-1}): 2241 (CN), 1720, 1710, 1700, 11695, 1647; MS (m/z): 197 (M$^+$), 187, 165, 154, 138, 136 (base peak), 108.

For compound (7): ^{1}H-NMR ($CDCl_3$) δ 6.95 (dt, J= 15.7 and 6.9 Hz, 1H), 5.83 (dt, J= 15.7 and 1.1 Hz, 1H), 4.40 (t, J= 6.4 Hz, 1H), 3.73 (s, 3H), 2.19–2.25 (m, 2H), 1.75–1.85 (m, 2H), 1.49–1.54 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 167.45 (s), 148.59 (d), 121.25 (d), 119.81 (s), 61.20 (d), 51.32 (q), 35.84 (t), 31.80 (t), 27.31 (t), 24.00 (t), -0.51 (q); IR (neat) (ν, cm^{-1}): 1719, 1656, 1255, 1200, 1114.

General Procedure for the Double Wittig Reaction

Ozone was introduced into a flask containing a cycloalkene in dichloromethane at –78 °C until the solution turned blue. The excess ozone was then excluded by nitrogen gas stream. 2.2 equivalents of $Ph_3P{=}CHCO_2Me$ or 2.2 equivalents of $Ph_3P{=}CHCOPh$ was added to the solution in one portion and the resulting solution was warmed up slowly to room temperature. The reaction was completed within 10-12 h. The reaction mixture was concentrated and purified by silica gel chromatography (hexane/ethyl acetate = 15:1) to isolate each product.

***trans, trans*-1,10-Diphenyl-2,8-decadiene-1,10-dione (8).**

Pale yellow solid, mp 66–67°C, 23% from cyclohexene. ^{1}H-NMR ($CDCl_3$) δ 7.90–7.95 (m, 4H), 7.40–7.59 (m, 6H), 6.85–7.13 (m, 4H), 2.34 (m, 4H), 1.59 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 190.57 (s), 149.03 (d), 137.76 (s), 132.53 (d), 128.38 (d), 126.04 (d), 32.40 (t), 27.63 (t); IR (CH_2Cl_2) (ν, cm^{-1}): 1667 (C=O), 1618 (C=C); MS (m/z): 318 (M^+), 213, 186, 105 (base peak); HRMS (m/z): 318.1622 (M^+, $C_{22}H_{22}O_2$, calcd 318.1620).

Dimethyl *trans, trans* - 2,7-nonadienedioate (9).

Colorless oil, 30% from cyclopentene. ^{1}H-NMR ($CDCl_3$) δ 6.95 (dt, J=15.7 and 6.9 Hz, 2H), 5.84 (dt, J=15.7 and 1.5 Hz, 2H), 3.72 (s, 6H), 2.25 (qd,J=7.0 and 1.5 Hz, 4H), 1.66 (qu, J=7.2 Hz, 2H); ^{13}C-NMR ($CDCl_3$) δ 166.49 (s), 147.95 (d), 121.24 (d), 51.01 (t), 31.05 (t), 25.98 (t); IR (neat) (ν, cm^{-1}): 1719 (C=O), 1655 (C=C); MS (m/z): 212 (M^+), 181, 152, 93, 81 (base peak); HRMS (m/z): 212.1043 (M^+, $C_{11}H_{16}O_4$ calcd 212.1049).

***trans, trans*-1,9-Diphenyl-2,7-nonadiene-1,9-dione (10).**

Pale yellow oil, 27% from cyclopentene. ^{1}H-NMR ($CDCl_3$) δ 7.90–7.95 (m, 4H), 7.41–7.60 (m, 6H), 6.88–7.20 (m, 4H), 2.39 (q, J=7.0 Hz, 4H), 1.76 (qu, J=7.3 Hz, 2H); ^{13}C-NMR ($CDCl_3$) δ 190.27 (s), 132.48(d), 128.30 (d), 126.22 (d), 31.90 (t), 26.44 (t); IR (neat) (v, cm^{-1}): 1668 (C=O), 1619 (C=C); MS (m/z): 304 (M^+), 199, 122, 105 (base peak), 77 HRMS (m/z): 304.1459 (M^+, $C_{21}H_{20}O_2$, calcd 304.1463).

Dimethyl *trans,,trans*-2,9-undecadienedioate (11).

Colorless oil, 31% yield from cycloheptene. ^{1}H-NMR ($CDCl_3$) δ 6.96 (dt, J= 15.6 and 7.0 Hz, 2H), 5.82 (dt, J= 15.6 and 1.6 Hz, 2H), 3.73 (s, 6H), 2.21 (m, 4H), 1.41–1.51 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ 167.01 (s), 149.21 (d), 120.96 (d), 51.28 (q), 31.93 (t), 28.48 (t), 27.68 (t); IR (neat) (v. cm^{-1}): 1704 (C=O), 1654 (C=C), 1432, 1313, 1282, 1199, 1143, 1039, 980; MS (m/z): 240 (M^+), 208, 176, 149, 121, 81 (base peak); HRMS (m/z): 240.1357 (M^+, $C_{13}H_{20}O_4$, calcd 240.1362).

