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Trapping Tetramethylene Biradical Intermediates in Cycloaddition Reactions of *p*-Methoxystyrene by Vinyl Copolymerization Reactions

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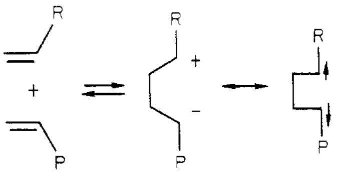
Tetramethylene biradical intermediates in cycloaddition reactions of *p*-methoxystyrene (**1**) with trimethyl ethylenetricarboxylate (**2**) at 70–116 °C and dimethyl cyanofumarate (**10**) at 28 °C were detected through the formation of alternating 1:1 copolymers **5** and **11**, identical with those formed by deliberate free-radical-initiated copolymerizations of these monomers. The rates were insensitive to solvent polarity. Free-radical inhibitors suppressed copolymerization and led instead to cycloadducts, dihydropyrans **3** and **12**, respectively, pointing to common intermediates in copolymerization and cycloaddition. Heating the kinetically favored dihydropyran **3** isomerized it to 1-butene **4**. Vacuum distillation of **3** gave **1** and **2**, while similar treatment of **12** gave copolymer by cycloreversion and spontaneous copolymerization. An ion-radical mechanism was excluded because deliberate generation of $\mathbf{1}^{+\cdot}$ in presence of **2** gave cyclodimer **8** or homopolymer **7**. Reaction of **1** with tetramethyl ethylenetetracarboxylate (**14**), which cannot copolymerize, led to cyclobutane **15** and traces of homopolymer **7** (some zwitterion character). The reactivity sequence **10** > **2** > **14** is dictated largely by resonance stabilization of and steric hindrance to tetramethylene formation. Consideration of the conformations available to tetramethylenes **16**–**18** provides a reasonable explanation of the results.

Reactions of electron-rich olefins with electron-poor olefins continue to attract the attention of both organic and polymer chemists. A bewildering variety of products is known to form in such reactions. These include cyclobutane derivatives, both cycloadducts and cyclodimers, 1-butenes, cyclohexanes (from two molecules of one olefin and one of the other), homopolymers of either or both olefins, and 1:1 alternating copolymers (for leading references, see ref 1–4).

The current interpretation implicates a tetramethylene intermediate which is a resonance hybrid[5,6] of zwitterion and singlet biradical.



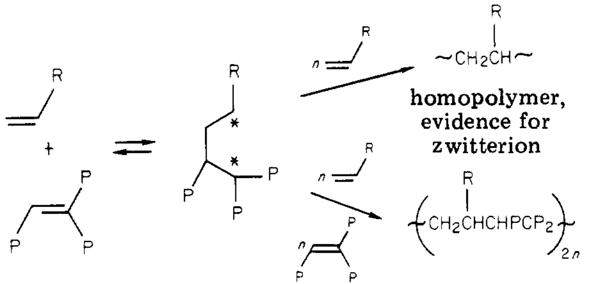
R = electron-rich substituent(s)
P = electron-poor substituent(s)

Zwitterionic character has been supported by substituent and solvent effects. The tetramethylene from vinyl ethers and tetracyanoethylene could be trapped by alcohols or unsaturated compounds, although trapping other tetramethylenes has not succeeded in many cases.[1,4]

The biradical nature also contributes to the ground state of tetramethylenes. This is especially prominent in cyclodimerization of styrene[7] and cycloadditions of fluoro olefins.[8]

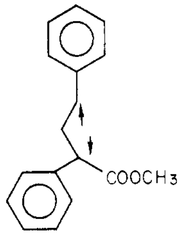
A fruitful study of the related trimethylenes was done by Cram and his colleagues.[9] They concluded that in ring-opening reactions of cyclopropanes, a spin-paired biradical (a) best represented the trimethylene from methyl 1,3-diphenylcyclopropanecarboxylate whereas a zwitterion (b) best described that from methyl 1-cyano-2-phenylcyclopropanecarboxylate.

Scheme I

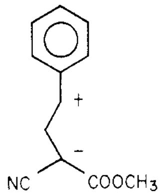


homopolymer, evidence for zwitterion

copolymer, evidence for biradical



a



b

It is not easy to diagnose biradical vs. zwitterionic contributions to the tetramethylene intermediate. We have been utilizing vinyl polymerization as a tool to help delineate the mechanism.[10,11] Under free-radical initiation, electron-poor trisubstituted ethylenes copolymerize with electron-rich vinyl monomers to form alternating 1:1 copolymers.[12] On the other hand, the latter readily undergo homopolymerization under cationic initiation. Accordingly, examination of the polymers formed in the *spontaneous* reactions of electron-rich with electron-poor olefins

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(1) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.

