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(*E*,*E*)-(η^6:η^6-1,4-Diphenyl-1,3-butadiene)bis(tricarbonylchromium) Dianion. Study of Its Chemistry and Reactivity

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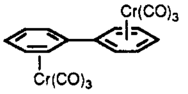
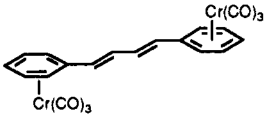
Reduction of (*E*,*E*)-(η^6:η^6-1,4-diphenyl-1,3-butadiene)bis(tricarbonylchromium) (1) with lithium naphthalenide followed by reaction with alkyl halides and acyl chlorides yields 1,4-dialkylated and 1,4-diacylated 1,4-diphenyl-2-butenes after oxidative cleavage of the chromium tricarbonyl moieties. The addition takes place exclusively in the 1,4-(benzylic) positions, resulting in a pair of diastereomers. The most likely mechanism involves an exo benzylic carbanion type attack of the dianion rather than a metal-assisted endo addition. Reaction of the dianion 2 with cyclopropylcarbinyl bromide and 6-bromo-1-hexene supports an inner-sphere polar S_N2 mechanism. Alkylation with long-chain electrophiles bearing polar and nonpolar functionalities opens up a convenient route to the preparation of potential monolayer-forming substances. Protonation with trifluoroacetic acid results in the formation of *trans*-1,4-diphenyl-2-butene.

Introduction

Since Dessy's original report on some of the redox properties of (η^6-benzene)tricarbonylchromium,[1] considerable interest regarding the generation of anionic species derived from (η^6-arene)tricarbonylchromium complexes has developed in recent years. Methods employed to date have varied from proton abstraction[2] to nucleophilic addition[3] to direct electrochemical reduction.[4] The structural aspects of this species, as well as the reactivity of (η^6-benzene)$Cr(CO)_3$ toward nucleophiles, have been thoroughly examined by Semmelhack, Kundig, and others.[3] While this study of the mono complexes of arenes has been well established, the study of the reactivity and reductive behavior of the bis complexes of arenes and other unsaturated compounds has been relatively new and is gaining rapid interest.[4i-k,5]

Table I. Electrochemical Results

compd[a]	$E_{1/2}$,[b] V	$E_{3/4} - E_{1/4}$,[c] mV	i_d, mA
	−1.606	30	2.60
	−1.407	20	1.80

[a] Approximately 3 mmol in propylene carbonate, 0.2 M TEAP, 0 °C, on the DME. [b] vs the Ag/AgCl, saturated NaCl(aq) reference electrode, ±0.005 V. [c] Values of $E_{3/4} - E_{1/4}$, on the order of 30 mV are indicative of a two-electron process.

We have been actively involved in the chemistry of the (arene)tricarbonylchromium complexes that undergo reductive rearrangements ($\eta^6 \rightarrow \eta^5$ and $\eta^6 \rightarrow \eta^4$). Previous work[4i,j,5] showed that the bis(tricarbonylchromium) complexes of biphenyl compounds reduced electrochemically by one electron per tricarbonylchromium group to give dianions which were stable under anhydrous, oxygen-free conditions. The electrochemical behavior of these conjugated bis complexes was found to be in marked contrast to the mono complexes of naphthalene[4k] and other monosubstituted (η^6-benzene)$Cr(CO)_3$ complexes where the reductions were by two electrons per $Cr(CO)_3$ group. The unusual stability of these dianions was attributed to a haptotropic rearrangement of (η^6:η^6-biphenyl)$[Cr(CO)_3]_2$ to a bis(η^5-cyclohexadienylidene)$[Cr(CO)_3]_2$ structure in which the η^5-cyclohexadiene rings maintained considerable conjugation throughout the connecting π system.

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(2) (a) Gracey, D. E. F.; Jackson, W. R.; Jennings, W. B.; Remmison, S. C.; Spratt, R. J. *J. Chem. Soc. B* **1969**, 1210. (b) Nicholas, K. M.; Kerber, R. C.; Steifel, E. I. *Inorg. Chem.* **1971**, *10*, 1519. (c) Ceccon, A.; Catelani, G. *J. Organomet. Chem.* **1974**, *72*, 179. (d) Ceccon, A. *J. Organomet. Chem.* **1974**, *72*, 189. (e) Jaouen, G.; Meyer, A.; Simmonneaux, G. *J. Chem. Soc., Chem. Commun.* **1975**, 813. (f) des Abbayes, H.; Boudeville, M. *J. Org. Chem.* **1977**, *42*, 4104. (g) Simmoneaux, G.; Jaouen, G. *Tetrahedron* **1979**, *35*, 2249. (h) Nesmeyanov, A. N.; Ustynyuk, N. A.; Novikova, L. N.; Rybina, T. N.; Ustynyuk, A.; Oprunenko, Y. F.; Trifonova, O. I. *J. Organomet. Chem.* **1980**, *184*, 63. (i) Ustynyuk, N. A.; Lokshin, B. V.; Oprunenko, Y. F.; Rozynatovsky, V. A.; Luzikov, Y. N.; Ustynyuk, Y. A. *J. Organomet. Chem.* **1980**, *202*, 279. (j) Brocard, J.; Couturier, D. *J. Chem. Soc., Chem. Commun.* **1981**, 1264. (k) Masters, N. F.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 955. (l) Jaouen, G.; Top, S.; Laconi, A.; Couturier, D.; Brocard, J. *J. Am. Chem. Soc.* **1984**, *106*, 2207. (m) Jaouen, G. *Pure Appl. Chem.* **1986**, *58*, 597. (n) Brocard, J.; Lebibi, J. *J. Organomet. Chem.* **1986**, *310*, C63. (o) Dickens, P. J.; Gilday, J. P.; Negri, J. T.; Widdowson, D. A. *Pure Appl. Chem.* **1990**, *62*, 575.

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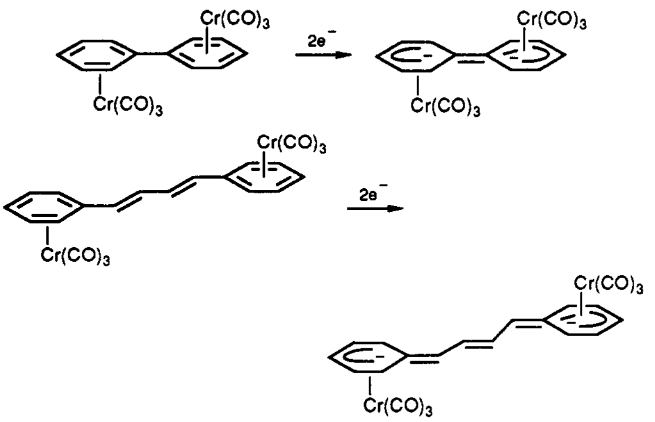


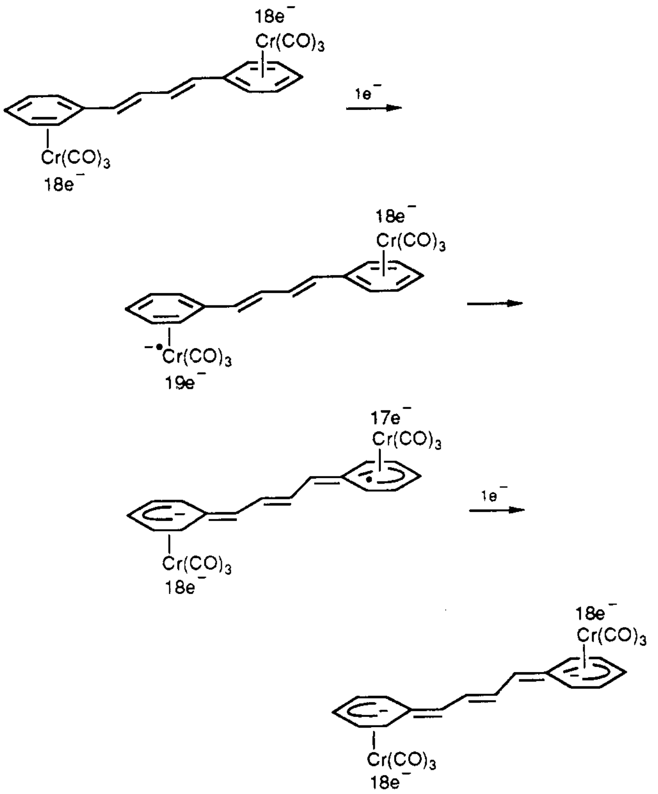
A similar behavior in this reductive rearrangement was further observed when this study was extended to the bis complexes of a long-chain conjugate system, viz. the bis(tricarbonylchromium) complexes of (E,E)-1,4-diphenyl-1,3-butadiene. Our initial report[6] indicated that these systems, upon chemical reduction, gave dianions which reacted smoothly with a variety of electrophiles to give an alkylated complex which, after decomplexation of the metallic moieties, gave good yields of disubstituted diphenyl butenes. In this paper, we wish to report on the electrochemistry, reactivity, and the synthetic utility of the dianions obtained from (E,E)-(η^6:η^6-1,4-diphenyl-1,3-butadiene)[Cr(CO)$_3$]$_2$ (1).

Results and Discussion

The preparation of 1 was carried out by standard methods.[7] (E,E)-1,4-diphenyl-1,3-butadiene and chromium hexacarbonyl were refluxed under argon for 5 days in a 10% solution of THF in n-butyl ether. The bis complex 1 was isolated by subliming off the unreacted chromium hexacarbonyl at 55 °C (3 mm) and the mono complex (E,E)-(1,4-diphenyl-1,3-butadiene)(Cr(CO)$_3$) at 165 °C (0.3 mm). Dissolving the bright red solid in THF followed by filtration through Celite to remove any decomposed material gave deep maroon-colored crystals of pure 1 in a 64% yield.

Nonaqueous electrochemical studies, cyclic voltametry, and polarography of 1 showed that it exhibited reductive characteristics very similar to other conjugated (arene)-bis(tricarbonylchromium) systems. The features of electrochemical reduction such as $E_{3/4} - E_{1/4}$ indicated that the reduction process involves a total of two electrons, one electron per chromium tricarbonyl group (Table I). The less negative reduction potential $E_{1/2} = -1.407$ V, relative to $E_{1/2} = -1.606$ V for the (η^6:η^6-biphenyl)[Cr(CO)$_3$]$_2$ complex, is due to the additional conjugation introduced through the four-carbon diene chain between the two –Cr(CO)$_3$ complexed phenyl rings. The cyclic voltammograms were found to be chemically reversible, demonstrating that the resulting dianion was persistent on that time scale. The i_a/i_c ratio at 0 °C was 0.8315 at a sweep rate of 100 mV/s.[8] The mechanism postulated for the two-electron reduction of 1 would thus be identical with the ECE process proposed for the (η^6:η^6-biphenyl)[Cr(CO)$_3$]$_2$ system[4i,j,5] (Scheme I).

Scheme I



Chemical reduction of 1 to generate dianion 2 was carried out by using lithium naphthalenide in THF. In a typical reaction, lithium naphthalenide in THF (2.7 equiv) was transferred under argon at –78 °C to a solution of 1 in THF/HMPA (ratio 6:1). An instantaneous color change from cherry red to a dark brown solution was observed. However, unlike the case of the biphenyl system where the dianion was stable and easily precipitated out as a fine brown powder, the dianion of 1 was soluble and did not precipitate out of solution. No solid precipitate was obtained even when the reaction mixture was brought up to room temperature. While acyl chlorides caused an instantaneous color change from dark brown to pale brown, the color change observed upon the addition of alkyl halides took place over the course of a few minutes. The color of the reaction mixture eventually faded completely to a pale orange or yellow above 0 °C. Decomplexation of the chromium tricarbonyl moieties was then accomplished by the addition of iodine at –78 °C.

