Electrochemical Studies of Seven Regioisomers of Tris[di(ethoxycarbonyl)methano][60]fullerene: Umpolung of Regiochemistry in Retro-Bingel Reactions and Walk-on-the-Sphere Rearrangements[§]

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Seven of the possible 46 constitutional isomers of tris[di(ethoxycarbonyl)methano[60]fullerene have been isolated and their electrochemical properties studied in CH_2Cl_2. A two-electron controlled potential electrolysis of each of these isomers results in competing retro-Bingel and isomerization reactions with preferential loss of one or two of the addends. PM3 and AM1 computational studies indicate that while the reactivity of neutral precursors is kinetically controlled, charging of the neutral species with two electrons results in an umpolung of reactivity and introduction of thermodynamic control. Lowering the electrolysis temperature increases the proportion of isomerization, and a new tris-isomer never obtained before via synthetic methods has been isolated.

Introduction

Several recent investigations of multiple additions to C_{60} have focused on the control of the regioselectivity in order to generate controlled three-dimensional frameworks on the fullerene surface.[1−20] Fine-tuning the electronic as well as the chemical properties of fullerene-based materials and their potential biological applications have been major thrusts for this endeavor.[21−25]

Oligoadducts have been prepared in many ways ranging from highly symmetrical and stereochemically defined structures to asymmetrical architectures.[1−20] A preferred method for their preparation has been cycloadditions to [6,6] double bonds.[1] These reactions, in general, are effectively irreversible, kinetically controlled reactions in which mixtures of regioisomers are obtained.[1,8] For example, the first cyclopropanation of C_{60} with diethylbromomalonate (the Bingel reaction) results in the monoaddition product $C_{61}(COOEt)_2$, which reduces the symmetry of C_{60}.[17] Second and third Bingel additions form the bis- and trisadducts, $C_{62}(COOEt)_4$ and $C_{63}(COOEt)_6$, respectively.[2,4,7,8,18,19] Seven out of eight possible bis-isomers are isolated after the second addition.[4] The *cis-1* isomer is sterically hindered and does not form (see inset in Figure 1). The product distribution of the other seven regioisomers (Figure 1) cannot be explained by thermodynamic factors since their quantum mechanically calculated heats of formation are very similar.[5,7] The preferred regiochemistry at room temperature appears to be kinetically controlled. AM1 calculations indicate that the preferred sites for nucleophilic attack on C_{61}-$(COOEt)_2$ exhibit enhanced orbital coefficients of low-lying molecular orbitals (LUMO) which correlate with the observed experimental yields.[5,7] However, it was recently discovered that, with the exception of the *cis-2* isomer which requires only one electron, a two-electron controlled potential electrolysis (CPE) of any isomer of bis-[di(ethoxycarbonyl)methano][60]fullerene results in the addends rearranging or "shuffling" on the fullerene surface.[26] Using this electrolytic reaction, the product distribution is the same regardless of which bis-isomer is used as starting material, but it is different from that