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0022-3263/81/1946-2948$01.25/0

Table I. Reaction of *p*-Methoxystyrene (1) with Trimethyl Ethylenetricarboxylate (2) at 70 and 116 °C[a]

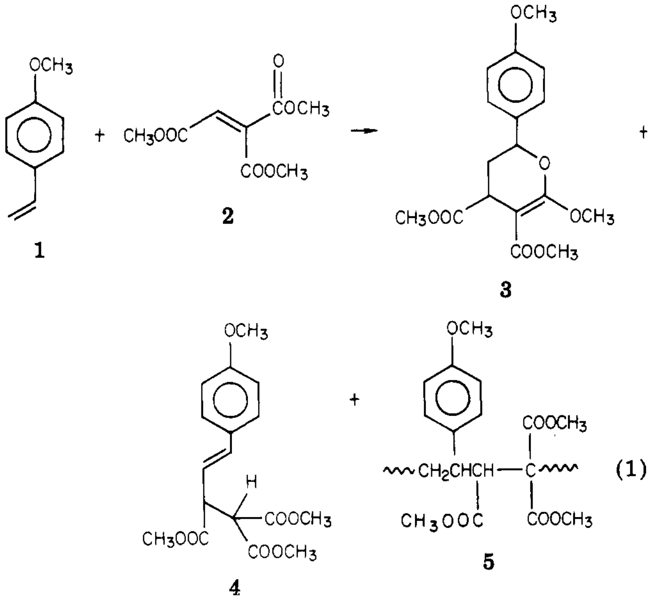
solvent	temp, °C	additives	% yield 3	% yield 4	% yield 5
none	70	none	5.5	0	65.5
	70	DPPH[b]	29.9	0	11.9
	116	none	0	0	67.7
	116	DPPH	0	32.2	0
benzene	70	none	trace	0	5.8
	70	DPPH or DPS[c]	trace	0	0
	116	DPPH	0	28.2	0
1,2-dichloroethane	70	none	17.2	0	17.6
	70	DPPH	18.3	0	0
	70	DPS	24.2	0	0
	116	DPPH	0	20.8	0
acetonitrile	70	none	trace	0	5.8
	70	DPPH	18.1	0	0
	70	DPS	21.7	0	0
	116	DPPH	0	17.1	0
benzaldehyde[d]	70	DPPH	0	10.4	0
Me_2SO[e]	75	DPPH	0	32.8	0

[a] Conditions: reagents 0.67 M, additives 1×10^{-3} M, reaction time 19 h, nitrogen atmosphere (except as noted). [b] DPPH = diphenylpicrylhydrazyl. [c] DPS = bis(4-hydroxy-3-*tert*-butyl-5-methylphenyl) sulfide. [d] 90 h. [e] 48 h.

will give evidence as to the nature of the tetramethylene intermediates (Scheme I).

Results

Trimethyl Ethylenetricarboxylate (2). The reaction of *p*-methoxystyrene (1) with trimethyl ethylenetricarboxylate (2) gave a bright yellow transient color and yielded both small molecules and macromolecules (eq 1; see Table I). The yields of 3 and 4 were generally measured by NMR methods. Dihydropyran 3 was isolated in crystalline form; mp 93–94 °C. Infrared and NMR spectra, as well as elemental analysis, confirmed the assigned structure. The 1-butene 4 was also isolated as a white powder, mp 73–74 °C. It was given the trans structure on the basis of NMR and IR spectra. Alternating copolymer 5,[12] a white noncrystalline solid, was characterized by elemental analysis and IR and NMR spectra. The products sought, but not found, were the cyclodimer of *p*-methoxystyrene, cyclohexane derivatives (from two molecules of one olefin and one of the other), double Diels–Alder adducts, and homopoly-*p*-methoxystyrene.



(1)

Temperature. Below 70 °C little reaction was observed. At 70 °C only dihydropyran 3 was formed in low yield. At 85 °C more total product, a mixture of dihydropyran and 1-butene 4, was obtained. At 115 °C only 1-butene 4 formed, in good yield. Copolymer 5 formation accompanied these reactions. Inasmuch as polymerization equals amplification, this should be a powerful method for studying reaction mechanism.

Here we examine the reactions of trimethyl ethylenetricarboxylate and dimethyl cyanofumarate with the electron-rich vinyl monomer *p*-methoxystyrene. Tetramethyl ethylenetetracarboxylate, which cannot copolymerize,[12] was included for comparison.

Free-Radical Inhibitors and Initiators. Diphenylpicrylhydrazyl (DPPH) and bis(4-hydroxy-3-*tert*-butyl-5-methylphenyl) sulfide (DPS) effectively inhibited the formation of copolymer 5. Yields of 3 and 4 were much higher in these inhibited reactions. Variation in DPPH concentrations in benzene showed no changes in yields. Oxygen (air) gave erratic yields of polymer but did not affect the yields of 4 and 5. Conversely, azobis(isobutyronitrile) (AIBN) gave good yields of the 1:1 alternating copolymer 5 and negligible yields of 3 and 4.

Solvents. At 70 °C, 1,2-dichloroethane or acetonitrile gave only slightly higher yields than benzene. The only solvents which gave 1-butene at 70–75 °C were Me_2SO and benzaldehyde. At 116 °C the yield of 1-butene 4 was similar in 1,2-dichloroethane, benzene, and acetonitrile.

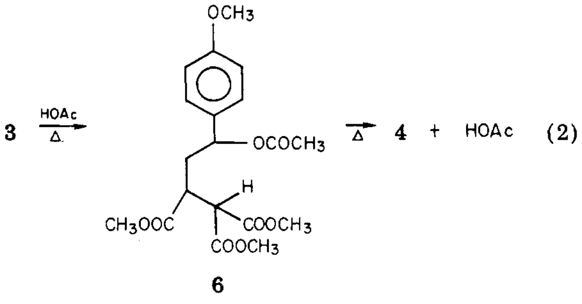
Trapping Attempts. A variety of reagents and solvents were examined as potential trapping agents for tetramethylene intermediates in the reaction of 1 and 2. These included thiophenol, methanol (these reacted with triester in blank runs), methoxyacetic acid, formic acid, trifluoroethanol, and nitrosobenzene (reacted with *p*-methoxystyrene). Acetonitrile or benzaldehyde, potential traps, gave no heterocyclic adduct. Metallic mercury[11] was without effect.