Attempts to characterize the structure of the dianion by NMR spectroscopy failed due to difficulties in handling these unstable solutions. Infrared spectroscopy proved to be more useful. An infrared spectrum of the dark brown solution obtained after reduction in THF was determined. The two sharp IR bands observed at 1962 and 1893 cm^{-1} for 1 disappeared upon formation of the dianion, while new bands appeared at 1904, 1814, and 1795 cm^{-1}. The observed new frequencies were totally consistent with the formation of the dianion and were similar to several analogues.[5b] Furthermore, the increase in the number of IR-active carbonyl bands from two to three suggests a lowering of symmetry at the chromium atoms and is also consistent with the proposed η^6 to η^5 rearrangement.[9,10]

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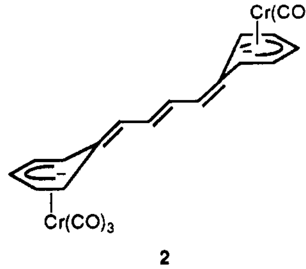
[7] (a) Feldkimel, M.; Cais, M. *Tetrahedron Lett.* **1961**, 444. (b) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1979**, *182*, 381. (c) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154.

[8] This number was complicated by adsorptions and therefore is not very accurate.

[9] For a theoretical discussion of geometrical deformation from planarity in η^5-cyclohexadienyl complexes, see: Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

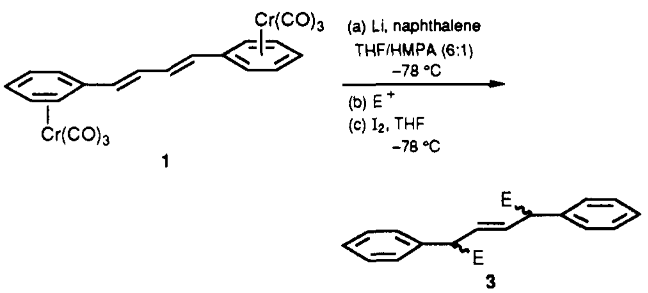


2

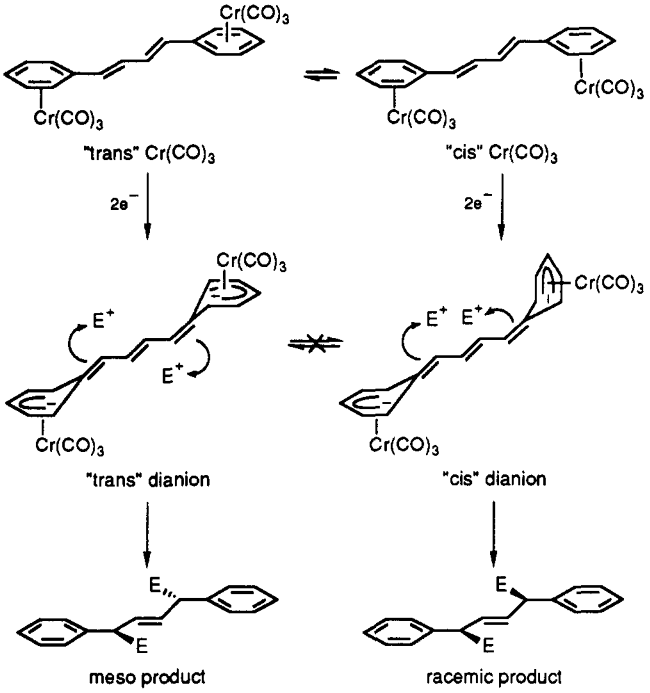
The proposed structure of 2 would be analogous to the biphenyl dianion with two distorted bis(η^5-cyclohexadienyl)tricarbonylchromium units connected by a conjugated four-carbon π system. The out of plane bending of the (η^5-cyclohexadienyl) moieties at the substituted carbon atom has been attributed in part to electronic factors[9] and is typical in cyclohexadienylmetal complexes.[11]

Reactions of dianion 2 with electrophiles was found to be highly regioselective, with attack occurring exclusively at the 1,4-positions (benzylic) (Scheme II and Table II). This is consistent with studies of stereospecific electrophilic attack at the benzylic positions of systems activated by a single Cr(CO)$_3$ group.[12] Significantly, 2 can be reacted stepwise with two different electrophiles (Table III). Accordingly, it is acting as a bis(benzylic) anionic species. The initial attack of 2 at one benzylic position and the second attack on the complexed 1-phenylallylic anion have been correlated with the LUMO–HOMO coefficients of the arene ligands[13,14] and are also found to be consistent with the conformational preferences of the Cr(CO)$_3$ group.[15]

Scheme II



Scheme III



The results of the reaction of dianion 2 with various electrophiles is shown in Table II. The reaction with acyl chlorides was very rapid, with the color change from dark brown to pale brown taking place within a few seconds. On the other hand the reaction with primary alkyl halides took a few minutes for the color change but yielded the dialkylated products in fair to good yields. While the reaction with allyl halides was rapid and did not yield any undesirable side products, the reaction with isopropyl bromide took place slowly and only in the presence of HMPA.[16]

The stereoselective and regioselective addition of the electrophiles could have occurred either by an exo benzylic carbanion S$_N$2 type attack or by a metal-assisted endo attack. Reactions of the benzylic type anions with both carbon and protic electrophiles have been found to result in exo addition of the electrophile. This observation has been explained as a function of the steric hindrance of the

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(10) For some (η^5-cyclohexadienyl)metal tricarbonyl complexes and their spectra, see: (a) Bird, P. H.; Churchill, M. R. *Chem. Commun.* **1967**, 777. (b) Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950. (c) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024. (d) Janse-Van Veuren, P.; Fletterick, R. J.; Meinwald, J.; Hughes, R. E. *Chem. Commun.* **1970**, 883, *J. Am. Chem. Soc.* **1971**, *93*, 4394. (e) Huttner, G.; Mills, O. S. *Chem. Ber.* **1972**, *105*, 3924. (f) Walker, P. J. C.; Mawby, R. *Inorg. Chim. Acta* **1973**, *7*, 621. (g) Bear, C. A.; Cullen, W. R.; Kutney, J. P.; Ridaura, V. E.; Trotter, J.; Zanarotti, A. *J. Am. Chem. Soc.* **1973**, *95*, 3058. (h) Connelly, N. G.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2334. (i) Pauson, P. L. *J. Organomet. Chem.* **1980**, *200*, 207. (j) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1980**, *102*, 3490. (k) Sievert, A. C.; Muetterties, E. Z. *Inorg. Chem.* **1981**, *20*, 2276. (l) Treichel, P. M.; Fivizzani, K. P.; Haller, K. J. *Organometallics* **1982**, *1*, 931. (m) Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053. (n) Green, J. C.; Kelly, M. R.; Payne, M. P.; Seddon, E. A.; Astruc, D.; Hamon, J.-R.; Michaud, P. *Organometallics* **1983**, *2*, 211. (o) Brookhart, M.; Lukacs, A. *Organometallics* **1983**, *2*, 649. (p) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (q) Le Rudulier, M.; Moinet, C. *J. Organomet. Chem.* **1988**, *352*, 337.

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(12) (a) Jaouen, G. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2, Chapter 2. (b) Jaouen, G.; Top, S.; McGlinchey, M. J. *J. Organomet. Chem.* **1980**, *195*, C5. (c) Lebibi, J.; Brocard, J.; Couturier, D. *Bull Soc. Chim. Fr.* **1982**, II, 357. (d) Davies, S. G.; Holman, N. J.; Laughton, C. A.; Mobbs, B. E. *Chem. Commun.* **1983**, 1316. (e) Caro, B.; LeBihan, J. Y.; Guillot, J. P.; Top, S.; Jaouen, G. *Chem. Commun.* **1984**, 602. (f) Halet, J. F.; Saillard, J. Y.; Caro, B.; LeBihan, J. Y.; Top, S.; Jaouen, G. *J. Organomet. Chem.* **1984**, *267*, C37. (g) Brocard, J.; Pelinski, L.; Lebibi, J. *J. Organomet. Chem.* **1986**, *309*, 299. (h) Brocard, J.; Lebibi, J. *J. Organomet. Chem.* **1987**, *320*, 295. (i) Le Bihan, J. Y.; Senechal-Tocquer, M. C.; Senechal, D.; Gentric, D.; Caro, B.; Halet, J. F.; Saillard, J. Y.; Jaouen, G.; Top, S. *Tetrahedron* **1988**, 3565.

(13) Values of coefficients are given by: Coulson, A.; Streitweiser, A. *Dictionary of π Electron Calculations*; W. H. Freeman and Co.; San Francisco, 1965; p 30.

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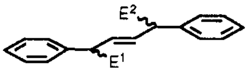
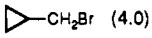
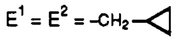
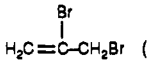
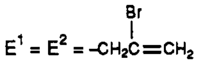
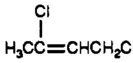
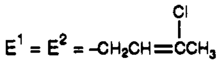
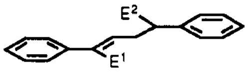
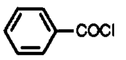
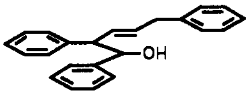
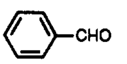
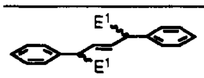
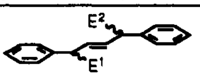
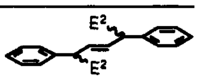
(16) For the reaction with *tert*-butyl bromide, no color change in the reaction mixture was observed even after 24 h. A very low yield of a mixture of monoalkylated alkenes and dienes was obtained.

Table II. Reduction of *E,E*-(η^6,η^6-1,4-Diphenyl-1,3-butadiene)bis(tricarbonylchromium) with Lithium Naphthalenide, Followed by Reaction with Electrophiles and Oxidation with Iodine

entry	reagent[a] (amt, equiv)	product	% yield[b]
		 **3**	
1	$H_3CCH_2CH_2CH_2Br$ (4.0)	**3a**: $E^1 = E^2 = -(CH_2)_3CH_3$	74[c]
2	$H_3CCH_2CH_2CH_2CH_2CH_2CH_2Br$ (4.0)	**3b**: $E^1 = E^2 = -(CH_2)_7CH_3$	40 (22)
3	$(H_3C)_2CHBr$ (5.5)	**3c**: $E^1 = E^2 = -CH(CH_3)_2$	67
4	$NCCH_2CH_2Br$ (3.0)	**3d**: $E^1 = E^2 = -(CH_2)_2CN$	49 (26)[d]
5	 (4.0)	**3e**: 	89
6	$H_2C{=}CHCH_2CH_2CH_2CH_2Br$ (4.0)	**3f**: $E^1 = E^2 = -(CH_2)_4CH{=}CH_2$	85
7	$H_2C{=}CHCH_2Br$ (3.7)	**3g**: $E^1 = E^2 = -CH_2CH{=}CH_2$	85
8	$HC{\equiv}CCH_2Br$ (4.0)	**3h**: $E^1 = E^2 = -CH_2C{\equiv}CH$	78
9	(*E*)-$H_3CCH{=}CHCH_2Cl$ (3.0)	**3i**: $E^1 = E^2 = -CH_2CH{=}CHCH_3$-(*E*)	76
10	 $H_2C{=}C(Br){-}CH_2Br$ (2.4)	**3j**:  $E^1 = E^2 = -CH_2C(Br){=}CH_2$	46
11	 $H_3CC(Cl){=}CHCH_2Cl$ (2.5)	**3k**:  $E^1 = E^2 = -CH_2CH{=}C(Cl)CH_3$	77
12	$(H_3C)_3CCOCl$ (2.2)	**3l**: $E^1 = E^2 = -CO(CH_3)_3$	67
		 **4**	
13	 (2.2)	**4a**: $E^1 = E^2 = -COC_6H_5$	75
14	H_3CCOCl (2.7)	**4b**: $E^1 = E^2 = -COCH_3$	40
15	$H_3CCH_2CH_2COCl$ (2.7)	**4c**: $E^1 = E^2 = -CO(CH_2)_2CH_3$	22
		 **5a**	
16	 (4.0)[e]		76

[a] The addition of alkyl halides was made at room temperature, while acyl chlorides were added at −78 °C. [b] All yields given are isolated. The figure in parentheses indicates the percentage isolated yield of the monoalkylated product. [c] An isolated yield of 66% was obtained when the reaction was carried out in the absence of HMPA. [d] An isolated yield of 37% was obtained when the reaction was carried out in the absence of HMPA. [e] The reaction was worked up with excess trifluoroacetic acid.

