washed with ether, acidified with concentrated hydrochloric acid, and extracted with ether. The combined ether extracts were concentrated under reduced pressure to give 197 mg of a tan solid. This material was purified by silica gel preparative thick-layer chromatography using a 40% ethyl acetate–hexane solution as the eluent to give 189 mg (82%) of 2,4′-biphenyldiol (**46**): mp 162–163 °C (lit.[56] mp 162–163 °C); IR (KBr) 3490 (br), 3360 (br), 1600, 1525, 1500, 1450, 1425, 1390, 1360, 1335, 1280, 1250, 1200, 1180, 1110, 840, and 770 cm^{-1}; NMR (360 MHz, $CDCl_3$) δ 4.86 (br s, 1 H), 5.13 (br s, 1 H), 6.92–7.00 (m, 4 H), 7.18–7.25 (m, 2 H), and 7.33–7.38 (m, 2 H); UV (95% ethanol) 291 (ϵ 2450) and 256 nm (3320). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.08; H, 5.26.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health. Use of the high field NMR spectrometer used in these studies was made possible through a NSF equipment grant.

Registry No. **3**, 54487-06-8; **3** (acid), 935-13-7; **3** (acid chloride), 54536-91-3; **5**, 54487-07-9; **8**, 105456-74-4; **9**, 117040-60-5; **10**, 117040-61-6; **11**, 105456-75-5; **11** (acid), 1456-08-2; **12**, 117040-62-7; **13**, 105456-77-7; **13** (acid), 92038-98-7; **14**, 113541-28-9; **15**, 113541-29-0; **16**, 117040-63-8; **16** (acid), 2745-26-8; **18**, 117040-64-9; **19**, 59554-98-2; **19** (acid), 5928-51-8; **20**, 117040-65-0; **21**, 58095-45-7; **22**, 105456-82-4; **22** (acid), 90048-04-7; **24**, 105456-83-5; **25**, 7339-87-9; **25** (2,4-dinitrophenyl hydrazone), 107455-76-5; **26**, 117040-66-1; **26** (acid), 16378-06-6; **27**, 117040-67-2; **28**, 117040-68-3; **30**, 10546-79-9; **30** (acid), 21683-86-3; **31**, 105456-80-2; **33**, 69888-44-4; **34**, 117040-69-4; **37**, 105456-81-3; **38**, 117040-70-7; **38** (acid), 91962-99-1; **39**, 117040-71-8; **40**, 117040-72-9; **41**, 117040-73-0; **42**, 105456-84-6; **42** (acid), 15433-88-2; **43**, 105456-85-7; **44**, 105456-86-8; **46**, 611-62-1; $Rh_2(OAc)_4$, 15956-28-2; $CH_2(CO_2H)_2$, 141-82-2; 3-formylbenzofuran, 4687-25-6; 3-(3-benzofuryl)acrylic acid, 114949-09-6.

Supplementary Material Available: Experimental details for the preparation of 3-(3-furyl)propionic acid as well as the final positions and thermal parameters of the X-ray analysis of 1,2-dihydrocyclopenta[*b*][1]benzopyran-3(9*H*)-one (**37**) (5 pages). Ordering information is given on any current masthead page.

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Selectivities in the Addition of Radicals Generated from Derivatives of 2-Bromomalonic Acid to Alkene Pairs[1]

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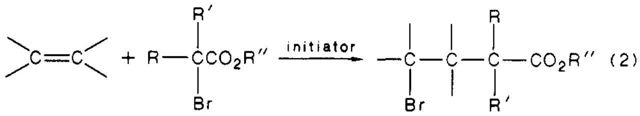
Direct competitions between 1-octene and three symmetrical tetraalkylethylenes for free radicals generated from derivatives of 2-bromomalonic acid were investigated. Despite the fact that these radicals are all electrophilic in nature, the less electron rich terminal alkene undergoes preferred reaction in many instances. This is principally caused by the steric demands of the attacking radical. Variation in both steric and electronic factors, however, lead to a wide range of relative reactivities.