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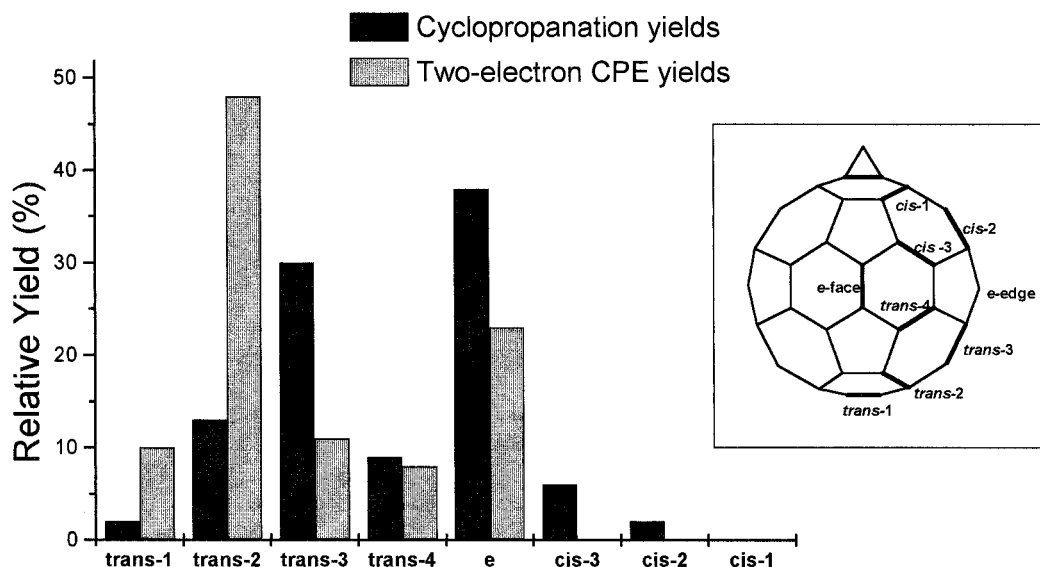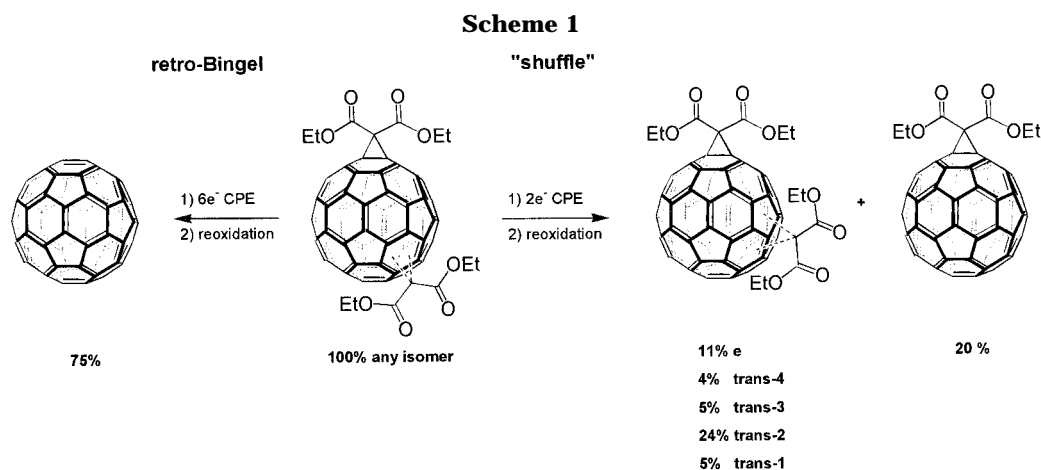
Figure 1. A comparison of the relative yields of Bingel bisadducts obtained by synthetic and electrolytic reactions.

Scheme 1

obtained during the second Bingel addition to the monoadduct, see Figure 1 and Scheme 1. For example, via the Bingel synthesis, the *trans-1* and *trans-2* adducts are produced in only 2% and 13% relative yields, respectively.[4] Via the "shuffle" (isomerization) electrolytic procedure, the corresponding yields are 10% and 48%.[26] Thus, the latter method may be used to produce larger amounts of bisadducts which are not readily available otherwise. It should also be noted here that if the electrolysis is not stopped after transferring two electrons but allowed to proceed to completion so that the current reaches background level, the result is the retro-Bingel reaction in which both addends are removed, and pure C_{60} is recovered in 75% yield, see Scheme 1.[27] This reaction has also been successfully utilized to obtain enantiomerically pure D_2-C_{76},[27] C_{2v}-symmetric C_{78},[28] D_2-C_{84}, D_{2d}-C_{84}, and another "new isomer" of C_{84}.[29]

There are 46 possible constitutional isomers for the tris-addition products of the Bingel reaction. Some of the

corresponding addition patterns with C_1-, C_2-, C_3-, or D_3-symmetry are inherently chiral.[4,9,30] As a consequence stereoisomerism due to one pair of enantiomers for each dissymmetric adduct has to be considered as well. So far, seven out of the 46 topologically possible constitutional isomers of $C_{63}(COOEt)_6$ (**1**−**7**, Chart 1) obtained by direct addition of bromo diethylmalonate have been isolated. Out of the remaining trisadducts, 36 involve *cis* addition patterns whose formation is therefore disfavored.[4,9] The remaining adducts without *cis* positions are **8**−**10**. Their formation by direct successive cyclopropanation of C_{60} is not preferred, and as a consequence they have not been isolated from the corresponding reaction mixtures. Trisadducts **1**−**7** involve exclusively the relative positional relationships *e*, *trans-4*, *trans-3*, and *trans-2*, since they were generated from the corresponding bisadducts with the same relative positional relationships, see Table 1. Whereas cyclopropanation of *e*-$C_{62}(COOEt)_4$ and *trans-2*-$C_{62}(COOEt)_4$ is comparatively regioselective with *e,e,e*-**1** and *e,trans-3,trans-2*-**3** being the main products, the malonate addition to *trans-3*-$C_{62}(COOEt)_4$ proceeds almost statistically with *trans-3,trans-3,trans-3*-**2** being the slightly favored regioisomer. An intermediate situation