Table III. Results of Mixed Alkylation Reactions: Reaction of Dianion 2 in Situ with Two Different Electrophiles

		product (% yield)[b]		
entry	reagent[a]			
1	$H_3CCH_2CH_2CH_2I/H_2C{=}CH{-}CH_2Br$	**3a** (24)	**3m** (40)	**3q** (10)
2	$H_3CCH_2CH_2I/H_2C{=}CH{-}CH_2OCOCH_3$[c]		**3n** (50)	**3q** (10)
3	$H_3C(CH_2)_6I/NC(CH_2)_6Br$		**3o** (44)	**3p** (10)
4	$H_3C(CH_2)_8Br/NC(CH_2)_6Br$		**3q** (46)	**3p** (20)
5	$H_3C(CH_2)_5Br/H_5C_2O_2C(CH_2)_5Br$	**3r** (13)	**3s** (31)	**3t** (22)
6	$H_3C(CH_2)_8Br/H_5C_2O_2C(CH_2)_4Br$	**3u** (17)	**3v** (46)	**3w** (23)
7	$H_3C(CH_2)_{11}Br/H_5C_2O_2C(CH_2)_{11}Br$		**3x** (22)	**3y** (24)
8	$H_3C(CH_2)_{15}Br/H_5C_2O_2C(CH_2)_{11}Br$	**3z** (11)	**3aa** (34)	**3y** (19)

[a] About 1.2 equiv of each reagent was used. [b] All yields given are isolated. [c] The allyl acetate was treated with $[(C_2H_5)_3P]_2PdCl_2$ (0.06 mmol) and DIPHOS (0.06 mmol) before reaction with the alkylated dianion 2.

$Cr(CO)_3$ group protecting one face of the ring as the electrophile reacts directly at the benzylic carbon.[3c,12f] Steric interactions of the entering electrophile with the $Cr(CO)_3$ group would therefore favor the formation of the exo isomer for a benzylic type attack.

On the other hand, a mechanism involving a metal-assisted electrophilic attack on an electron-rich tricarbonyl dianion complex has been reported in the literature. Protonation of the (η^4-naphthalene)tricarbonylchromium dianion has been suggested to occur via a metal-assisted endo mechanism on the basis of NMR data.[4k] A metal-assisted endo process is also postulated by Kundig in his work on acylation transfer to the (η^5-cyclohexadienyl)tricarbonylchromium anion.[3i,j,l,m] Cooper has also shown that protonation and carboxylation of activated benzene in $[Cr(\eta^4\text{-}C_6H_6)CO_3]^{2-}$ is a metal-assisted endo delivery.[17] Although the possibility of a metal-mediated attack does exist for 2, the likelihood of it taking place is less since no product of phenyl ring alkylation was obtained from any

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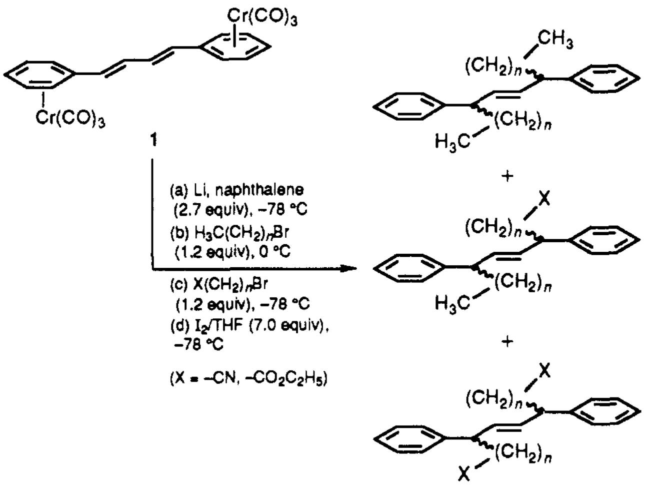
[17] (a) Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644. (b) Corrella, J. A., II; Cooper, N. J. *J. Am. Chem. Soc.* **1990**, *112*, 2832.

Scheme IV

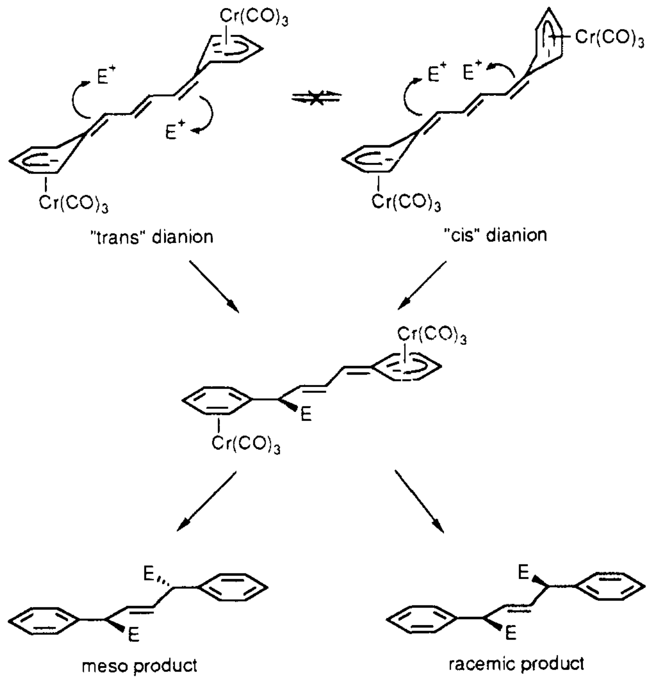


of the reactions and it would be difficult for the sterically hindered chromium atoms to direct the electrophile exclusively to the more distant benzylic position.

The formation of products from a metal-assisted alkylation of the phenyl ring, leading to a cyclohexadiene system with an exocyclic double bond, has been reported.[18] However, no such product was observed in our study. Their absence could possibly be ascribed to the preferential formation of an aromatic ring system instead of a cyclohexadiene unit bearing an exocyclic olefin moiety.

It should also be noted that there are two prochiral centers present in the 1,4-benzylic positions of 1. Reactions at these sites would lead to the formation of the *dl* and meso diastereomers. Unlike the $(\eta^6{:}\eta^6\text{-biphenyl})[Cr(CO)_3]_2$ dianion, the $Cr(CO)_3$ groups in 2 are widely separated in space and therefore have less interaction with each other. The dianion 2 possesses sterically accessible benzylic sites and would more closely resemble the benzylic anion intermediates obtained from the deprotonation of alkyl-substituted (η^6-arene)tricarbonylchromium systems.[2] A possible explanation for the 1:1 ratio observed for the racemic and meso diastereomers generated from 2 is shown in Scheme III. It is likely that the energy difference between the cis and trans conformers of 1 having the two $Cr(CO)_3$ groups on the same and opposite sides of the plane described by the four-carbon diene unit and the 1-carbon of each phenyl ring is quite small. As reduction occurs, with the postulated concurrent rearrangement to a bis(η^5-cyclohexadienylidene) structure, sufficient double-bond character is induced between the 1-carbon of each phenyl ring and the adjacent carbon atom, which may prevent any rotation along these bonds. This would result in 2 existing as a mixture of two isomers that may not interconvert. It is quite likely that each $Cr(CO)_3$ group in the cis and trans dianion 2 exclusively controls the stereochemistry of the adjacent benzylic site, overriding the steric interactions of the neighboring chiral center. Accordingly, the "trans" dianion 2 would yield the *meso*-1,4-diphenyl-2-butene while the *racemic* diastereomer would be generated from the "cis" dianion. Similar results have been observed by our group in related work carried out on the (*E*)-($\eta^6{:}\eta^6$-stilbene)bis(tricarbonylchromium) dianion.[5c]

There is another possible explanation for the formation of diastereomers. The "trans" dianion after initial alkylation would yield the alkylated allyl benzyl monoanion.



If there is rotation about the phenyl–benzylic position, alkylation would result in two diastereomers. This possibility cannot be ruled out because the energy barrier for this rotation is not known.

The assignment of the trans orientation of the 2,3 central double bond in the alkylated products and one acylated product (31) is based upon the formation of *trans*-1,4-diphenyl-2-butene, which was obtained exclusively when 2 was quenched with trifluoroacetic acid.[19,20] The fact that no *cis*-1,4-diphenyl-2-butene was produced suggests that the formation of the dianion has been stereospecific.

The reaction with acyl chlorides yielded only one product, which resulted from isomerization of the 2,3 central double bond to the 1,2-position (compounds 4a–c). This is attributed to the inherent high acidity of the benzylic protons, which are also α to a carbonyl group. Treatment of 2 with succinyl or adipoyl chloride failed to yield any cyclized products.

Another important question is whether the reactions with electrophiles are occurring via an inner-sphere polar mechanism or via an electron-transfer mechanism. The use of radical probes, 6-halo-1-hexene[21] and (halomethyl)cyclopropanes,[22] for the presence of a single electron-transfer (SET) mechanism were employed. Treatment of 1 with lithium naphthalenide followed by reaction with (1-bromomethyl)cyclopropane and 6-bromo-1-hexene resulted in clean alkylation at the benzylic positions with no ring opening or cyclization (Table II, entries 5 and 6). Although the possibility of a SET mechanism cannot be completely ruled out for either the initial or the second

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[18] (a) Blagg, J.; Davies, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1283. (b) Heppert, J. A.; Thomas-Miller, M. E.; Milligan, M. L.; Takusagawa, F.; Aubé, J. *Organometallics* **1988**, *7*, 2581. (c) Heppert, J. A.; Aubé, J.; Thomas-Miller, M. E.; Milligan, M. L.; Takusagawa, F. *Organometallics* **1990**, *9*, 727. (d) Blagg, J.; Davies, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1133.

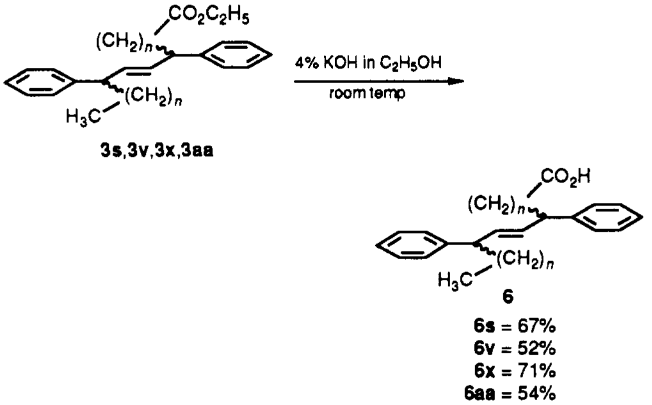
[19] *E*-1,4-Diphenyl-2-butene: lit. mp 43–45 °C. Blum, J.; Becker, Y. *J. Chem. Soc., Perkin Trans. 2* **1972**, 982.

[20] *Z*-1,4-Diphenyl-2-butene: (a) lit. bp 176–178 °C (17 mm). Neher, R. *Helv. Chim. Acta* **1963**, *46*, 1083. (b) lit. bp 89–90 °C (0.02 mm). Lambert, J. B.; Mark, H. W.; Magyar, E. S. *J. Am. Chem. Soc.* **1977**, *99*, 3059.

[21] San Fillippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

[22] (a) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8. (b) Krusic, J. C.; Levisalles, J.; Normant, J.-M.; Rose, E. *J. Am. Chem. Soc.* **1977**, *99*, 250. (c) Matthew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981.