The last decade has observed a renewed interest in the development of free-radical reactions suitable for synthetic purposes. The formation of carbon–carbon bonds by the addition of carbon free radicals to unsaturated molecules has received particular attention.[2] Several of these processes show stereospecificity as well as the expected regiospecificity and have been utilized in the synthesis of complex natural products.[3,4] Despite this resurgence of interest, and the fact that such radical additions were initially characterized over 50 years ago by Kharasch and his co-workers,[5] the factor(s) mainly responsible for the regiochemistry of the rate-determining step (eq 1) still remain controversial. Is this preferred addition to the

$$RCH{=}CH_2 + Z^\bullet \rightarrow R\dot{C}HCH_2Z \qquad (1)$$

terminal end of the double bond associated with the electronic factors that make a secondary radical more stable than its primary counterpart, or, rather, is this the result of steric factors that make the terminal position more accessible? In all probability both must play some role. Tedder and Walton have suggested that several factors are operative in this process.[6] This view has been further substantiated by Giese[7] and by Münger and Fischer.[8]

Recent results obtained in this laboratory were also relevant to this question.[9] The esters of 2-bromo carboxylic acids add readily to alkenes via a radical pathway (eq 2).[10] In competitive additions between 1-methyl-



$$\mathrm{{>}C{=}C{<}} + R-\overset{R'}{\underset{Br}{C}}CO_2R'' \xrightarrow{\text{initiator}} -\underset{Br}{C}-C-\overset{R}{\underset{R'}{C}}-CO_2R'' \qquad (2)$$

cyclohexene and 1-octene for a series of carbethoxyalkyl radicals, it was observed that the former compound always underwent preferential reaction. This was somewhat surprising as most of these carbethoxyalkyl radicals show modest nucleophilic character.[9] These results were rationalized in terms of the relative position of the transition

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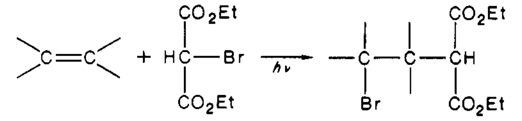
state along the reaction coordinate. The alkene pair used in the above case might not be optimal, however, since potential steric hindrance is not maximized in the asymmetrically trisubstituted double bond of 1-methylcycohexene.

Concurrently with the above experiments, Boldt and co-workers investigated the reactivities of several alkenes toward radical addition of bromomalononitrile.[11] Absolute values of rate constants were carefully obtained. The authors chose to correlate their findings with the superdelocalizabilities of the starting alkene. This is essentially a parameter associated with the ground state of the unsaturated molecule. Its use could be justified on the assumption that free radical additions should have relatively early transition states.[12] Calculations for the addition of methyl radical to ethene[13] and propene[14] indicate only slight perturbation of the alkene structure in the transition state. It would be expected, however, that changing either the inherent electronic stability or the steric demands of the attacking radical could lead to a later transition state. Tricyanomethyl radical is known to be a particularly persistent species.[15] The dicyanomethyl radical is less persistent. It has been reported to undergo dimerization at close to the diffusion-controlled limit.[15] It should still, however, be a more stable species than methyl. It has been observed that even a single cyano group can markedly favor radical formation at an adjacent position.[16] Dicyanomethyl radical is also of relatively small size. The results of Boldt et al. have been interpreted as being indicative of little steric control in their system.[11] It would be expected, however, that this attacking radical will have only modest steric requirements. It is interesting to note that the series (*Z*)-2-pentene, (*Z*)-4-methyl-2-pentene, and (*Z*)-4,4-dimethyl-2-pentene shows decreasing relative reactivities of 1:0.36:0.21. The regiochemistry of addition of dicyanomethyl radical to the latter two of these systems is contrary to the predictions based upon superdelocalizability. Both of these observations argue that some steric control is operative even with this relatively small attacking radical.