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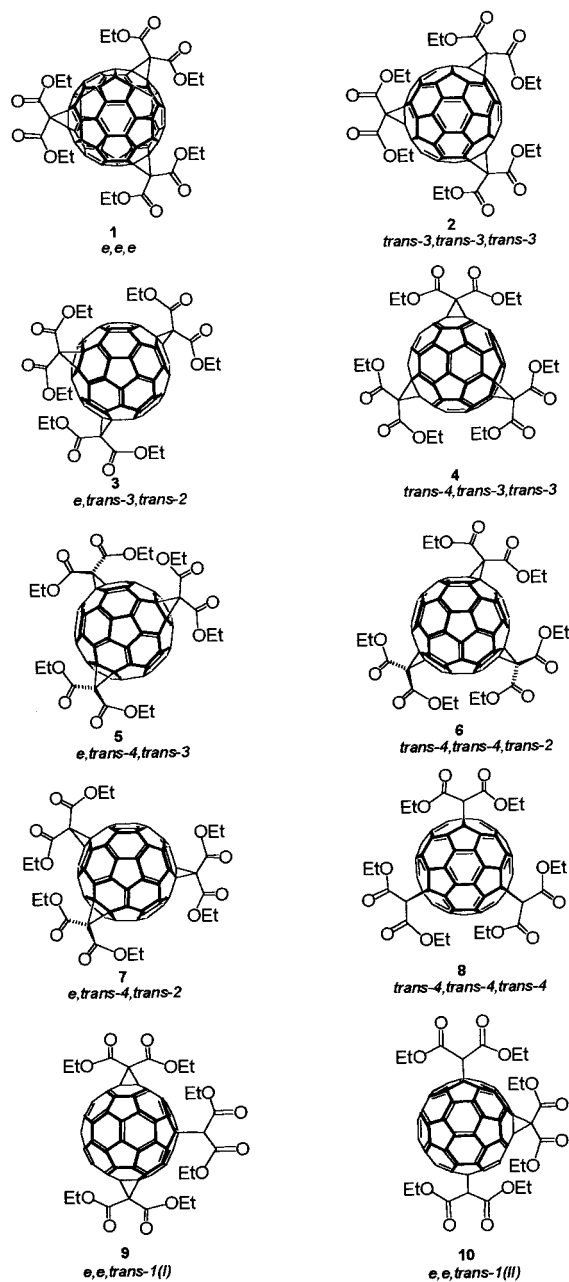(30) Djojo, F.; Hirsch, A. *Eur. J. Org. Chem.* **1999**, 3027−3039.

Chart 1

1
e,e,e

2
trans-3,trans-3,trans-3

3
e,trans-3,trans-2

4
trans-4,trans-3,trans-3

5
e,trans-4,trans-3

6
trans-4,trans-4,trans-2

7
e,trans-4,trans-2

8
trans-4,trans-4,trans-4

9
e,e,trans-1(I)

10
e,e,trans-1(II)

Table 1. Symmetry and Synthetic Yield of the Seven Tris Bingel Isomers in This Study

compd		symmetry	yield (%) (starting from)			
			e	*t4*	t3	t2
[*e,e,e*]	**1**[a]	C_3	35.3			
[*t3,t3,t3*]	**2**[a]	D_3			28.5	
[*e,t3,t2*]	**3**[a]	C_1	47.8		27.5	86.5
[*t4,t3,t3*]	**4**	C_s		26.6	24.3	
[*e,t4,t3*]	**5**[a]	C_1	16.9	44.2	19.7	
[*t4,t4,t2*]	**6**[a]	C_2		10.3		
[*e,t4,t2*]	**7**[a]	C_1		18.9		13.5

[a] These trisadducts have an inherently chiral addition pattern. Only one enantiomer of the racemic mixtures is depicted in formulas **1**−**3** and **5**−**7**.

is represented by the cyclopropanation of *trans-4*-C_{62}-(COOEt)$_4$, where four out of the five possible regiosiomers of $C_{63}(COOEt)_6$ involving at least one *trans-4* position were formed in a nonstatistical ratio. The main product in this reaction is *e,trans-4,trans-3*-**5**. Quantum mechan-