Scheme V



3s,3v,3x,3aa

6

6s = 67%
6v = 52%
6x = 71%
6aa = 54%

step,[23,24] the above two results do suggest that direct substitution by an inner-sphere polar S_N2 pathway is the likely mechanism. Entries 8, 9, and 11 of Table II further indicate that S_N2 processes are favored over S_N2' for both the initial as well as the second attack.

Having established an initial success in mixed alkylation, i.e. introduction of one substituent at one benzylic position followed by trapping the other anionic benzylic position with a different alkyl halide, we were interested in extending this methodology toward the synthesis of novel molecules that could be used for monolayers and Langmuir–Blodgett films. These compounds could have been possibly used as bistable materials by photochemically inducing cis/trans isomerizations. Most monolayer-forming substances are amphiphatic molecules containing alkyl chains of 12 or more carbon atoms.[25] Long-chain carboxylic acids, alcohols, oximes, ketones, amines, ammonium salts, sulfates, and sulfonates have been used most frequently as monolayer-forming substances. Treatment of 2 with a nonpolar long-chain electrophile followed by a long-chain electrophile with a polar substituent at one end could result in such a monolayer-forming amphiphatic molecule.

Reduction of 1 with lithium naphthalenide followed by in situ reaction with two different long-chain electrophiles resulted in a statistical mixture of three products, the two products of dialkylation with the same electrophile and the product of mixed alkylation (Scheme IV and Table III). For our study, long-chain functionalized and simple (nonfunctionalized) alkyl halides were used as our electrophiles. Among the functionalized alkyl halides, halonitriles did react well. However, it was not convenient to convert the nitrile into a more polar carboxylic acid group under conditions that would not cause any undesirable side reactions. Long-chain bromo esters[26] were therefore used, since the ester functionality in the alkylated product after isolation could easily be converted to the more polar carboxylic acid upon mild hydrolysis.

The mixed alkylated product after separation and purification was subjected to hydrolysis. Saponification of the separated product with 4% KOH in ethanol gave the corresponding carboxylic acid derivatives in the yields shown in Scheme V. All of the product carboxylic acids were either colorless or pale yellow viscous oils. As none of these new materials were solids, they yielded poorly defined Langmuir–Blodget films and this phase of the study was discontinued.

Conclusion

Reduction of (*E,E*)-(η^6:η^6-1,4-diphenyl-1,3-butadiene)-bis(tricarbonylchromium) (1) with lithium naphthalenide results in the formation of a dianion that undergoes alkylation with a variety of electrophiles in the 1,4-position. The alkylation proceeds in a stepwise manner, thereby allowing the introduction of two different electrophiles. This regioselective addition results in the formation of two diastereomeric dialkylated (*E*)-1,4-diphenyl-2-butenes, indicating that attack of the dianion is a benzylic type nucleophilic attack. Reaction with radical probes such as (1-bromomethyl)cyclopropane and 6-bromo-1-hexene gave no products that would indicate the presence of any single electron transfer or radical processes in the mechanism of the reaction. Protonation of the dianion 2 was found to be stereospecific, leading to the formation of *trans*-1,4-diphenyl-2-butene, which can be easily converted to the natural product 1,4-diphenyl-2,3-butanediol.[27]

Experimental Section

General Procedures. ^1H NMR and ^{13}C NMR spectra were obtained on a 360-MHz Nicolet NIC-360 and 50-MHz VXR-200 superconducting NMR spectrometers, respectively. For ^1H NMR spectroscopy all peaks were referenced to tetramethylsilane, while for ^{13}C NMR spectroscopy all peaks were referenced to the central peak of the $CDCl_3$ triplet. Multiple-intensity peaks in ^{13}C NMR spectra are referred to as nX, where n is the intensity relative to 1. IR spectra were recorded neat between NaCl plates or as KBr disks either on a Perkin-Elmer 283 spectrophotometer or on an Analect RFX-65 FTIR spectrometer interfaced with an Analect ATC-652 286 FTIR data system. High-resolution mass spectra were obtained by the Midwest Regional Center for Mass Spectrometry, University of Nebraska-Lincoln, Lincoln, NE.

Purification of the crude reaction mixture was carried out by means of either column chromatography using hexane as the eluant and silica gel (E. Merck No. 7734, 70-234 μmesh size) as the stationary phase or preparative thick-layer chromatography using hexane as the eluant and 20 cm × 20 cm silica gel GF plates of 1000-μm thickness (Analtech Catalog No. 02013) or 2000-μm thickness (Analtech Catalog No. 02015). More difficult separations for purification were performed either on a Harrison Research Model 7924 T 25 chromatotron using hexane as the eluant and 1 mm thick rotors of silica gel 60PF-254 containing gypsum (E. Merck, Catalog No. 7740) as the stationary phase or by preparative reversed-phase thick-layer chromatography using 10% H_2O in H_3CCN as the eluant and 20 cm × 20 cm PLKC-18F linear K plates of 1000-μm thickness (Whatman Catalog No. 4800-840).

All manipulations were carried out on a dual manifold providing vacuum and dry argon. The Linde prepurified grade argon was further purified by passing it through a 150 °C catalyst column (BASF R3-11) and then through a column of phosphorus pentoxide followed by a column of granular potassium hydroxide. Tetrahydrofuran (THF) and n-butyl ether were freshly distilled under argon from sodium/potassium alloy. Hexamethylphosphoric triamide (HMPA) was dried by storing over 13X molecular sieves (predried under argon at 350 °C for 4 h). Lithium and naphthalene were cut and weighed in a Vacuum Atmosphere Co. argon drybox.

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[23] The SET mechanism is favored by the presence of small amounts of transition metals. This was evident by the dimerization of ketyls to give pinacols, during the addition of Grignard reagents to ketones. Ashby, E. C.; Buhler, J. D.; Lopp, I. G.; Wieseman, T. L.; Bowers, J. S.; Laemmle, J. T. *J. Am. Chem. Soc.* **1976**, *98*, 6561.

[24] About 10% of benzil was obtained in the reaction with benzoyl chloride (Table II, entry 13).

[25] Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley Interscience Publications: New York, 1982; pp 78–99.

[26] About 3.0 mmol of the long-chain bromo carboxylic acids were dissolved in 8.0 mL of C_2H_5OH. Acetyl chloride (4.2 mmol) was added, and the reaction mixture was refluxed for 2 h. After cooling, the reaction mixture was diluted with ether and the ether solution was washed with saturated $NaHCO_3$ solution, water and saturated NaCl solutions and dried over $MgSO_4$. The crude long-chain bromo ester obtained after rotary evaporation of the solvent ether was purified by means of column chromatography using 12% ethyl acetate in hexane as the solvent system.

[27] (a) Hill, R. K.; Bradberry, T. F. *Experientia* **1982**, *38*, 70. (b) Crotti, P.; Ferretti, M.; Macchia, F.; Stoppioni, A. *J. Org. Chem.* **1984**, *49*, 4706.

Electrochemistry Experiments. All electrochemistry experiments were performed by using a PAR Model 173 potentiostat/galvanostat equipped with *iR* feedback compensation in conjunction with a PAR Model 174 polarographic analyzer, a PAR Model 175 universal programmer, and a PAR Model 179 digital coulometer. Electrochemical data were recorded on a Hewlett-Packard Model 7004B X-Y plotter.

All electrochemical experiments were performed in anhydrous solvents under an argon atmosphere in a jacketed electrochemical cell. The working electrode for cyclic voltammetry was a hanging-mercury-dropping Electrode (HMDE), which was equipped with a micrometer device that produced an electrode area of 1.38 ± 0.05 mm^2 for every two divisions. A dropping-mercury electrode (DME) with a drop knock of 1 drop/s was employed for polarographic studies. The reference electrode used was Ag/AgCl, saturated NaCl(aq) (±0.042 V from saturated calomel electrode), buffered from the bulk electrochemical solution by means of a glass frit. The auxiliary electrode was a platinum screen, similarly buffered with a frit. The electrolyte salts, tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP), were dried under vacuum at 100 °C for 10 h prior to use. Propylene carbonate (PC) was vacuum-distilled by using a spinning band distillation apparatus and stored over molecular sieves until needed.

Preparation of (*E*,*E*)-(η^6:η^6-1,4-Diphenyl-1,3-butadiene)bis(tricarbonylchromium) (1). A 500-mL round-bottomed flask was charged under argon with 5.21 g (25.2 mmol) of (*E*,*E*)-1,4-diphenyl-1,3-butadiene and 13.9 g (63.2 mmol) of $Cr(CO)_6$ in 350 mL of a 10% solution of THF in *n*-butyl ether. The reaction mixture was refluxed for a period of 5 days, during which time it developed a red precipitate. The reaction mixture was cooled and then suction-filtered to remove 10.8 g of the precipitated red solid. Sublimation at 55 °C (0.3 mm) resulted in removal of 2.80 g of unreacted $Cr(CO)_6$. (*E*,*E*)-(η^6-1,4-Diphenyl-1,3-butadiene)tricarbonylchromium was removed by sublimation (0.004 Torr at 170 °C). The red bis complex 1 was dissolved in THF and filtered through Celite to remove any decomposed material. Rotary evaporation of THF yielded 7.72 g (64%) of deep maroon-colored crystals of 1. ^{1}H NMR (acetone-d_6): δ 7.01 (dd, 2 H, *J* = 14.82, 2.90 Hz), 6.42 (dd, 2 H, *J* = 14.81, 2.89 Hz), 5.88 (dd, 4 H, *J* = 6.14, 1.55 Hz), 5.70 (t, 4 H), 5.60 (t, 2 H). ^{13}C NMR (acetone-d_6): δ 234.45, 131.76, 131.21, 106.91, 94.79, 93.97, 93.29. IR (THF): 2976, 1962, 1893, 1078 cm^{-1}. Mass spectrum, *m*/*e* (ion, relative intensity): 477 (M$^+$, 5), 394 (4), 258 (100), 52 (45). High-resolution mass spectrum calcd for $C_{22}H_{14}Cr_2O_6$: 477.9600. Found: 477.9611.

Preparation of (*E*)-1,4-Diphenyl-2-butene. Lithium (13.6 mg, 1.98 mmol) and naphthalene (291 mg, 2.27 mmol) were stirred in 10 mL of THF at ambient temperature for 2 h. This solution was then transferred to a stirred solution of 1 (350 mg, 0.73 mmol) in 25 mL of THF and 2.5 mL of HMPA at −78 °C. After 10 min at −78 °C, 2.5 mL of HMPA was added to the reaction mixture. After another 15 min at −78 °C, the CF_3CO_2H (501 mg, 4.4 mmol) was syringed neat into the reaction mixture. An instantaneous color change from dark brown to pale orange was observed. The reaction mixture was stirred at −78 °C for 1 h and then at room temperature for 2 h. It was then quenched at −78 °C with a solution of I_2 (1.30 g, 5.12 mmol) in 10 mL of THF. After overnight stirring, the resultant dark solution was diluted with ether. The ether solution was washed three times with saturated $Na_2S_2O_3$ solution, twice with water, and once with saturated NaCl solution and dried over $MgSO_4$. Filtration followed by rotary evaporation of the solvent gave the crude product, which was purified by preparative TLC to yield 0.117 24 g (77%) of the pure product.[19]

(*E*)-1,4-Diphenyl-2-butene. Mp: 40.5–42.0 °C. ^{1}H NMR (CDCl$_3$): 7.25–7.30 (m, 4 H), 7.17–7.21 (m, 6 H), 5.66 (m, 2 H), 3.35 (d, 4 H). ^{13}C NMR (CDCl$_3$): δ 140.69, 130.40, 128.49 (2X), 128.36 (2X), 125.94, 38.94. IR (neat): 3080, 3061, 3022, 2959, 2899, 2831, 1602, 1493, 1451, 1429, 1075, 1029, 973 cm^{-1}.