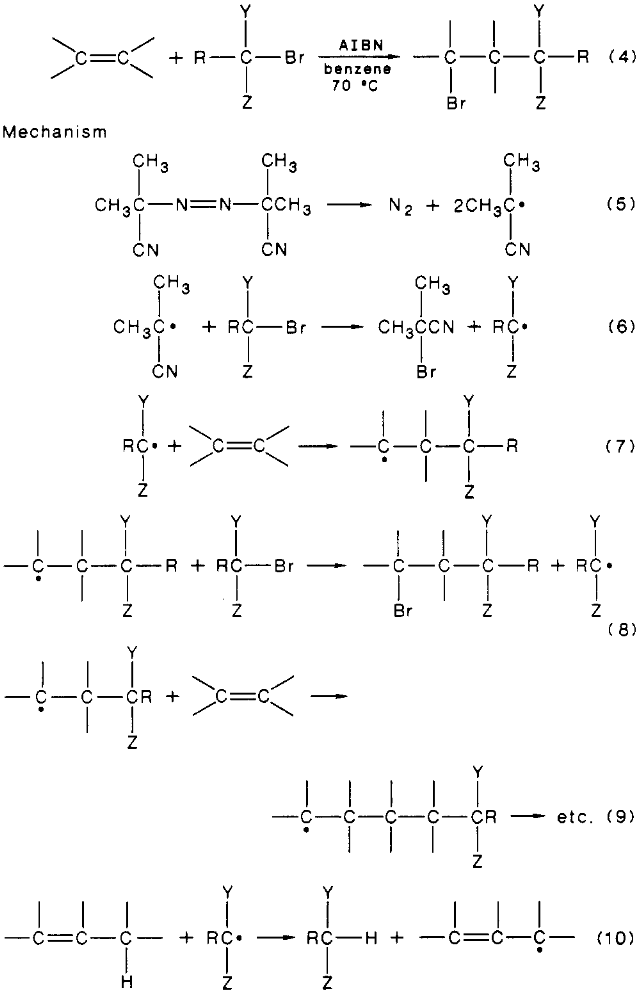
Giese, Horler, and Leising have investigated the addition of the related dicarbethoxymethyl radical, generated from diethyl 2-bromomalonate, to alkenes (eq 3).[17] This radical was shown to be an extremely electrophilic species. One would expect even greater electrophilicity for the dicyanomethyl radical. Replacement of the hydrogen on the radical carbon by an alkyl group might decrease the degree of electrophilic character of the radical as well as lead to an increased stabilization due to a captodative effect.[18] Such radicals should still be electrophilic in nature.

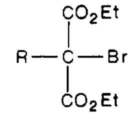


$$\mathrm{>C{=}C<} + \mathrm{HC(CO_2Et)_2Br} \xrightarrow{h\nu} \mathrm{-C(Br)-C-CH(CO_2Et)_2} \qquad (3)$$

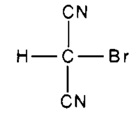
The present paper will describe the results of direct competition between pairs of alkenes for the radicals generated from diethyl 2-bromomalonate, **1a**, three diethyl 2-alkyl-2-bromomalonates, **1b–d**, 2-bromomalonitrile, **2**, and ethyl bromocyanoacetate, **3**. All the radicals formed from these precursors should be electrophilic as discussed above. The radical generated from **3** would predictably possess both an electrophilicity and steric demands intermediate between the corresponding radicals formed from **1a** and **2**.

Scheme I

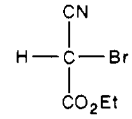




1a, R = H
b, R = CH_3
c, R = CH_3CH_2
d, R = $(CH_3)_2CH$



2



3

Three symmetrical tetraalkylethylenes were competitively reacted against 1-octene for the bromo esters and bromo nitriles shown above. Reactions were carried out at 70 °C in benzene solution under a nitrogen atmosphere at reduced pressure. AIBN was used to initiate the reaction. An internal standard (chlorobenzene, bromobenzene, or 1,2-dichlorobenzene) necessary for subsequent GLC analyses was present in all samples. Scheme I shows the generalized overall reaction (eq 4) and the key steps of the mechanistic sequence. Initiation of the chain reaction is shown in eq 5 and 6 while eq 7 and 8 describe the propagating steps. Possible telomerization (eq 9) was militated aginst by the presence of a large excess of radical precursor, which should favor process 8. Good material balance between connsumption of total alkene and radical precursor indicates that polymerization does not appre-