Table 2. Half-Wave Reduction Potential (V vs Fc/Fc⁺) of C_{60} Trisadducts in 0.1 mol dm³ Bu$_4$NPF$_6$ in CH$_2$Cl$_2$

compd	E_1	E_2	E_3	E_4	E_5
[*e,e,e*]-**1**	−1.32 (57)	−1.53 (63)	N.O.[a]	−2.11[b]	−2.29[b]
[*t3,t3,t3*]-**2**	−1.29 (68)	−1.46 (76)	N.O.	−2.14[b]	−2.31[b]
[*e,t3,t2*]-**3**	−1.25 (62)	−1.52 (83)	−1.87[b]	−2.12[b]	−2.29[b]
[*t4,t3,t3*]-**4**	−1.17 (77)	−1.51 (117)	−1.87[b]	−2.08[b]	−2.30[b]
[*e,t4,t3*]-**5**	−1.16 (76)	−1.52 (93)	−1.85[b]	−2.18[b]	N.O.
[*t4,t4,t2*]-**6**	−1.16 (66)	−1.52 (83)	−1.81[b]	−2.16[b]	N.O.
[*e,t4,t2*]-**7**	−1.17 (72)	−1.54 (92)	−1.82[b]	−2.17[b]	N.O.

[a] Not observed. [b] Reported as peak potentials due to irreversibility.

ical calculations on some of the precursor bisadducts showed that the sites of preferred attacks exhibit pronounced frontier orbital coefficients.[7]

Recently, a one-step, tether-directed, regioselective synthesis was reported for the preparation of trisadducts of cyclotriveratrylene (CTV)-C_{60}, in which the C_3 symmetrical *e,e,e* and the D_3 *trans-3,trans-3,trans-3* structures were exclusively isolated.[20] In vitro studies have demonstrated that the water-soluble carboxylic acid analogues, $C_{63}(COOH)_6$, of both of these isomers are potent free radical scavengers and exhibit biological activity by fully blocking *N*-methyl-D-aspartate (NMDA) receptor-mediated toxicity.[24]

The high probability that both the retro-Bingel and the "shuffling" reactions occur in tris[di(ethoxycarbonyl)-methano][60]fullerene led to the present study. The principal goal was to investigate the relative rates of the "shuffling" and retro-Bingel reactions in an effort to make either or both synthetically useful procedures with trisadducts. The possibility of using the shuffling to improve the yields of those tris-isomers whose formation is not favored via the Bingel synthesis was very attractive. An evident additional incentive was the possibility of making other tris-isomers which had not been detected before.

This paper is a full account of the results obtained during the systematic investigation of the cyclic voltammetry and bulk electrolysis properties of C_{60} trisadducts **1**−**7**.

Results and Discussion

The half-wave reduction potentials for **1**−**7** were determined using cyclic voltammetry (Pt electrode) prior to CPE. These values are reported in Table 2 vs Fc/Fc⁺. Figure 2 shows a series of cyclic voltammograms for the [*e,e,e*] isomer, **1**, as representatives of the typical voltammograms for these compounds at room temperature. A quick inspection of this figure and the values reported in Table 2 seems to indicate that the first and second reductions are reversible if the scan is reversed after the first and/or second reduction peak. Notice, however, the appearance of a small (irreversible) oxidation peak at −1.02 V when the potential is reversed after the second reduction. The appearance of this peak may indicate the formation of a new product at the second reduction potential. As the CV potential is scanned more cathodically, the formation of a multitude of oxidation peaks, including the growth of the peak at −1.02 V, upon scan reversal at −2.60 V is observed. In most cases the oxidation peaks are irreversible and do not correspond to any reduction peak, indicating the presence of an EC mechanism with the concomitant formation of one or more new products after the second reduction.
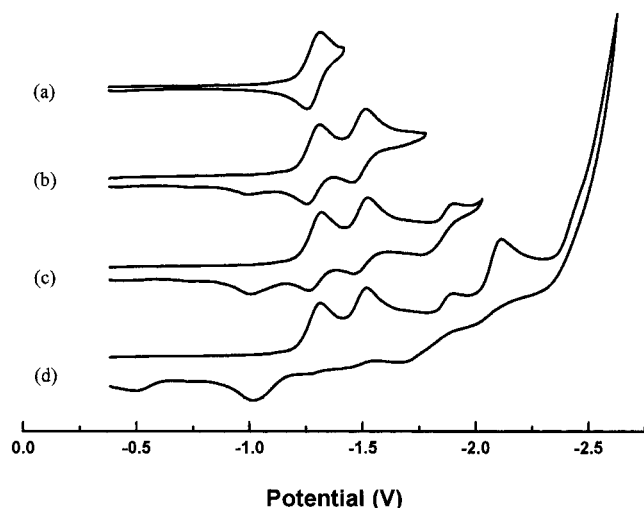
Figure 2. Cyclic voltammograms of trisadduct **1** in 0.1 mol dm^{-3} Bu$_4$NPF$_6$ in CH$_2$Cl$_2$ using a scan rate of 200 mV s^{-1} reversing the scan after the (a) first, (b) second, (c) third, and (d) fourth reduction waves.
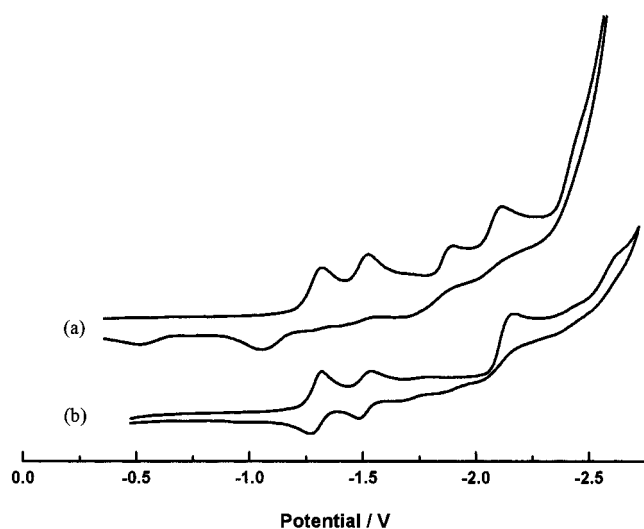