General Procedure for the Reduction of (*E*,*E*)-(η^6:η^6-1,4-Diphenyl-1,3-butadiene)bis(tricarbonylchromium) (1), Followed by Reaction with Electrophiles and Oxidation with Iodine. Lithium (10.6 mg, 1.54 mmol) and naphthalene (291 mg, 2.27 mmol) were stirred under argon at room temperature in 10 mL of THF until all the lithium pieces were consumed (about 2 h). The dark green lithium naphthalenide solution was then transferred through a cannula under argon to a cherry red stirred solution of 1 (350 mg, 0.73 mmol) in 30 mL THF and 3 mL of HMPA at −78 °C. The resultant dark solution was stirred at −78 °C for 15 min, after which an additional 3 mL of HMPA was syringed into the reaction mixture. After stirring for an additional 15 min at −78 °C, the electrophile (see Table II for amounts) was syringed neat into the reaction mixture. The reaction mixture was stirred overnight, during which time it warmed to room temperature. The color had become pale yellow. The reaction flask was once again cooled to −78 °C, and the contents were quenched with iodine (1.30 g, 5.12 mmol) in 20 mL of THF. The quenched solution was stirred as it gradually warmed to room temperature (about 8 h). The reaction mixture was diluted with diethyl ether, and the ether solution was washed three times with saturated $Na_2S_2O_3$ solution, twice with water, and once with saturated NaCl solution and dried over $MgSO_4$. Filtration followed by rotary evaporation of the solvent ether gave the crude product, which was purified by chromatography.

(*E*)-5,8-Diphenyl-6-dodecene (3a). ^{1}H NMR (CDCl$_3$): δ 7.20 (m, 10 H), 5.61 (m, 2 H), 3.24 (m, 2 H), 1.70 (m, 4 H), 1.28 (m, 8 H), 0.87 (t, 6 H). ^{13}C NMR (CDCl$_3$): δ 145.60, 145.50, 133.90, 133.70, 128.30, 127.60, 125.90, 48.75, 48.68, 35.90, 35.80, 29.90, 29.80, 22.60, 13.99, 13.95. IR (neat): 3020, 2920, 2850, 1600, 1490, 1450, 1375, 1025, 961, 685 cm^{-1}. Mass spectrum, *m*/*e* (ion, relative intensity): 320 (M$^+$, 14), 263 (M − C_4H_9, 100), 244 (67), 207 (46), 174 (54), 117 (50). High-resolution mass spectrum calcd for $C_{24}H_{32}$: 320.2504. Found: 320.2509.

(*E*)-8,11-Diphenyl-9-octadecene (3b). ^{1}H NMR (CDCl$_3$): δ 7.22–7.29 (m, 4 H), 7.12–7.18 (m, 6 H), 5.57–5.58 (dd, 1 H, *J* = 4.54 Hz), 5.54–5.56 (dd, 1 H, *J* = 4.56 Hz), 3.16–3.24 (m, 2 H, *J* = 4.34 Hz), 1.65 (q, 4 H), 1.23 (broad m, 20 H), 0.56 (t, 6 H). ^{13}C NMR (CDCl$_3$): δ 145.55, 145.49, 133.83, 133.63, 128.29, 127.57, 125.85, 48.78, 48.68, 36.20, 36.08, 31.89, 31.85, 29.58, 29.52, 29.29, 29.23, 27.68, 27.56, 22.69, 14.11. IR (neat): 3070, 3030, 2930, 2860, 1610, 1495, 1455, 970, 750, 690 cm^{-1}. Mass spectrum, *m*/*e* (ion, relative intensity) 404 (M$^+$, 1), 306 (4), 215 (6), 117 (49), 91 (100). High-resolution mass spectrum calcd for $C_{30}H_{44}$: 404.3443. Found: 404.3463.

(*E*)-2,7-Dimethyl-3,6-diphenyl-4-octene (3c). ^{1}H NMR (CDCl$_3$): δ 7.17 (m, 10 H), 5.65 (m, 2 H), 2.91 (m, 2 H), 1.90 (broad m, 2 H), 0.83 (d, 6 H), 0.71 (d, 6 H). ^{13}C NMR (CDCl$_3$): δ 144.90, 133.50, 128.20, 128.00, 125.80, 56.90, 33.10, 21.10, 20.60. IR (neat): 3020, 2950, 1600, 1490, 1445, 1380, 1365, 1260, 1021, 960, 685 cm^{-1}. Mass spectrum, *m*/*e* (ion, relative intensity): 292 (M$^+$, 3), 249 (M − C_3H_7, 19), 206 (9), 193 (12), 117 (99), 91 (100). High-resolution mass spectrum calcd for $C_{22}H_{28}$: 292.2191. Found: 292.2191.

(*E*)-1,8-Dicyano-3,6-diphenyl-4-octene (3d). ^{1}H NMR (CDCl$_3$): 7.20 (m, 10 H), 5.68 (m, 2 H), 3.37 (m, 2 H), 1.90–2.20 (broad m, 8 H). ^{13}C NMR (CDCl$_3$): δ 141.90, 141.70, 133.10, 132.90, 128.60, 128.20, 127.10, 127.00, 126.70, 119.10, 47.11, 47.07, 30.90, 15.04, 14.98. IR (neat): 3020, 2960, 2240, 1600, 1492, 1452, 1420, 1171, 1025, 968, 903 cm^{-1}. Mass spectrum, *m*/*e* (ion, relative intensity): 314 (M$^+$, 3), 260 (M − $(CH_2)_2CN$, 5), 210 (25), 170 (40), 117 (40), 91 (100). High-resolution mass spectrum calcd for $C_{22}H_{22}N_2$: 314.1783. Found: 314.1802.

(*E*)-1,6-Dicyclopropyl-2,5-diphenyl-3-hexene (3e). ^{1}H NMR (CDCl$_3$): δ 7.15–7.28 (m, 10 H), 5.64–5.68 (m, 2 H), 3.34–3.39 (m, 2 H), 1.46–1.64 (m, 4 H), 0.52–0.62 (m, 2 H), 0.30–0.43 (m, 4 H), −0.58–0.72 (m, 4 H). ^{13}C NMR (CDCl$_3$): δ 145.31, 145.24, 133.57, 133.40, 128.27, 128.23 (2X), 127.65 (2X), 127.38, 125.87, 49.17, 49.14, 41.54, 41.48, 9.36, 9.33, 4.74, 4.65, 4.57. IR (neat): 3070, 3000, 2910, 1605, 1495, 1450, 1015, 820, 750, 695 cm^{-1}. Mass spectrum, *m*/*e* (ion, relative intensity): 316 (M$^+$, 1), 261 (M − *c*$C_3H_5CH_2$, 14), 205 (25), 117 (100). High-resolution mass spectrum calcd for $C_{24}H_{28}$: 316.2191. Found: 316.2195.

(*E*)-7,10-Diphenyl-1,8,15-hexadecatriene (3f). ^{1}H NMR (CDCl$_3$): δ 7.22–7.29 (m, 5 H), 7.13–7.18 (m, 5 H), 5.66–5.82 (m 2 H, C proton of ABC pattern), 5.54–5.58 (m, 2 H), 4.86–4.99 (m, 4 H, A and B protons of ABC pattern), 3.16–3.23 (m, 2 H), 1.93–2.03 (m, 4 H), 1.66 (m, 4 H), 1.29–1.41 (m, 4 H), 1.11–1.27 (m, 4 H). ^{13}C NMR (CDCl$_3$): δ 145.36, 145.27, 138.97, 133.79, 133.58, 128.41, 128.28 (2X), 127.50 (2X), 125.87, 114.21, 114.16, 114.11, 48.66, 48.59, 35.94, 35.84, 33.66, 33.62, 33.57, 28.84, 28.79, 27.10, 27.01. IR (neat): 3061, 3026, 2928, 2855, 1640, 1600, 1492, 1452, 992, 909, 758, 698 cm^{-1}. Mass spectrum, *m*/*e* (ion, relative intensity): 372 (M$^+$, 1), 289 (M − C_8H_{11}, 6), 117 (39), 91 (100). High-resolution mass spectrum calcd for $C_{28}H_{36}$: 372.2817. Found: 372.2818.

(*E*)-4,7-Diphenyl-1,5,9-decatriene (3g). ^{1}H NMR ($CDCl_3$): δ 7.24–7.29 (m, 4 H), 7.14–7.19 (m, 6 H), 5.49–5.77 (m, 2 H, C proton of ABC pattern), 4.89–5.00 (m, 4 H, AB protons of ABC pattern), 3.29–3.36 (m, 2 H), 2.41–2.46 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 144.33, 136.69, 133.44, 132.96, 128.43, 128.30, 127.66, 127.48, 127.34, 126.08, 125.98, 116.09, 48.56, 48.42, 40.46, 40.32. IR (neat): 3076, 3062, 3026, 3003, 2976, 2924, 2860, 1639, 1601, 1493, 1452, 1440, 1415, 1074, 995, 971, 912 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 288 (M$^+$, 1), 247 (M − C_3H_5, 21), 205 (M − C_6H_{11}, 63), 117 (59), 91 (100). High-resolution mass spectrum calcd for $C_{22}H_{24}$: 288.1878. Found: 288.1890.

(*E*)-4,7-Diphenyl-5-decen-1,9-diyne (3h). ^{1}H NMR ($CDCl_3$): δ 7.19–7.24 (m, 4 H), 7.13–7.15 (m, 6 H), 5.68–5.72 (m, 2 H), 3.46–3.48 (m, 2 H), 2.47–2.55 (overlapping d, 4 H, $^4J_{HH}$ = 2.59 Hz), 1.83–1.91 (overlapping t, 2 H, $^4J_{HH}$ = 2.60 Hz). ^{13}C NMR ($CDCl_3$): δ 142.78, 132.84, 132.62, 128.35, 127.58, 126.58, 82.49, 82.43, 69.99, 69.89, 47.18, 47.08, 25.72, 25.60. IR (neat): 3280, 3060, 3030, 2910, 2110, 1600, 1490, 1450, 1430, 1300, 965, 750, 690 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 284 (M$^+$, 1), 245 (M − C_3H_3, 58), 205 (65), 129 (29), 91 (100). High-resolution mass spectrum calcd for $C_{22}H_{20}$: 284.1565. Found: 284.1561.

(*E,E,E*)-5,8-Diphenyl-2,6,10-dodecatriene (3i). ^{1}H NMR ($CDCl_3$): δ 7.14–7.29 (m, 10 H), 5.51–5.62 (m, 2 H), 5.14–5.45 (m, 4 H), 3.06–3.66 (m, 2 H), 2.34–2.45 (m, 4 H), 1.47–1.65 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ 145.03, 144.78, 144.74, 144.71, 133.57, 133.27, 132.92, 129.31, 129.19, 128.36, 128.23 (2X), 127.57 (2X), 126.43, 126.39, 125.93, 125.90, 48.95, 48.85, 39.28, 39.12, 17.98, 17.91, 17.87. IR (neat): 3050, 2900, 1600, 1495, 1450, 960, 690 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 316 (M$^+$, 1), 261 (M − C_4H_7, 14), 205 (31), 117 (84), 91 (100), 55 (51). High-resolution mass spectrum calcd for $C_{24}H_{28}$: 316.2191. Found: 316.2185.