***trans, trans*-1,11-Diphenyl-2,9-undecadiene-1,11-dione (12).**

Pale yellow oil, 26% from cycloheptene. ^{1}H NMR ($CDCl_3$) δ 7.90–9.75 (m, 4H), 7.27–7.59 (m, 6H), 6.84–7.11 (m, 4H), 2.33 (m, 4H), 1.40–1.64 m, 6H); ^{13}C-NMR ($CDCl_3$) δ 190.79 (s), 149.52 (d), 137.91 (s), 132.55 (d), 128.45 (d), 126.00 (d), 32.61 (t), 28.77 (t), 27.92 (t); IR (neat) (v, cm^{-1}): 1667 (C=O), 1618 (C=C); MS (m/z): 332 (M^+), 105 (base peak), 91, 77; HRMS (m/z): 332.1746 (M^+, $C_{23}H_{24}O_2$,calcd 332.1776).

Dimethyl *trans,trans*-2,10-dodecadienedioate (13).

Colorless oil, 42% yield from cyclooctene. ^{1}H-NMR ($CDCl_3$) δ 6.96 (dt, J= 15.7 and 7.0 Hz, 2H), 5.82 (dt, J= 15.6 and 1.6 Hz, 2H), 3.72 (s, 6H), 2.20 (qd, J= 6.9 and 1.2 Hz, 4H), 1.31–1.70 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 167.024 (s), 149.40 (d), 120.85 (d), 51.27 (q), 32.01 (t), 28.74 (t), 27.78 (t); IR (neat) (ν, cm^{-1}): 1710 (C=O), 1650 (C=C); HRMS (m/z): 254.1524 (M$^+$, $C_{14}H_{22}O_4$, calcd 254.1518).

***trans,trans*-1,12-Diphenyl-2,10-dodecadiene-1,12-dione (14).**

Pale yellow solid, mp 62–63°C, 26% from cyclooctene. ^{1}H-NMR ($CDCl_3$) δ 7.90–7.95 (m, 4H), 7.44–7.54 (m, 6H), 6.84–6.92 (m, 4H), 2.31 (m, 4H), 1.38–1.53 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 190.62 (s), 149.59 (d), 137.80 (s), 132.41(d), 128.32 (d), 125.80 (d), 32.56 (t), 28.81 (t), 27.87 (t); IR (CH_2Cl_2) (ν, cm^{-1}): 1666 (C=O), 1618 (C=C); MS (m/z): 346 (M$^+$), 241, 227, 159, 105 (base peak), 77; HRMS(m/z): 346.1941 (M$^+$, $C_{24}H_{26}O_2$, calcd 346.1933).

Dimethyl *cis*-1,3-cyclopentane-*trans,trans*-diacrylate (15).

Colorless oil, 36% from norbornylene. ^{1}H-NMR ($CDCl_3$) δ 6.93 (dd, J= 15.6 and 8.0 Hz, 2H), 5.81 (dd, J= 15.6 and 1.0 Hz, 2H), 3.73 (s, 6H), 2.74 (m, 2H), 1.89–2.03 (m, 4H), 1.59 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 167.03 (s), 152.17 (d), 119.53 (d), 51.35 (q), 42.60 (t), 38.89 (t), 31.15 (t); IR (neat) (ν, cm^{-1}): 1713 (C=O), 1652 (C=C); MS (m/z): 238 (M$^+$), 206 (base peak), 178, 146, 119, 81; HRMS (m/z): 238.1205 (M$^+$, $C_{13}H_{18}O_4$, calcd 238.1196).

cis-1,3-Cyclopentane-_trans,trans_-diacrylophenone (16).

Colorless oil, 25% from norbornylene. ^{1}H-NMR ($CDCl_3$) δ 7.90–7.95 (m, 4H), 7.41–7.60 (m, 6H), 6.84–7.11 (m, 4H), 2.89 (m, 2H), 1.30-2.21 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ 190.87 (s), 152.45 (d), 137.92 (s), 132.64 (d), 128.49 (d), 124.46 (d), 43.36 (t), 39.33 (t), 31.49 (t), 28.30 (t); IR (neat) (ν cm^{-1}): 1667 (C=O), 1618 (C=C); MS (m/z): 330 (M$^+$), 225, 105 (base peak), 77; HRMS (m/z): 330.1620 (M$^+$, $C_{23}H_{22}O_2$, calcd 330.1620).

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