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Table I. Relative Reactivities of Tetramethylethylene/1-Octene toward Various Radicals at 70 °C

radical	(precursor)	k_{rel}	no. of runs
$H\dot{C}(CN)_2$	(**2**)	5.77 ± 0.28	5
$H\dot{C}(CN)CO_2Et$	(**3**)	2.96 ± 0.15	6
$H\dot{C}(CO_2Et)_2$	(**1a**)	0.76 ± 0.03	6
$Me\dot{C}(CO_2Et)_2$	(**1b**)	0.35 ± 0.02	6
$Et\dot{C}(CO_2Et)_2$	(**1c**)	0.08 ± 0.02	4
$i\text{-}Pr\dot{C}(CO_2Et)_2$	(**1d**)	0.11 ± 0.03	5

Table II. Relative Reactivities Tetraethylethylene/1-Octene toward Various Radicals at 70 °C

radical	(precursor)	k_{rel}	no. of runs
$H\dot{C}(CN)_2$	(**2**)	1.27 ± 0.03	5
$H\dot{C}(CN)CO_2Et$	(**3**)	*a*	
$H\dot{C}(CO_2Et)_2$	(**1a**)	0.08 ± 0.04[b]	6
$Me\dot{C}(CO_2Et)_2$	(**1b**)	$<4 \times 10^{-3}$	6

[a] Indeterminable due to poor GLC separation. Allylic hydrogen atom abstraction may predominate. [b] Corrected value; 88 ± 4% of total reactivity due to allylic hydrogen atom abstraction.

ciably occur. Allylic hydrogen atom abstraction (eq 10) was not expected to be an important competing reaction since it had not been observed in prior studies.[5,9,11,17] To our surprise, this process became a major pathway of reaction for certain of the systems investigated.

Tetramethylethylene, TME (2,3-dimethyl-2-butene), is the smallest of the tetraalkylethylenes investigated. In competitive reaction with 1-octene for the series of radicals discussed above, a reactivity range of over 50 was observed. With dicyanomethyl radical as the attacking species, TME was nearly 6 times more reactive than 1-octene. While neither of these alkenes were investigated by Boldt et al., we feel that the above value compares favorably with that of approximately 15 for the relative reactivity of 2,3-dimethyl-2-pentene to 1-pentene, which they observed if differences in temperature are taken into consideration.[11] As the steric demands of the attacking radical increases, there is a corresponding increase in the tendency to react at the terminal double bond of 1-octene. In considering the entire series, this must be considered as a reversal, not a loss, of selectivity. No allylic hydrogen atom abstraction was observed in the reactions involving this pair of alkenes. Data for these relative reactivities are found in Table I.

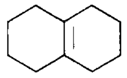
Tetraethylethylene, TEE (3,4-diethyl-3-hexene), should have a much less accessible double bond. The relative reactivities of the TEE/1-octene system are given in Table II. TEE is virtually unreactive with **1b**. It was, therefore, decided not to investigate systems that would involve even bulkier radicals. In reaction with the dicyanomethyl radical, TEE is only slightly (ca. 27%) more reactive than 1-octene. It is felt that the decrease in selectivity is attributable to steric factors. To our initial surprise, the predominent reaction of TEE with the radicals derived from **1a** and **3** was allylic hydrogen atom abstraction. In the former instance ca. 88% of TEE disappeared by this pathway. It is reasonable to expect that the secondary allylic hydrogen atoms in TEE are much more labile than their primary counterparts in TME. The analogous benzylic systems have been studied in detail. Ethylbenzene exhibits greater hydrogen atom lability than toluene. Depending upon the identity of the abstracting agent, the relative reactivities of these compounds may reach a value of 50.[19] When this factor is reinforced by the relative accessibilities of the double bonds in the alkenes under consideration, an explanation for preferred allylic hydrogen atom abstraction from TEE presents itself. Huyser has noted similar effects in the reaction of alkenes with the radical(s) generated from bromotrichloromethane.[20]