(*E*)-2,9-Dibromo-4,7-diphenyl-1,5,9-decatriene (3j). ^{1}H NMR ($CDCl_3$): δ 7.24–7.30 (m, 4 H), 7.14–7.20 (m, 6 H), 5.63–5.64 (m, 2 H of minor diastereomer), 5.59–5.61 (m, 2 H of major diastereomer), 5.39 (s, 2 H of minor diastereomer), 5.34 (s, 2 H of major diastereomer), 5.31 (s, 2 H of minor diastereomer), 5.27 (s, 2 H of major diastereomer), 3.67–3.71 (m, 2 H), 2.71–2.74 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 142.89, 142.83, 132.86, 132.79, 132.62, 132.05, 128.62, 128.38 (2X), 127.65 (2X), 127.61 (2X), 126.42, 126.35, 118.56, 47.83, 47.66, 46.49, 46.28. IR (neat): 3084, 3059, 3026, 2933, 2908, 1630, 1601, 1493, 1452, 1429, 1190, 968, 889, 785, 736, 698 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 327 (6), 325 (5), 245 (7), 206 (47), 205 (72), 91 (100). High-resolution mass spectrum calcd for $C_{22}H_{22}Br_2$: 446.0068. Found: 446.0064.

(*E,E,E*)-2,11-Dichloro-5,8-diphenyl-2,6,10-dodecatriene (3k). ^{1}H NMR ($CDCl_3$): δ 7.25–7.31 (m, 4 H), 7.15–7.21 (m, 6 H), 5.55–5.68 (m, 2 H), 5.19–5.43 (m, 2 H), 3.28–3.36 (m, 2 H), 2.54–2.71 (m, 4 H), 1.93–2.07 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ 145.27, 144.13, 144.05, 143.95, 143.92, 136.22, 133.36, 133.05, 132.91, 132.71, 132.10, 131.63, 131.60, 131.56, 131.02, 130.92, 128.53, 128.44, 128.38, 128.19, 128.12, 127.51, 127.29, 127.26, 126.22, 126.20, 126.15, 123.92, 123.83, 123.73, 123.46, 122.07, 121.96, 121.93, 48.29, 47.82, 46.99, 42.95, 38.21, 37.94, 37.90, 35.59, 35.07, 34.95, 34.88, 26.33, 26.30, 26.26, 26.19, 26.15, 26.08. IR (neat): 3082, 3060, 3026, 2976, 2951, 2918, 2850, 1664, 1601, 1493, 1450, 1431, 1379, 970, 758, 698 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 386 (M + 2, 0.28), 384 (M$^+$, 1.06), 383 (4), 349 (M − 35, 0.68), 297 (6), 295 (18), 206 (27), 117 (100), 91 (62). High-resolution mass spectrum calcd for $C_{24}H_{26}Cl_2$: 384.1412. Found: 384.1365.

(*E*)-4,5-Diphenyl-2,2,9,9-tetramethyl-5-decen-3,8-dione (3l). ^{1}H NMR ($CDCl_3$): δ 7.15–7.36 (m, 10 H), 5.81–5.86 (dd, 2 H), 4.83–4.85 (dd, 2 H, *J* = 5.18, 2.44 Hz), 1.11 (s, 11 H), 1.06 (s, 4 H), 0.91 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 213.46, 138.82, 138.76, 131.92, 130.88, 128.70, 128.58, 128.39, 128.06, 127.02, 126.89, 55.40, 50.34, 45.44, 45.37, 26.67, 26.34, 26.30, 26.06. IR (neat): 2950, 1700, 1470, 1450, 1365, 1060, 1040, 725, 610 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 376 (M$^+$, 0.74), 319 (M − *t*-C_4H_9, 0.17), 291 (M − *t*-C_5H_9O, 1.46), 206 (M − 2*t*-C_5H_9O, 2.86), 117 (7), 85 (22), 57 (100). High-resolution mass spectrum calcd for $C_{26}H_{32}O_2$: 376.2402. Found: 376.2386.

1,2,5,6-Tetraphenyl-2-hexen-1,6-dione (4a). ^{1}H NMR ($CDCl_3$): δ 7.85–7.90 (two overlapping dd, 4 H, *J* = 12.91, 12.79, 1.39 Hz), 7.15–7.53 (m, 16 H), 6.21 (d, 1 H, *J* = 7.45 Hz), 4.69 (t, 1 H), 2.88–2.96 (m, 1 H), 2.57–2.66 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 198.82, 198.36, 142.22, 138.62, 136.99, 136.60, 136.35, 133.52, 132.95, 129.72, 129.29, 129.05, 128.77, 128.68, 128.59, 128.55, 128.49, 128.13, 127.83, 127.26, 126.01, 53.98, 34.02. IR (neat): 3060, 3025, 2920, 1740, 1665, 1600, 1560, 1500, 1450, 1350, 1240, 1220, 1175, 1010, 950, 930, 890, 750, 696 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 416 (M$^+$, 4), 311 (M − C_6H_5CO, 33), 105 (100), 77 (41). High-resolution mass spectrum calcd for $C_{30}H_{24}O_2$: 416.1776. Found: 416.1530.

3,6-Diphenyl-3-octen-2,7-dione (4b). ^{1}H NMR ($CDCl_3$): δ 7.27–7.34 (m, 6 H), 7.05–7.08 (dd, 2 H, *J* = 7.78, 1.70 Hz), 6.89–6.92 (dd, 2 H, *J* = 7.69, 1.76 Hz), 6.69–6.73 (2d, 1 H, *J* = 7.12, 7.08 Hz), 3.66–3.70 (2d, 1 H, *J* = 6.62, 6.61 Hz), 2.69–2.77 (m, 1 H), 2.39–2.49 (m, 1 H), 2.15 (s, 3 H), 2.01 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 206.80, 198.42, 144.26, 140.53, 137.65, 135.64, 129.32, 129.12, 128.24, 127.67, 127.54, 58.82, 31.90, 28.87, 27.40. IR (neat): 3050, 3015, 2910, 1720, 1670, 1640, 1600, 1495, 1355, 1155, 780, 690 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 292 (M$^+$, 18), 249 (M − CH_3CO, 100), 232 (8), 117 (12), 115 (16), 105 (24). High-resolution mass spectrum calcd for $C_{20}H_{20}O_2$: 292.1563. Found: 292.1462.

5,8-Diphenyl-5-dodecen-4,9-dione (4c). ^{1}H NMR ($CDCl_3$): δ 7.24–7.35 (m, 6 H), 7.05–7.07 (dd, 2 H, *J* = 7.78, 1.70 Hz), 6.90–6.93 (dd, 2 H, *J* = 7.72, 1.70 Hz), 6.65–6.69 (2d, 1 H, *J* = 7.11, 7.06 Hz), 3.65–3.70 (2d, 1 H, *J* = 6.71 Hz), 2.65–2.75 (m, 1 H), 2.33–2.51 (m, 1 H), 2.38 (t, 2 H), 2.28 (t, 2 H), 1.44–1.56 (m, 4 H), 0.83 (t, 3 H), 0.76 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 209.07, 200.85, 143.98, 139.35, 137.77, 135.83, 129.35, 128.98, 128.28, 128.23, 127.50, 127.43, 58.05, 43.52, 41.44, 32.00, 17.79, 17.18, 13.68, 13.48. IR (neat): 3028, 2962, 2874, 1713, 1674, 1651, 1598, 1074, 763, 701 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 348 (M$^+$, 8), 277 (M − C_3H_7CO, 37), 187 (M − C_3H_7CO + $C_6H_5CH_2$, 4), 105 (38), 91 (64), 71 (100). High-resolution mass spectrum calcd for $C_{24}H_{28}O_2$: 348.2089. Found: 348.2083.

(*E*)-1,2,5-Triphenyl-3-penten-1-ol (5a). ^{1}H NMR ($CDCl_3$): δ 7.00–7.30 (m, 15 H), 4.64 (m, 2 H), 3.50 (m, 1 H), 2.60–2.90 (broad m, 3 H). ^{13}C NMR ($CDCl_3$): δ 141.80, 140.30, 133.60, 128.40, 128.20, 128.00, 127.90, 127.50, 127.30, 126.90, 126.60, 126.30, 126.10, 77.40, 58.90. IR (KBr): 3800, 3030, 2880, 1600, 1490, 1450, 1260, 1190, 1017, 905 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 314 (M$^+$, 3), 296 (46), 223 (54), 205 (85), 107 (100), 91 (96), 79 (51). High-resolution mass spectrum calcd for $C_{23}H_{22}O$: 314.1671. Found: 314.1672.

General Procedure for Mixed Alkylation Reactions. Reduction of (*E,E*)-(η^6:η^6-1,4-Diphenyl-1,3-butadiene)bis(tricarbonylchromium) (1) with Lithium Naphthalenide Followed by Reaction with Two Electrophiles. Lithium (13.6 mg, 1.98 mmol) and naphthalene (291 mg, 2.27 mmol) were stirred under argon at room temperature in 10 mL of THF until all the lithium pieces were consumed. The dark green solution was transferred under argon to a stirred solution of 1 (350 mg, 0.73 mmol) in 25 mL of THF and 2.5 mL of HMPA at −78 °C. After stirring for 10 min at −78 °C, an additional 3.0 mL of HMPA was syringed in. After another 5 min at −78 °C, the first electrophile (the nonpolar alkyl halide) (1.2 equiv) was syringed neat into the reaction mixture. Stirring of the pale brown reaction mixture was then carried out at −78 °C for 10 min and at room temperature for 60 min. The reaction mixture was once again cooled to −78 °C and the second electrophile (the polar group containing alkyl halide) (1.2 equiv) was syringed neat into the reaction mixture. The reaction mixture was stirred at −78 °C for 10 min and allowed to stir overnight, during which time it warmed to room temperature. The reaction flask was cooled to −78 °C, and the contents were quenched with a solution of iodine (1.30 g, 5.12 mmol) in 20 mL of THF. The quenched solution was allowed to warm to room temperature and then was diluted with ether. The ether solution was washed three times with saturated $Na_2S_2O_3$ solution, twice with water, and once with saturated NaCl solution and then dried over $MgSO_4$. Filtration followed by rotary evaporation of the solvent gave the crude product. The crude product was purified by preparative TLC using about 5% ethyl acetate in hexane as the eluant.

(*E*)-4,7-Diphenyl-1,5-undecadiene (3m). ^{1}H NMR ($CDCl_3$): δ 7.20 (m, 10 H), 5.60–5.80 (broad m, 3 H), 5.00 (broad m, 2 H), 3.38 (m, 1 H), 3.25 (m, 1 H), 2.51 (m, 2 H), 1.72 (dd, 2 H), 1.20–1.40 (broad m, 4 H), 0.91 (m, 3 H). ^{13}C NMR ($CDCl_3$): δ 145.50, 144.50, 136.90, 134.50, 134.30, 133.00, 132.90, 128.30, 127.70, 127.60, 127.43, 127.39, 126.10, 125.90, 116.00, 48.75, 48.62, 48.50, 40.50, 40.40, 35.90, 35.80, 29.85, 29.79, 22.63, 22.60, 14.00. Mass spectrum, *m/e* (ion, relative intensity): 304 (M^+, 1), 263 ($M - C_3H_5$, 19), 207 (6), 185 (6), 147 (6), 117 (62), 91 (100). High-resolution mass spectrum calcd for $C_{23}H_{28}$: 304.2191. Found: 304.2197.

(*E*)-4,7-Diphenyl-1,5-decadiene (3n). ^1H NMR ($CDCl_3$): δ 7.22–7.30 (m, 4 H), 7.13–7.21 (m, 6 H), 5.52–5.80 (m, 1 H, C proton of ABC pattern), 5.57–5.61 (m, 2 H), 4.81–5.08 (m, 2 H, AB protons of ABC pattern), 3.29–3.35 (m, 1 H), 3.19–3.26 (m, 1 H), 2.41–2.51 (m, 2 H), 1.60–1.70 (m, 2 H), 1.14–1.38 (m, 2 H), 0.75–0.95 (overlapping t, 3 H). ^{13}C NMR ($CDCl_3$): δ 145.24, 145.22, 145.19, 144.48, 144.43, 136.83, 136.74, 136.65, 134.31, 134.11, 133.94, 132.83, 132.69, 132.52, 132.41, 128.43, 128.39, 128.31 (2X), 128.27 (2X), 127.64 (2X), 127.61 (2X), 127.58, 127.55, 127.42, 127.36, 127.32, 126.03, 125.94, 125.87, 125.76, 116.15, 115.95, 48.58, 48.44, 48.38, 43.83, 43.73, 43.54, 43.49, 41.28, 41.12, 40.53, 40.41, 39.27, 39.10, 38.30, 38.20, 20.73, 20.68, 20.65, 14.13, 13.99. IR (neat): 3080, 3060, 3026, 3001, 2956, 2927, 2870, 1639, 1601, 1493, 1452, 1072, 1030, 991, 970, 912 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 290 (M^+, 1), 249 ($M - C_3H_5$, 45), 205 (5), 91 (100). High-resolution mass spectrum calcd for $C_{22}H_{26}$: 290.2034. Found: 290.2044.