Attempts to trap the tetramethylene of 1 and 2 at 70–75 °C in excesses of dimethyl maleate (16:1), *N*-phenylmaleimide (2:1), and maleic anhydride (5:1) failed to yield the expected cyclohexanes but yielded the copolymer of 1 and dimethyl maleate, the copolymer of 1 and *N*-phenylmaleimide, and homopoly-*p*-methoxystyrene (7), respectively. With NO the 1-butene 4 and unidentified oligomers formed.

Cycloreversions and Solvolyses of Dihydropyran 3. Heating 3 alone at 75 °C overnight gave copolymer 5 and also traces of 1 and 2. Heating 3 at 115 °C in the presence of DPPH converted it completely to 1-butene 4. Vacuum distillation of 3 gave back 1 and 2. Heating 3 in deuterioacetonitrile for 43 h at 75 °C in the presence of DPPH gave 1-butene 4 and traces of 1 and 2.

Heating 3 in methanol at 86 °C for 5 h gave no reaction but at 126 °C for 16 h gave 1 and 2 as its methanol adduct. Left in methanol at 28 °C for 10 days, 3 gave 1-butene 4.

Heating 3 at 70 °C in acetic acid for 48 h gave acetate 6 in good yield (eq 2). The latter, heated alone, gave



(2)

Table II. Photochemical Reactions of *p*-Methoxystyrene with Trimethyl Ethylenetricarboxylate[a] in Acetonitrile

additives	time, h	yield, g (% yield) 8	9	5	7
air, 1,4-dicyanobenzene	46.5	0.13 (24.3)	0	0.211 (31.4)	0
air	162	0	0	0.005[b]	0
air, 4,4'-dimethoxybenzophenone	144	0	trace	0.241 (35.9)	0
air, 4,4'-dimethoxybenzophenone, DPPH	144	0	0.019 (3)	0	trace

[a] See Experimental Section for conditions. [b] And oligomer.

Table III. Reaction of Dimethyl Cyanofumarate with *p*-Methoxystyrene[a]

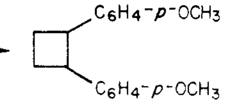
solvent	additives	time, h	% yield 12	11
none	none	0.1	0	98
CD_3CN	DPPH (0.01 g)	118	33.7	28.1
CH_3CN	DPS (0.01 g)	114.5	50.8	0
CH_3CN	di-*tert*-butylnitroxide	114.5	49.5	0

[a] See Experimental Section for details.

1-butene 4 and acetic acid. Acetic acid, in blank experiments, did not react with triester and reacted only very slowly with *p*-methoxystyrene. A mixture of the monomers in acetic acid in the presence of DPPH at 75 °C gave acetate 6 (30.7%). This probably formed by acetolysis of 3 as in Scheme II.

Photochemical and One-Electron-Oxidation Reactions. *p*-Methoxystyrene (1) and triester 2 were irradiated by UV light at 40 °C in acetonitrile (Table II). Irradiating 1 and 2 in the presence of 1,4-dicyanobenzene gave the known[13] cyclodimer 8 of *p*-methoxystyrene (eq 3), along

$$1 + 2 \xrightarrow[\text{CH}_3\text{CN}]{\text{1, 4- DCB, } h\nu}$$



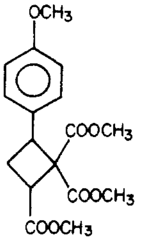
+ 5 (3)

8

with copolymer 5. *p*-Methoxystyrene and the triester in acetonitrile in the presence of ferric perchlorate[14] at 28 °C yielded only homo-*p*-methoxystyrene (7) and left the triester unreacted.

Ultraviolet irradiation of 1 and 2 in acetonitrile in presence of 4,4'-dimethoxybenzophenone and DPPH gave a low yield of cyclobutane adduct 9 (mp 133–134 °C).