Table III. Relative Reactivities Δ^9-Octalin/1-Octene toward Various Radicals at 70 °C

radical	(precursor)	k_{rel}	no. of runs
$H\dot{C}(CN)_2$	(**2**)	4.42 ± 0.21	5
$H\dot{C}(CN)CO_2Et$	(**3**)	2.40 ± 0.14	6
$H\dot{C}(CO_2Et)_2$	(**1a**)	0.82 ± 0.06[a]	5
$Me\dot{C}(CO_2Et)_2$	(**1b**)	0.38 ± 0.03	6
$Et\dot{C}(CO_2Et)_2$	(**1c**)	0.15 ± 0.03	6

[a] Corrected value; 34 ± 2% of total reactivity due to allylic hydrogen atom abstraction.

The steric accessibility of a double bond may be increased by its incorporation into a cyclic unit. Huyser, for example, has observed in this study of the reaction of alkenes with bromotrichloromethane that the addition/allylic hydrogen atom abstraction ratio of 3.5 in 3-heptene is increased to 5.5 in cycloheptene.[20] With precidents such as this in mind, the reactivities of Δ^9-octalin (1,2,3,4,5,6,7,8-octahydronaphthalene), 4, relative to 1-octene were obtained for our series of radicals. Results are presented in Table III. Although the double bond in this alkene should be electronically equivalent to that in TEE, its pattern of reactivity much more closely resembles that found for TME. This is attributed to the greater steric accessibility of the double bond in the rigid system. This effect also leads to a decrease in the amount of allylic hydrogen atom abstraction by the dicarbethoxymethyl radical relative to that observed for TEE.



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While we have chosen to emphasize steric factors in rationalizing our observations, it must be admitted that slight electronic differences exist among the radicals utilized. To partially evaluate this effect, we prepared the di-*tert*-butyl ester of 2-bromomalonic acid. Direct competition between TME and 1-octene for the radical generated from this precursor yields a relative reactivity of 0.18 ± 0.03. The corresponding diethyl ester was much less selective, showing a relative reactivity of 0.76 ± 0.03. The greater selectivity of the former system is unlikely to be due to electronic factors as the point of structural variation is three atoms removed from the radical site.

It is felt that these results illustrate the predominance of steric factors in controlling the additions of bulky radicals to tetraalkylethylenes. The relative importance of steric and electronic factors in controlling radical addition to less hindered double bonds should be variable. Also, the inherent steric and electronic demands of the attacking radical must greatly influence these variable effects.

Experimental Section

Materials. With the exception of di-*tert*-butyl 2-bromomalonate, all radical precursors were prepared by direct bromination of commercially available compounds.[21-23] Solvent, internal GLC standards, AIBN, 1-octene, and tetramethylethylene were

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purchased. All were purified before use and exhibited physical properties in agreement with literature values. Δ^9-Octalin was prepared[24] and purified[25] by procedures in the literature. Tetraethylethylene was prepared by a modified Eastwood procedure.[26] Physical properties agreed with literature values, and proton NMR indicated no spurious signals.

The di-*tert*-butyl ester of 2-bromomalonic acid was prepared from the nonbrominated ester. This, in turn, was prepared from the acid by the method of Raha.[27] The bromination was carried out by the procedure developed by Hori et al.[28] The yield was 60%. The following physical properties were observed: bp 62 °C (1 Torr); $n^{21}{}_{\mathrm{D}}$ 1.4437; ^{1}H NMR (CDCl$_3$) δ 1.45 (s, 18 H), 4.6 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 163.32 (s), 83.54 (s), 45.43 (s), 27.44 (s); IR (KBr) 1756 cm^{-1} (C=O); MS, *m/e* 297, 295 (M$^+$), 241, 239 (M$^+$ - C$_4$H$_8$).