(*E*)-1-Cyano-7,10-diphenyl-8-heptadecene (3o). ^1H NMR ($CDCl_3$): δ 7.23–7.29 (m, 4 H), 7.12–7.20 (m, 6 H), 5.57–5.59 (m, 1 H), 5.54–5.56 (m, 1 H), 3.19 (m, 2 H), 2.17–2.30 (m, 2 H), 1.48–1.69 (m, 6 H), 1.20–1.38 (m, 16 H), 0.83–0.88 (two t, 3 H). ^{13}C NMR ($CDCl_3$): δ 145.45, 145.29, 145.19, 145.07, 134.07, 133.76, 133.47, 133.31, 128.37, 128.26, 127.79, 127.47, 127.44, 127.33, 127.26, 125.91, 125.83, 125.74, 119.71, 48.69, 48.61, 48.55, 43.72, 36.06, 35.99, 35.90, 35.80, 31.87, 31.81, 31.77, 29.49, 29.44, 29.22, 29.16, 28.63, 28.51, 28.45, 27.60, 27.49, 27.22, 27.09, 25.26, 25.16, 22.60, 16.98, 14.05. IR (neat): 3050, 3030, 2920, 2850, 2240, 1600, 1490, 1455, 1025, 965, 755, 690 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 415 (M^+, 3), 316 ($M - C_7H_{15}$, 33), 305 ($M - (CH_2)_6CN$, 13), 215 (48), 117 (100). High-resolution mass spectrum calcd for $C_{30}H_{41}N$: 415.3239. Found: 415.3250.

(*E*)-1,16-Dicyano-7,10-diphenyl-8-hexadecene (3p). ^1H NMR ($CDCl_3$): δ 7.25–7.30 (m, 4 H), 7.12–7.20 (m, 6 H), 5.54–5.59 (m, 2 H), 3.16–3.21 (m, 2 H), 2.19–2.34 (m, 4 H), 1.50–1.71 (m, 6 H), 1.18–1.45 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 145.16, 144.98, 133.76, 133.51, 128.34, 127.46, 127.41, 125.97, 119.74, 48.63, 35.84, 35.76, 28.64, 28.58, 28.50, 28.46, 27.25, 27.09, 25.25, 25.16, 25.09, 17.00. IR (neat): 3060, 3030, 2920, 2860, 2240, 1600, 1485, 1450, 960, 750, 695 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 426 (M^+, 2), 316 ($M - (CH_2)_6CN$, 43), 226 (90), 117 (100). High-resolution mass spectrum calcd for $C_{30}H_{38}N_2$: 426.3035. Found: 426.3063.

(*E*)-1-Cyano-7,10-diphenyl-8-nonadecene (3q). ^1H NMR ($CDCl_3$): δ 7.22–7.29 (m, 4 H), 7.15 (broad s, 6 H), 5.45–5.62 (m, 2 H), 3.19 (s, 2 H), 2.26 (m, 2 H), 1.51–1.67 (broad m, 6 H), 1.14–1.40 (broad s, 20 H), 0.87 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 145.43, 145.27, 145.17, 145.05, 134.06, 133.75, 133.45, 133.29, 128.39 (2X), 128.25 (2X), 127.46 (2X), 127.43, 127.24, 125.92, 125.83, 119.70, 48.67, 48.60, 48.54, 43.72, 36.04, 35.98, 35.89, 35.79, 31.86, 29.55, 29.51, 29.48, 29.26, 28.62, 28.51, 28.46, 27.59, 27.47, 27.22, 27.09, 25.26, 25.16, 22.64, 17.01, 16.98, 14.07. IR (neat): 3060, 3025, 2925, 2854, 2247, 1601, 1493, 1464, 1452, 970, 760, 700 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 443 (M^+, 1), 316 ($M - C_9H_{19}$, 11), 243 (16), 91 (100). High-resolution mass spectrum calcd for $C_{32}H_{45}N$: 443.3552. Found: 443.3548.

(*E*)-7,10-Diphenyl-8-hexadecene (3r). ^1H NMR ($CDCl_3$): δ 7.24–7.29 (m, 4 H), 7.13–7.18 (m, 6 H), 5.54–5.58 (m, 2 H), 3.18–3.21 (m, 2 H), 1.64 (m, 4 H), 1.13–1.27 (m, 16 H), 0.82–0.88 (overlapping t, 6 H). ^{13}C NMR ($CDCl_3$): δ 145.51, 145.45, 133.79, 133.59, 128.25 (2X), 127.53 (2X), 125.80, 48.74, 48.64, 36.16, 36.04, 31.81, 31.71, 29.25, 29.18, 27.60, 27.47, 22.63, 22.59, 14.07. IR (neat): 3082, 3060, 3026, 3001, 2954, 2925, 2854, 1601, 1493, 1452, 968 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 376 (M^+, 1), 291 ($M - C_6H_{13}$, 21), 206 ($M - 2C_6H_{13}$, 5), 117 (24), 91 (100). High-resolution mass spectrum calcd for $C_{28}H_{40}$: 376.3130. Found: 376.3127.

(*E*)-Ethyl 7,10-Diphenyl-8-hexadecenoate (3s). ^1H NMR ($CDCl_3$): δ 7.21–7.28 (m, 4 H), 7.12–7.17 (m, 6 H), 5.54–5.58 (m, 2 H), 4.06–4.13 (m, 2 H), 3.19 (broad s, 2 H), 2.22 (m, 2 H), 1.49–1.69 (m, 6 H), 1.21–1.32 (broad s, 12 H), 1.23 (t, 3 H), 0.82–0.87 (overlapping t, 3 H). ^{13}C NMR ($CDCl_3$): δ 173.72, 145.43, 145.33, 145.25, 145.16, 133.94, 133.70, 133.60, 133.41, 128.25 (2X), 127.49 (2X), 125.86, 125.82, 60.09, 48.63, 48.56, 36.10, 36.00, 35.87, 34.29, 34.25, 31.77, 31.71, 29.20, 29.15, 29.03, 28.96, 27.56, 27.44, 27.23, 27.11, 24.87, 24.82, 22.59, 22.55, 14.22, 14.03. IR (neat): 3026, 2927, 2856, 1736, 1601, 1493, 1452, 1373, 1178, 1030, 970 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 434 (M^+, 3), 432 ($M - H_2$, 4), 389 ($M - OC_2H_5$, 12), 349 ($M - C_6H_{13}$, 21), 291 ($M - C_8H_{15}O_2$, 25), 260 ($M - C_{13}H_{18}$, 22). High-resolution mass spectrum calcd for $C_{30}H_{42}O_2$: 434.3185. Found: 434.3167.

(*E*)-Diethyl 7,10-Diphenyl-8-hexadecenedioate (3t). ^1H NMR ($CDCl_3$): δ 7.24–7.29 (m, 4 H), 7.12–7.17 (m, 6 H), 5.53–5.59 (m, 2 H), 4.08–4.13 (m, 4 H), 3.17–3.20 (m, 2 H), 2.18–2.27 (m, 4 H), 1.51–1.67 (m, 8 H), 1.20–1.32 (broad s, 8 H), 1.24 (t, 3 H), 1.23 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 173.73, 145.20, 145.07, 133.76, 133.52, 128.29 (2X), 127.49 (2X), 127.46 (2X), 125.90, 60.09, 48.58, 35.83, 35.75, 34.29, 34.25, 29.02, 28.96, 27.21, 27.11, 24.85, 24.81, 24.74, 14.22. IR (neat): 3026, 2979, 2931, 2856, 1736, 1601, 1493, 1464, 1452, 1373, 1180, 1032, 972 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 492 (M^+, 1), 349 (11), 259 (25), 117 (50), 91 (100). High-resolution mass spectrum calcd for $C_{32}H_{44}O_4$: 492.3240. Found: 492.3239.

(*E*)-10,13-Diphenyl-11-docosene (3u). ^1H NMR ($CDCl_3$): δ 7.17–7.23 (m, 4 H), 7.08–7.13 (m, 6 H), 5.49–5.53 (m, 2 H), 3.13–3.16 (m, 2 H), 1.55–1.64 (m, 4 H), 1.15–1.21 (broad s, 28 H), 0.24 (t, 6 H). ^{13}C NMR ($CDCl_3$): δ 145.51, 145.56, 133.79, 133.60, 128.26 (2X), 127.52 (2X), 125.82, 48.75, 48.64, 36.17, 36.05, 31.90, 29.61 (2X), 29.54 (2X), 29.34, 27.65, 27.53, 22.69, 14.11. IR (neat): 3060, 3026, 2954, 2925, 2854, 1601, 1493, 1466, 1452, 970 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 460 (M^+, 3), 333 ($M - C_9H_{19}$, 61), 117 (76), 91 (100). High-resolution mass spectrum calcd for $C_{34}H_{52}$: 460.4069. Found: 460.4075.

(*E*)-Ethyl 6,9-Diphenyl-7-octadecenoate (3v). ^1H NMR ($CDCl_3$): δ 7.21–7.28 (m, 4 H), 7.12–7.17 (m, 6 H), 5.48–5.58 (m, 2 H), 4.08 (m, 2 H), 3.19 (m, 2 H), 2.21 (s, 2 H), 1.55–1.72 (m, 6 H), 1.18–1.30 (broad s, 19 H), 0.87 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 173.65, 145.39, 145.26, 145.08, 144.99, 134.03, 133.79, 133.47, 133.29, 128.30 (2X), 128.26 (2X), 127.50 (2X), 127.29, 125.94, 125.84, 60.11, 48.70, 48.65, 48.49, 48.44, 36.10, 36.02, 35.68, 35.59, 34.26, 34.23, 31.87, 29.57, 29.55, 29.51, 29.29, 27.60, 27.50, 27.12, 27.03, 24.87, 24.84, 22.66, 14.21, 14.09. IR (neat): 3060, 3026, 2925, 2854, 1736, 1601, 1493, 1464, 1452, 1373, 1178, 1030, 970 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 335 ($M - C_9H_{19}$, 2), 333 ($M - C_7H_{13}O_2$, 3). High-resolution mass spectrum calcd for $C_{32}H_{44}O_2$: 460.3441. Found: 460.3341.

(*E*)-Diethyl 6,9-Diphenyl-7-tetradecenedioate (3w). ^1H NMR ($CDCl_3$): δ 7.24–7.29 (m, 4 H), 7.11–7.20 (m, 6 H), 5.49–5.58 (m, 2 H), 4.08 (m, 4 H), 3.19–3.21 (m, 2 H), 2.17–2.30 (m, 4 H), 1.55–1.71 (m, 8 H), 1.21 and 1.22 (two overlapping t, 6 H). ^{13}C NMR ($CDCl_3$): δ 173.66, 144.99, 144.86, 133.71, 133.49, 128.32 (2X), 127.48 (2X), 127.45 (2X), 127.25, 125.95, 60.10, 48.47, 48.44, 35.65, 35.57, 34.23, 34.21, 27.09, 27.01, 24.86, 24.82, 14.20. IR (neat): 3060, 3026, 2979, 2933, 2858, 1734, 1601, 1493, 1452, 1373, 1253, 1178, 1030, 972 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 419 ($M - OC_2H_5$, 2), 335 ($M - (CH_2)_4CO_2C_2H_5$, 3), 91 (100). High-resolution mass spectrum calcd for $C_{30}H_{38}O_4$: 462.2770. Found: 462.2769.