$$1 + 2 \xrightarrow[\text{4,4'- dimethoxybenzophenone, DPPH}]{h\nu}$$

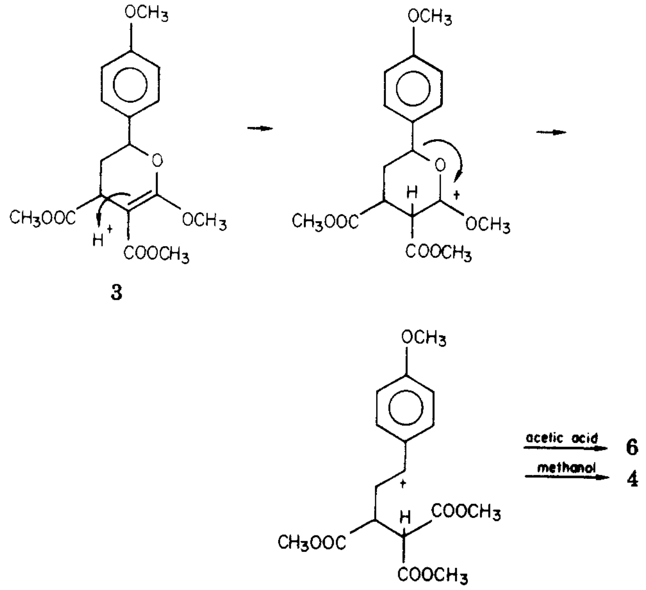


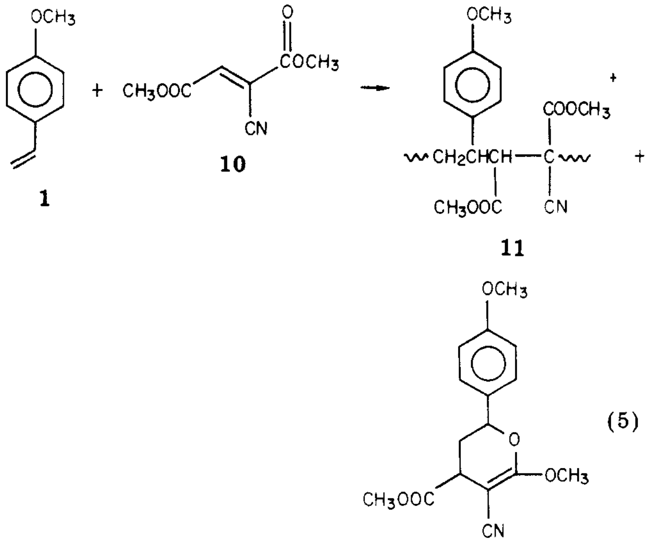
(4)

9

Dimethyl Cyanofumarate. A trisubstituted electrophilic olefin of greater reactivity,[12] dimethyl cyanofumarate (10), was allowed to react with *p*-methoxystyrene (Table III). In bulk the reagents formed a bright yellow mixture, and then an immediate exothermic reaction occurred to form 1:1 alternating copolymer 11 in ~99% yield[12] (eq 5).

Scheme II



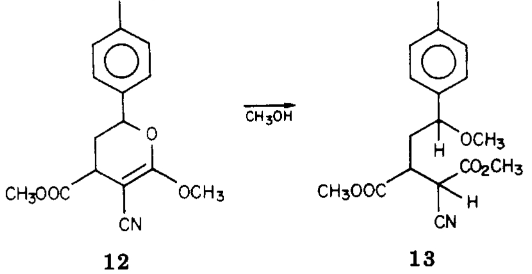


(5)

This reaction proceeded equally rapidly in total darkness.

In acetonitrile-d_3 solution containing DPS as an inhibitor after 48 h at 28 °C, dihydropyran 12, along with other products, was observed by NMR.

Cycloreversions and Solvolysis of Dihydropyran 12. Attempts to isolate and purify 12 led only to copolymer formation, even in the presence of DPPH. After a few days in methanol at 28 °C, 12 yielded the solvolysis product 13 (eq 6).



(6)

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[13] Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, *53*.

[14] Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.

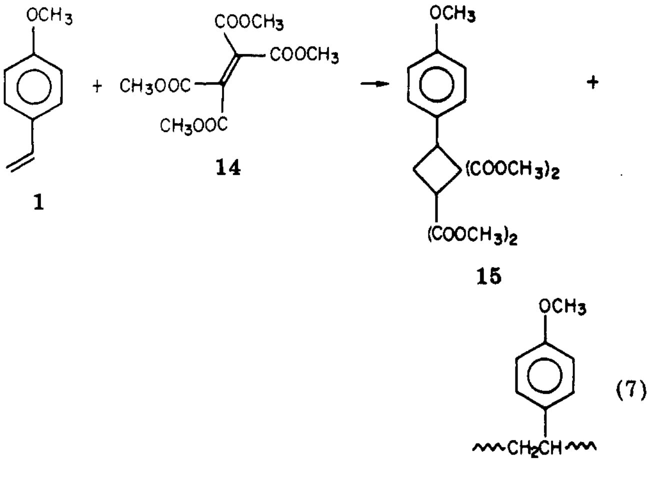
Table IV. Reaction of *p*-Methoxystyrene with Tetramethyl Ethylenetetracarboxylate at 116 °C[a]

run	time, h	solvent	% yield 15	% yield 7
1	40	none	trace	
2	44.5	none	3.7	0
3	65.5	none	9.3	0
4	40	1,2-dichloroethane	trace	5.6
5	44.5	1,2-dichloroethane	trace	7.1

[a] See Experimental Section for details.

Trapping Experiments. *N*-Phenylmaleimide (2:1 molar excess) was used to try to trap the tetramethylene from **10** and **1** at room temperature (28 °C) but yielded a copolymer of **1** and the maleimide. Maleic anhydride and dimethyl maleate stopped the copolymerization of **1** and **10** but did not stop the formation of **12**.

Tetramethyl Ethylenetetracarboxylate. Tetramethyl ethylenetetracarboxylate (**14**) was less reactive than trimethyl ethylenetricarboxylate, requiring higher temperatures to react. It gave cyclobutane adduct **15** at 116 °C (Table IV) in bulk. When 1,2-dichloroethane was used as solvent, the product was homopoly-*p*-methoxystyrene (**7**, eq 7). Cyclobutane **15** was obtained in crystalline form; mp 136–137 °C. Infrared, NMR, and elemental analyses were consistent with the structure. Homopolymer **7**, a white powder, was characterized by comparison of its NMR spectrum with that of authentic homo-*p*-methoxystyrene. Its infrared spectrum showed a carbonyl absorption peak even after repeated refluxing with methanol to remove unreacted **14**.