Determination of Selectivities. A standard competitive kinetic approach was used.[29] Stock solutions of a tetraalkylethylene, 1-octene, radical precursor, internal GLC standard, AIBN (radical chain initiator), and benzene (solvent) were prepared in approximate relative molar ratios of 1:1:4:1:0.1:13. The solution was divided among several reaction tubes. Air was removed from the samples by repeated freeze–thaw cycles. Tubes were sealed while samples were under a nitrogen atmosphere at reduced pressure. One tube was reserved as a starting mixture sample and the remainder were put in a 70.0 ± 0.1 °C constant-temperature bath for times varying from 4 to 90 h. Relative rates of disappearance of the two competing alkenes were determined by GLC evaluation of relative concentrations. All GLC analyses were carried out on a Varian 200 chromatograph. A 15 ft × $^1/_4$ in. packed column of 5% SE-30 on Cromosorb-W was used throughout this study. The reaction times employed corresponded to 4–90% disappearance of each alkene in any given run.

Acknowledgment. One of us (A.J.A.) wishes to express gratitude to the Oregon State University Undergraduate Honors Program for providing financial support.

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Preparations and Reactions of Symmetrical Dimethylenebiphenyl Dianions; Conformations of [0.*n*]-*o*-Cyclophanes. A Simple NMR Method for Determining Twist Angles in Biphenyls†

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With *n*-butyllithium/potassium *tert*-butoxide, a proton is removed from each methyl group of the symmetrical dimethylbiphenyls to give dianions in good yield. The reactions of these dianions with alkyl halides, dialkyl sulfates, trimethylchlorosilane, trimethylchlorogermane, α,ω-dihalides, and oxidizing agents were found to provide the best routes to many symmetrically substituted biphenyls, including [0.*n*]- and [0.*n*.0.*n*]cyclophanes. NMR and molecular mechanical studies of some of these cyclophanes gave information on their preferred conformations. An NMR method for determining the angle of twist in biphenyls from the chemical shifts of the ortho hydrogens is developed.

Preparation and Reactions of Dianions from the Dimethylbiphenyls. Dianions formed from the xylenes by the removal of a proton from each methyl group are useful intermediates for the preparation of symmetrically substituted benzenes, [*n*]cyclophanes, and [*n*.*n*]-cyclophanes.[3] We now report that analogous preparations of dianions **1** from the symmetrical dimethylbiphenyls **2a** followed by reactions with similar electrophiles and oxidizing agents provide in most cases the best routes to biphenyl derivatives **2b–i**, [0.*n*]cyclophanes **3**, [0.*n*.0.*n*]-cyclophanes **4**, and miscellaneous cyclophanes **5–8** (Chart I). In a related study, dianion *o*-**1** with lithium and magnesium rather than potassium counterions was prepared from *o*-**2a** and reacted with Me$_2$SiCl$_2$ to give a good yield of **5**.[4]

Our yields are given in Table I. The Me$_2$SO$_4$ and Et$_2$SO$_4$ reactions indicate the yields of each of the dianions **1** to be at least 84%.[5] Monoalkylated products **9** can arise either from undermetalation or from the dianion **1** obtaining a proton and an alkyl group rather than the desired two alkyl groups. The yield dropped considerably with the secondary halide *i*-PrBr, with electron transfer possibly becoming the predominant mechanism. With *t*-BuI, dialkylation (presumably entirely by electron transfer) rose to a respectable 44% in the para case, but, due to severe steric interactions, no di- or even monoalkylation product was detected in the ortho case. Instead, oxidation to

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† Dedicated to George H. Büchi on his 65th birthday.

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[5] These dianions have calculated resonance energies per atom (REPA's) of 0.068, 0.067, and 0.070, respectively (kindly provided by B. A. Hess and L. J. Schaad), which suggest that they should be readily preparable; see Bates et al. (Bates, R. B.; Hess, B. A.; Ogle, C. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052) for REPA's for many other delocalized dianions.