(*E*)-Ethyl 13,16-Diphenyl-14-octacosenoate (3x). ^1H NMR ($CDCl_3$): δ 7.13–7.18 (m, 6 H), 5.54–5.58 (m, 2 H), 4.11 (q, 2 H), 3.18–3.21 (m, 2 H), 2.28 (t, 2 H), 1.61–1.66 (m, 6 H), 1.19–1.27 (broad s, 33 H), 1.25 (t, 3 H), 0.88 (t, 3 H). ^{13}C NMR ($CDCl_3$): δ 173.86, 145.49, 145.43, 133.78, 133.59, 128.24 (2X), 127.51 (2X), 125.80, 60.10, 48.72, 48.62, 45.11, 36.14, 36.63, 34.38 (2X), 32.64, 31.91, 29.64 (5X), 29.56 (5X), 29.43 (3X), 29.36 (3X), 29.25 (2X), 29.22, 29.13 (2X), 28.85, 27.62, 27.51, 26.86, 24.98, 22.67, 14.24 (2X), 14.09. IR (neat): 3060, 3026, 2924, 2852, 1738, 1601, 1493, 1466, 1453, 1371, 1178, 1032, 970 cm^{-1}. High-resolution FAB mass spectrum gave a peak for ($M + H - H_2$) at 601 and for ($M - H + 2Li$) at 615.

(*E*)-Diethyl 13,16-Diphenyl-14-octacosenedioate (3y). ^1H NMR ($CDCl_3$): δ 7.22–7.29 (m, 4 H), 7.13–7.18 (m, 6 H), 5.54–5.58 (m, 2 H), 4.12 (q, 4 H), 3.17–3.20 (m, 2 H), 2.28 (t, 4 H), 1.59–1.66 (m, 8 H), 1.19–1.28 (broad s, 32 H), 1.25 (t, 6 H). ^{13}C NMR ($CDCl_3$): δ 173.88, 145.49, 145.41, 133.78, 133.57, 128.25 (2X), 127.53 (2X), 125.81, 60.11, 48.71, 48.63, 36.13, 36.03, 34.39 (2X), 29.56 (3X), 29.51 (2X), 29.44, 29.26, 27.61, 27.51, 24.98 (2X), 14.25.

IR (neat): 3026, 2978, 2924, 2852, 1736, 1601, 1493, 1464, 1452, 1178, 1032, 970 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 660 (M$^+$, 1), 658 (M – H$_2$, 1), 615 (2), 117 (65), 91 (100). FAB mass spectrum gave a peak for (M + Li) at 667. High-resolution mass spectrum calcd for $C_{44}H_{68}O_4$: 660.5118. Found: 660.5146.

(*E*)-17,20-Diphenyl-18-hexatriacontene (3z). ^{1}H NMR (CDCl$_3$): δ 7.23–7.29 (m, 4 H), 7.13–7.18 (m, 6 H), 6.54–6.58 (m, 2 H), 3.18–3.21 (m, 2 H), 1.62–1.69 (m, 4 H), 1.25 (broad s, 56 H), 0.89 (t, 6 H). ^{13}C NMR (CDCl$_3$): δ 145.52, 145.46, 133.79, 133.60, 128.26 (2X), 127.52 (2X), 125.82, 48.74, 48.63, 36.17, 36.05, 31.93 (2X), 29.71, 29.67, 29.61, 29.54, 29.37 (2X), 27.64, 22.70 (2X), 14.12 (2X). IR (neat): 3060, 3028, 2951, 2916, 2848, 1601, 1493, 1471, 1452, 968, 754, 696 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 656 (M$^+$, 1), 654 (M – H$_2$, 1), 117 (54), 91 (100). High-resolution mass spectrum calcd for $C_{48}H_{80}$: 656.6260. Found: 656.6241.

(*E*)-Ethyl 13,16-Diphenyl-14-dotriacontenoate (3aa). ^{1}H NMR (CDCl$_3$): δ 7.24–7.28 (m, 4 H), 7.13–7.17 (m, 6 H), 5.54–5.58 (m, 2 H), 4.11 (q, 2 H), 3.17–3.21 (m, 2 H), 2.27 (t, 2 H), 1.59–1.66 (m, 6 H), 1.19–1.25 (m, 49 H), 0.88 (t, 3 H). ^{13}C NMR (CDCl$_3$): δ 173.80, 145.47, 145.40, 133.78, 133.59, 128.23 (2X), 127.50 (2X), 125.80, 60.08, 48.72, 48.63, 36.14, 36.03, 34.37, 31.91, 29.69 (3X), 29.65 (2X), 29.56 (2X), 29.43, 29.35, 29.25, 29.14, 27.61, 24.98, 22.67, 14.23, 14.09. IR (neat): 3060, 3026, 2924, 2852, 1738, 1601, 1466, 1452, 1178, 698 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 658 (M$^+$, 1), 656 (M – H$_2$, 2), 613 (1), 117 (68), 91 (100). FAB mass spectrum gave peaks for (M + H – H$_2$) at 657, for (M + Li) at 665, and for (M – H + 2Li) at 671. High-resolution mass spectrum calculated for $C_{46}H_{74}O_2$: 658.5689. Found: 658.5580.

General Procedure for the Hydrolysis of the Long-Chain Monoesters Obtained from the Mixed Alkylation Reactions. The ester dissolved in 4.0 mL of C_2H_5OH was added to about 8.0 mL of 4% KOH solution (0.4 g of KOH in 7.5 mL of H_2O and 2.5 mL of C_2H_5OH). The reaction mixture was stirred at room temperature for 6 h, refluxed for 90 min, and then stirred at room temperature for 1 h. The reaction mixture was concentrated by rotary evaporation of the solvent. The reaction flask was then cooled in an ice bath, and the contents were diluted with 10 mL of saturated NaCl solution and then acidified with HCl. The acidic solution was extracted twice with ether, and the combined ether extracts were then washed twice with saturated NaCl solution and dried over anhydrous Na_2SO_4. Filtration followed by rotary evaporation of the solvent gave the crude product which was purified by preparative TLC.

(*E*)-7,10-Diphenyl-8-hexadecen-1-oic Acid (6s). Yield: 67% isolated from **3s**. ^{1}H NMR (CDCl$_3$): δ 7.22–7.29 (m, 4 H), 7.13–7.18 (m, 6 H), 5.54–5.58 (m, 2 H), 3.18–3.61 (m, 2 H), 2.30 (m, 2 H), 1.52–1.70 (m, 6 H), 1.15–1.37 (broad s, 12 H), 0.82–0.84 (t, 3 H). ^{13}C NMR (CDCl$_3$): δ 179.93, 145.44, 145.34, 145.23, 145.14, 134.02, 133.76, 133.53, 133.35, 128.30 (2X), 128.28 (2X), 127.50 (2X), 127.30, 125.92, 125.85, 48.72, 48.67, 48.63, 48.57, 36.11, 36.00, 35.85, 35.75, 33.95, 33.91, 31.79, 31.73, 29.22, 29.17, 28.93, 28.86, 27.59, 27.47, 27.22, 27.10, 24.56, 24.51, 22.62, 22.58, 14.07. IR (neat): 2450–3500, 3084, 3060, 3025, 3001, 2927, 2856, 1709, 1601, 1493, 1452, 1286, 970 cm^{-1}. High-resolution FAB mass spectrum gave peaks for (M + Li) at 413 and for (M – H + 2Li) at 419. Exact mass calcd for $C_{28}H_{38}O_2Li$, i.e. (M + Li): 413.2262. Found: 413.3031.

(*E*)-6,9-Diphenyl-7-octadecen-1-oic Acid (6v). Yield: 52% isolated from **3v**. ^{1}H NMR (CDCl$_3$): δ 7.24–7.29 (m, 4 H), 7.13–7.19 (m, 6 H), 5.54–5.58 (m, 2 H), 3.16–3.22 (m, 2 H), 2.23–2.32 (two overlapping t, 2 H), 1.56–1.72 (m, 6 H), 1.20–1.30 (m, 16 H), 0.87 (t, 3 H). ^{13}C NMR (CDCl$_3$): δ 178.65, 145.43, 145.30, 145.06, 144.95, 134.17, 133.89, 133.37, 133.20, 128.35 (2X), 128.29 (2X), 127.52 (2X), 127.28, 125.98, 125.86, 48.70, 48.47, 48.41, 36.08, 35.99, 35.66, 35.56, 33.73, 31.89 (2X), 29.70 (2X), 29.58 (3X), 29.55 (3X), 29.30 (2X), 27.61, 27.51, 27.06, 26.97, 24.98, 24.52, 22.67 (2X), 14.10 (2X). IR (neat): 2400–3400, 3060, 3026, 2925, 2854, 1709, 1601, 1493, 1452, 1412, 1284, 1232, 970 cm^{-1}. Mass spectrum, *m/e* (ion, relative intensity): 434 (M$^+$, 1), 333 (7), 307 (12), 117 (51), 91 (100). High-resolution mass spectrum calcd for $C_{30}H_{42}O_2$: 434.3185. Found: 434.3191.

(*E*)-13,16-Diphenyl-14-octacosen-1-oic Acid (6x). Yield: 71% isolated from **3x**. ^{1}H NMR (CDCl$_3$): δ 7.23–7.29 (m, 4 H), 7.12–7.48 (m, 6 H), 5.54–5.58 (m, 2 H), 3.18–3.21 (m, 2 H), 2.34 (t, 2 H), 1.60–1.66 (m, 8 H), 1.19–1.25 (broad s, 36 H), 0.88 (t, 3 H). ^{13}C NMR (CDCl$_3$): δ 178.95, 145.50, 145.44, 133.70, 133.58, 128.26 (2X), 127.53 (2X), 125.81, 125.73, 72.27, 61.84, 48.73, 48.63, 36.15, 36.04, 33.87, 31.92, 29.65 (3X), 29.58 (3X), 29.42, 29.36, 29.24, 29.07, 27.63, 27.52, 24.69, 22.69, 14.11. IR (neat): 2400–3651, 3082, 3060, 3026, 2925, 2852, 1709, 1601, 1483, 1464, 1452, 1284, 933, 721, 698 cm^{-1}. High-resolution FAB mass spectrum calculated for $C_{40}H_{61}O_2K_2$, i.e. (M – H + 2K)$^+$: 651.6771. Found: 651.3917.

(*E*)-13,16-Diphenyl-14-dotriaconten-1-oic Acid (6aa). Yield: 54% isolated from **3aa**. ^{1}H NMR (CDCl$_3$): δ 7.23–7.29 (m, 4 H), 7.13–7.18 (m, 6 H), 5.54–5.58 (m, 2 H), 3.16–3.21 (m, 2 H), 2.34 (t, 2 H), 1.58–1.66 (m, 6 H), 1.25 (broad s, 44 H), 0.88 (t, 3 H). ^{13}C NMR (CDCl$_3$): δ 179.19, 145.49, 145.44, 133.78, 133.58, 128.25 (2X), 127.53 (2X), 125.82, 48.72, 48.63, 36.15, 36.04, 33.89, 31.92, 29.70 (6X), 29.58 (3X), 29.43, 29.36, 29.24, 29.07, 27.63, 27.52, 24.68, 22.69, 14.11. IR (neat): 2400–3375, 3060, 3026, 2922, 2852, 1709, 1601, 1493, 1466, 1286, 968, 755, 698 cm^{-1}. High-resolution FAB mass spectrum gave peaks for (M + Li) at 637, (M – H + 2Li) at 643, and (M + Na) at 653. Exact mass calculated for $C_{44}H_{70}O_2Na$, i.e. (M + Na): 653.5274. Found: 653.5282.

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