1 + **14** → **15** + **7** (7)

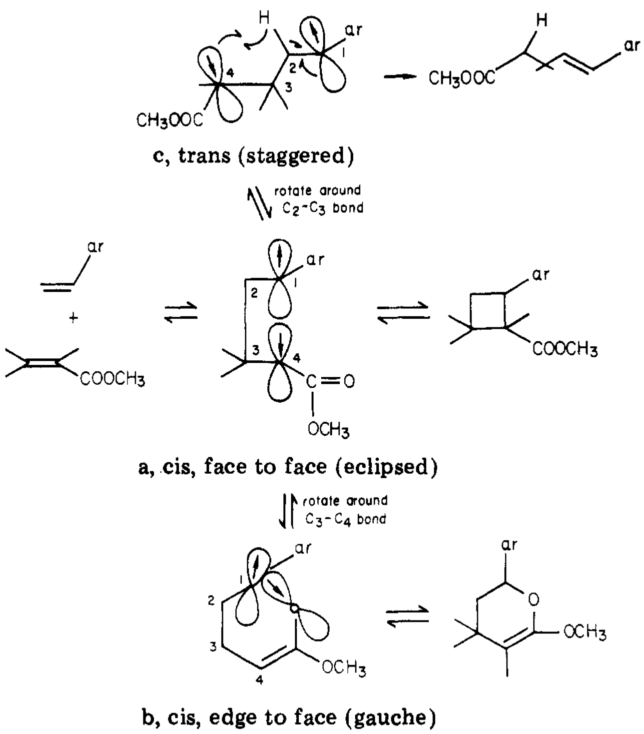
Exposure of a mixture of **1** and **14** to free radicals from AIBN at 70 °C gave no copolymer.

Discussion

When **1** and **2** react at 70–116 °C, small molecules **3** and **4** and alternating copolymer **5** are formed. Dihydropyran **3**, formed at 75 °C, is the kinetically controlled product. It isomerizes to the more thermodynamically stable **4** at 115 °C (at atmospheric pressure). Heating **3** under vacuum regenerates **1** and **2**. These results can be accommodated by considering the conformational isomers of a tetramethylene intermediate **16** (Scheme III). Following Cram,[9] cis face-to-face **16a**, stabilized by overlap of the p orbitals, may form first. This can undergo facile rotation around the C_3–C_4 bond, giving cis edge-to-face **16b** which can reversibly collapse to **3**. Rotation around the C_2–C_3 bond gives *trans*-**16c** and leads to 1-butene **4**.

Biradical character is indicated by the spontaneous formation of an alternating copolymer identical with that formed by deliberate free-radical-induced copolymerization of **1** and **2**. The copolymer is formed either from the forward reaction of **1** and **2** or in the cycloreversion of **3**. Biradical character for **16** is further supported by the comparable yields of **3** and **4** obtained in polar solvents with those in benzene. Trapping experiments did not succeed, indicating that **16** is highly reactive and too short-lived to trap. (Moreover, the trapping agents used were probably more suitable for zwitterionic than biradical intermediates.)

Scheme III[a]



c, trans (staggered)

a, cis, face to face (eclipsed)

b, cis, edge to face (gauche)

[a] **16a–c**, tetramethylene from **1** and **2**; **17a–c**, tetramethylene from **1** and **10**; **18a–c**, tetramethylene from **1** and **14**; ar, *p*-methoxyphenyl.

Formation of dihydropyran **3** and **12** by internal O-alkylation of an ester is very unusual. Presumably the avoidance of cyclobutane ring strain in the ${}_{\pi}2 + {}_{\pi}2$ cycloadducts is involved. Further work will be reported separately.[15]

Dimethyl cyanofumarate **10** reacts similarly with *p*-methoxystyrene. The biradical nature for tetramethylene intermediate **17** is strongly demonstrated by the spontaneous formation of copolymer **11** even at 25 °C, where no adventitious thermal initiation is possible. As in the case of **2**, dihydropyran formation is kinetically favored, and no cyclobutane forms.

Tetramethyl ethylenetetracarboxylate did not copolymerize with *p*-methoxystyrene even when free-radical initiator was deliberately added, so that in that case we could not test for the biradical nature of tetramethylene **18** by copolymer formation.

Here cis face-to-face **18a** does collapse to cyclobutane adduct because of the additional carbomethoxy substituent. Rotation about the C_3–C_4 bond may be impeded, or **18a** may be favored by a conformational "*gem*-dimethyl effect". Moreover, a 1,3-diaxial carbomethoxy–aryl interaction in a putative dihydropyran may intervene. Rotation around C_2–C_3 is also difficult, as evidenced by failure to form 1-butene.

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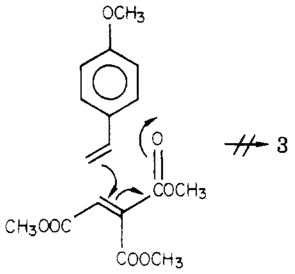
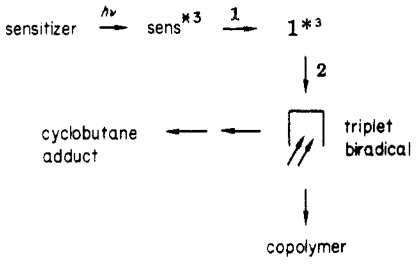
(15) Hall, H. K., Jr.; Rasoul, H. A. A.; Abdelkader, M.; Nogues, P.; Sentman, R. C., submitted for publication in *Tetrahedron Lett.*

Scheme IV



Scheme V



Inasmuch as the stabilizing groups in **18** are identical with those in **16**, trapping experiments failed as before.

The contrast between the results with **2** and **14** shows that the groups at positions 1 and 4 of the tetramethylene do not alone determine its behavior. This can also be seen by contrast with Cram's trimethylene (b) which, although having terminal groups similar to those of tetramethylene **17**, behaved as zwitterion.

Evidence against Dihydropyran Formation by Concerted Cycloaddition. Dihydropyran **3** might form through a hetero-Diels–Alder $_{\pi}2 + _{\pi}4$ cycloaddition. By use of the principle of microscopic reversibility, the retro-Diels–Alder mechanism should occur to form **1** and **2** only. But the opening of **3** in CD_3CN and methanol in the presence of DPPH yielded mostly 1-butene **4**. These results (as well as the spontaneous copolymerizations), seen in both forward and reverse reactions, are against a Diels–Alder mechanism (Scheme IV).

Evidence against Cation Radical Intermediates. Ferric perchlorate[14] and 1,4-dicyanobenzene[13] are well-known to form cation radicals from donor olefins, thermally and photochemically, respectively. Deliberately generated *p*-methoxystyrene cation radicals reacted preferentially with the parent donor olefin to form the corresponding homopolymer or cyclodimer even in the presence of trisubstituted olefin. Only when the known triplet transfer agent 4,4′-dimethoxybenzophenone was added could a low yield of cyclobutane **9** be isolated, clearly by a different mechanism, perhaps (see Scheme V).

This conclusion is supported by recent results of Lewis, Ho, and DeVoe.[16] These investigations examined the cycloaddition of *n*-isobutylpyrrolidine to dimethyl fumarate. Thermal cycloaddition proceeded via a 1,4-zwitterionic tetramethylene, whereas photocyclization proceeded via exciplex and radical ion pair, the former leading to a different cycloadduct than that obtained thermally.

A second criterion also speaks against electron-transfer and ion radical involvement. Because of the known larger electron affinity of CN vs. $COOCH_3$, the rate sequence in that case should be dimethyl cyanofumarate > tetraester > triester. However, this is not observed. Tetraester **14** was less reactive than triester **2**. This is attributed to greater steric hindrance at the β-position of **14**. This is incidental evidence for bond formation and a tetramethylene intermediate, inasmuch as **14** would be more reactive than **2** if a single electron transfer was occurring.

Finally, the high reactivity of **10** compared to **2** can be explained by a flat planar structure for the former,[17] permitting extensive delocalization of radical character.

Zwitterionic Character of Tetramethylene Intermediates. We have stressed the biradical character of tetramethylenes. However, as stated in the beginning of this paper, the tetramethylenes must be regarded as resonance hybrids of a zwitterion and spin-paired biradical.[5]

In the present work zwitterionic character for **18** was demonstrated by the cationic homopolymerization of *p*-methoxystyrene. 1,2-Dichloroethane-promoted homopolymerization is often observed.[18] Because radical copolymerization does not occur between **1** and **14**, homopolymerization, and zwitterionic character, can be detected.

Moreover the rate sequence *p*-(dimethylamino)styrene[10] > *p*-methoxystyrene > styrene supports ionic contributions to the tetramethylenes **16**–**18**.

In our work it is reasonable that *p*-methoxyphenyl, less able to stabilize positive charge, should give a biradical tetramethylene whereas Dunn's tetramethylene[10] from *p*-(dimethylamino)styrene should behave only as a zwitterion.

Experimental Section

Instrumentation. NMR spectra were taken with a Varian T-60 nuclear magnetic resonance spectrometer. Infrared data were obtained from Perkin-Elmer 337 and 710A spectrometers, standardized with polystyrene. Melting points were obtained from a Thomas-Hoover capillary melting point apparatus.

Materials. Aldrich chemicals were used except as otherwise specified.

Reactants. Trimethyl ethylenetricarboxylate (**2**) was synthesized according to Daly's procedure,[12] except that in the synthesis of the intermediate trimethyl 1,1,2-ethanetricarboxylate, before the slurry was poured in ice and water, most of the methanol was removed on a rotary evaporator. The trimethyl ethylenetricarboxylate was obtained pure after distillation and recrystallization from ether in 53.8% yield from the ethane.

Dimethyl cyanofumarate (**10**) was synthesized by following Daly's procedure too. The exception is that the temperature was kept below 0 °C, and, finally, cold hydrochloric acid was added to neutralize the excess of triethylamine. Pure dimethyl cyanofumarate was obtained after distillation and recrystallization from ether in 33.7% yield from dimethyl 1-bromo-1-cyanosuccinate.

Typical Experimental Procedure. In general the reactions were run in a pressure tube and under a nitrogen atmosphere, except in the case of dimethyl cyanofumarate where the reactions were run at ambient pressure and in a 25-mL round-bottomed flask. The polymer was precipitated by anhydrous ether or methanol, redissolved in 2 mL of acetone, reprecipitated by the same solvent, filtered, dried, and finally weighed. The yield of copolymer was calculated from the total weight of the acceptor and donor. After rotoevaporation of methanol or ether, the filtrate mixture was weighed, and an NMR spectrum was taken from which the yield was calculated.

Poly(*p*-methoxystyrene-*alt*-trimethyl ethylenetricarboxylate) (5).[12] To a solution of 4 mmol (0.536 g) of *p*-methoxystyrene and 4 mmol (0.808 g) of triester **2** in 6 mL of benzene was added 10 mg of azobis(isobutyronitrile) (AIBN). The mixture was placed in a pressure tube which was capped and degassed with argon. The reaction mixture was heated to 72 ± 1 °C overnight. The copolymer was precipitated in 50 mL of methanol, filtered, dissolved in 3 mL of acetone, reprecipitated with 30 mL of methanol, and finally washed with 20 mL of

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methanol. The dried copolymer **5** (0.27 g, 20%) was obtained as a white powder: IR (KBr) 2950 (m), 1740 (s), 1600 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.2–3.8 (m, 16 H), 6.35–7.2 (m, 4 H).

Dimethyl 2-(*p*-Methoxyphenyl)-6-methoxy-3,4-dihydro-2*H*-pyran-4,5-dicarboxylate (3). A solution containing 404 mg (2 mmol) of triester **2**, 268 mg (2 mmol) of *p*-methoxystyrene, and 10 mg of DPPH in 3 mL of 1,2-dichloroethane under nitrogen was heated in an oil bath at 70 °C for 20 h. The cooled solution was stirred overnight at 0.5 mm to remove solvent and *p*-methoxystyrene. Ether (20 mL) was added and the solution cooled to −76 °C. After 24 h, crystallization was complete. The ether supernatant was removed with a pipet. The crystalline materials were dissolved in chloroform and passed through a silica gel column to remove polar impurities. The chloroform was rotoevaporated, and the residue was recrystallized from ether at −76 °C to give 0.123 g (18.3%) of dihydropyran **3**: mp 93–94 °C; IR (KBr) 2950 (w, CH), 1730 (m, C=O), 1660 (m, C=CO$_2$), 1610 (s, C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.2 (m, 2 H, CH$_2$), 3.5 (q, 4, J = 10 Hz, 1 H, HCCO$_2$CH$_3$), 3.7, 3.75, 3.8, and 3.85 (4 s, 12 H, OCH$_3$), 5.2 (q, 4, J = 10 Hz, 1 H, HCO), 6.8–7.4 (A$_2$B$_2$, 4 H, aromatic). Anal. Calcd for $C_{17}H_{20}O_7$: C, 60.7; H, 6.0. Found: C, 60.7; H, 5.8.

Trimethyl 1-(*p*-Methoxyphenyl)-1-butene-3,4,4-tricarboxylate (4). The reaction was carried out as above, but at 116 °C. The mixture was cooled and 1,2-dichloroethane was rotoevaporated. The mixture was heated in a vacuum distillation apparatus to 120 °C (0.1 mm), whereupon *p*-methoxystyrene and triester distilled. The residue was cooled, dissolved in chloroform, and passed through a silica gel column, and the solvents were rotoevaporated. Crystallization in 20 mL of ether at −76 °C gave 0.14 g (20.8%) of **4** as a white powder: mp 73–74 °C; IR (KBr) 2950 (w, CH), 1730 (s, C=O), 1610 (m, C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.7, 3.8, and 3.85 (3 s, 13 H, OCH$_3$ and CH), 4.05 (m, 1 H, CH(CO$_2$CH$_3$)$_2$), 5.95 and 6.05 (dd, 2, J = 14 Hz, 1 H, HC=C β to aromatic ring), 6.6 (d, J = 14 Hz, 1 H, C=CH α to aromatic ring), 6.8–7.4 (A$_2$B$_2$, 4 H, aromatic). Anal. Calcd for $C_{17}H_{20}O_7$: C, 60.7; H, 6.0. Found: C, 60.6; H, 6.2.

Trimethyl 1-(*p*-Methoxyphenyl)-1-acetoxy-3,4,4-butanetricarboxylate (6). The reaction was carried out like the previous ones at 75 °C in acetic acid. The mixture was cooled at room temperature, and the solvent and *p*-methoxystyrene were removed under vacuum at room temperature (0.1 mm). The acetate and triester were separated by chromatography. The mixture was dissolved in chloroform and eluted through a silica gel column by a mixture of 50/50 chloroform and pentane, and the solvents were rotoevaporated to yield 0.243 g (30.5%) of the acetate **6** as an oil which was sensitive to heat. (This oil under heat gave the 1-butene **4**): IR (neat) 2925 (w, CH), 1730 (s, C=O), 1660 (w, C=O, α to aromatic ring), 1600 (w, C=C) cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 2.0–2.5 (m, 2 H, CH$_2$), 2.1 and 2.15 (2 s, 3 H, O=CCH$_3$), 3.2 (m, 1 H, HCCO$_2$Me), 3.75–3.9 (4 s, 12 H, OCH$_3$), 3.95 (d, 1 H, HC(CO$_2$Me)$_2$), 5.8 (t, 1 H, HCOC(O)CH$_3$), 6.8–7.42 (A$_2$B$_2$, aromatic). Anal. Calcd for $C_{19}H_{24}O_9$: C, 57.6; H, 6.1. Found: C, 57.1; H, 6.3. The sample lost weight during the analysis at the rate of 6 μg/min. The acetate was heated to give **4** which gave a better analysis.

Trimethyl 1-(*p*-Methoxyphenyl)-2,2,3-cyclobutanetricarboxylate (9). A solution containing 404 mg (2 mmol) of triester **2**, 268 mg (2 mmol) of *p*-methoxystyrene, 226 mg of 4,4′-dimethoxybenzophenone, and 10 mg of DPPH in 4 mL of acetonitrile in a quartz tube was irradiated by UV light at 40 °C (in a UV reactor) for 6 days. The mixture was dripped into 40 mL of methanol to yield a trace of precipitate which is the homopolymer of *p*-methoxystyrene. The solvent was rotoevaporated, and to the mixture was added 50 mL of pentane in which the sensitizer is slightly soluble. The solution is separated from the crystals of 4,4′-dimethoxybenzophenone. To the solution was added 20 mL of dichloroethane, and the solution was left at −76 °C to yield 0.019 g (3%) of cyclobutane adduct after two successive crystallizations: mp 133–134 °C; IR (KBr) 2750 (w, CH), 1730 (s, C=O), 1600 (w, C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.5–3.1 (m, 2 H, CH$_2$), 3.45 (q, 1 H, CH), 3.25, 3.72, 3.76, and 3.88 (4 s, 12 H, OCH$_3$), 4.15 (q, 8, J = 10 Hz, 1 H, CH α to phenyl group), 6.7–7.4 (A$_2$B$_2$, 4 H, aromatic). Anal. Calcd for $C_{17}H_{20}O_7$: C, 60.7; H, 6.0. Found: C, 60.7; H, 5.9.

Methyl 2-(*p*-Methoxyphenyl)-6-methoxy-5-cyano-3,4-dihydro-2*H*-pyran-4-carboxylate (12) and Poly(*p*-methoxystyrene-*alt*-dimethyl cyanofumarate) (11). A solution containing 0.134 g (1 mmol) of **1**, 0.169 g (1 mmol) of **10**, and 0.01 g of DPPH in 1.5 mL of CD$_3$CN in an NMR tube was left for 66.5 h at room temperature. By NMR we observed copolymer, dihydropyran, and starting material. After 118 h the solution was dripped into methanol to yield 0.085 g (28.1%) of copolymer which was separated by filtration. After rotoevaporation of the solvent, we added acetone–pentane (1:100) and placed the solution at −76 °C to yield 0.102 g (33.7%) of crystals of **12**, which melted at room temperature and copolymerized when left at room temperature overnight. For **12**: IR (neat) 2950 (w, CH), 2200 (w, CN), 1730 (m, C=O), 1660 (m, C=CO$_2$), 1610 (s, C=C) cm^{-1}; ^{1}H NMR 2.08–2.4 (m, 2 H, CH$_2$), 3.08–4.4 (m, 10 H, OMe and HCCO$_2$Me), 5.1 (q, 1 H, 4, J = 8 Hz, CH), 6.8–7.5 (m, 4 H, aromatic). For copolymer **11**: IR (KBr) 2950 (w, CH), 1730 (s, C=O), 1600 (m, C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.45–2.7 (m, 3 H), 2.85–3.6 (m, 1 H, HCCO$_2$CH$_3$), 3.6–3.9 (m, 6 H, OCH$_3$), 6.45–7.10 (m, 4 H, aromatic).

Dimethyl 1-(*p*-Methoxyphenyl)-1-methoxy-4-cyano-3,4-butanedicarboxylate (13). Dimethyl cyanofumarate (0.169 g, 1 mmol) was dissolved in 2 mL of 1,2-dichloroethane, to which was added (0.5 g, 5 mmol) of maleic anhydride. Separately 0.134 g (1 mmol) of *p*-methoxystyrene was dissolved in 2 mL of 1,2-dichloroethane. The two solutions were mixed and allowed to react at room temperature (28 °C) for 119 h. The reaction was quenched with 50 mL of methanol; no precipitation occurred. The solution was left at 28 °C for a few days, and then the solvent was rotoevaporated. We isolated **13** from the mixture by high-pressure chromatography on a silica gel column with pentane/chloroform (50/50): 0.174 g (51.9%); an oil; IR (neat) 2950 (m, CH), 1730 (s, C=O), 1610 (m, C=C); ^{1}H NMR (CDCl$_3$) δ 1.9–2.3 (m, 2 H, CH$_2$), 3 and 3.1 (s, 3 H, OCH$_3$ α to phenyl), 3.25–3.5 (m, 1 H), 3.6–3.9 (s, 9 H, OCH$_3$), 4–4.25 (m, 2 H), 6.7–7.25 (A$_2$B$_2$, 4 H, aromatic). Anal. Calcd for $C_{17}H_{21}O_6N$: C, 60.9; H, 6.3; N, 4.2. Found: C, 61.0; H, 6.3; N, 3.9.

Tetramethyl 1-(*p*-Methoxyphenyl)-2,2,3,3-cyclobutanetetracarboxylate (15). A mixture of 268 mg (2 mmol) of *p*-methoxystyrene and 520 mg (2 mmol) of tetraester **14** was placed in a pressure tube which was capped and heated to 116 °C for 65.5 h. The mixture was dissolved in 20 mL of ether to remove unreacted tetraester crystals, and then the unreacted *p*-methoxystyrene was removed under vacuum (0.1 mm) at room temperature. The cyclobutane was crystallized twice from ether to yield 73 mg (9.3%) of white crystalline **15**: mp 136–137 °C; IR (KBr) 2950 (m, CH), 1740 (s, C=O), 1610 (m, C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.35–2.7 (q, 8, J = 12 Hz, 2 H, CH$_2$), 3.3, 3.78, and 3.85 (3 s, 15 H, OCH$_3$), 4.4–4.75 (q, 8, J = 12 Hz, 1 H, CH), 6.75–7.4 (A$_2$B$_2$, 4 H, aromatic). Anal. Calcd for $C_{19}H_{22}O_9$: C, 57.9; H, 5.6. Found: C, 58.3; H, 5.8.

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Registry No. **1**, 637-69-4; **2**, 51175-48-5; **3**, 77321-34-7; (*E*)-**4**, 77321-35-8; **5**, 77321-32-5; **6**, 77321-36-9; **7**, 24936-44-5; *cis*-**8**, 52498-14-3; *trans*-**8**, 52498-15-4; **9**, 77321-37-0; (*E*)-**10**, 54797-29-4; **11**, 77321-33-6; **12**, 77321-38-1; **13**, 77400-16-9; **14**, 1733-15-9; **15**, 77321-39-2.