Figure 3. Cyclic voltammograms of trisadduct **1** in 0.1 mol dm^{-3} Bu$_4$NPF$_6$ in CH$_2$Cl$_2$ using a scan rate of 200 mV s^{-1} at (a) room temperature and (b) −40 °C.

The voltammetric response for compound **1** was also studied at a lower temperature (Figure 3). At −40 °C the chemical reaction that follows the electrochemical one at room temperature is slowed, as evidenced by the increased reversibility of the first and second reductions when the potential is scanned cathodically throughout the potential window of the solvent.

On the basis of the voltammetric information, it was assumed that the compound would be stable at least in its monoanionic state at room temperature (RT). However, CPE performed on this compound at RT at the first reduction potential did not stop automatically, i.e., the current did not reach background level. Therefore, after a current corresponding to exactly 1 electron equivalent had been reached, the electrolysis was interrupted. Analysis of the isolated products after reoxidation showed that 15% of the material was converted to other products although a substantial amount of unreacted starting material (85%) was recovered. Interestingly, the products included five of the bisadducts (mostly the *e*-isomer) as well as one other trisadduct isomer and even some

monoadduct. An EC mechanism is obviously operative already at the first reduction potential.

A new electrolysis was then carried out at the second reduction potential and manually interrupted after a charge corresponding to 2 electron equivalents had been passed. After reoxidation to the neutral state the products were isolated and analyzed (see Experimental Section). Table 3 shows a summary of the relative product distribution results obtained from the HPLC analysis of the electrolysis products of **1**. Also in the same table are the results obtained for **2**−**7**, all of which were electrolyzed under the same conditions as **1**, see Experimental Section for details.

A mixture of mono-, bis-, and trisadducts (and in one case C$_{60}$) was obtained in every case. Quantitative analyses show that all seven isomers preferentially undergo removal of one or two of the addends (the retro-Bingel reaction) to form bis- and monoadduct(s) over rearrangement (shuffle) to form other trisadducts. It is noteworthy, however, that the bisadducts formed in larger amounts for each of the compounds correspond to simple removal of one of the addends without any apparent further rearrangement of the remaining two addends. Shuffling of the newly formed bisadducts occurs only to a small extent. This can be concluded by simple inspection of the percentage of bisadducts formed. For example, of the five bisadducts formed from the loss of one addend by the [*t4,t3,t3*] isomer, **4**, 35% corresponds to the *trans-4* bisadduct and 50% to the *trans-3*, while the *e*, *trans-2*, and *trans-1* bisadducts were each produced in 5% relative yields. Thus, no preferential pattern of relative distribution such as the one mentioned in the Introduction and presented in Table 1 is observed in the present case.[26]

In all cases a relatively large fraction of material remained on the silica column during purification of the electrolysis products (with pure toluene) prior to HPLC analysis; see Experimental Section for details of the procedure followed. This material is very polar and could only be extracted using a large proportion of ethyl acetate, which brought with it some supporting electrolyte. We presume that this material must contain the removed addend(s), but we do not have direct proof of this. A new separation/isolation procedure is being devised to identify the nature of this product, since this is crucial for a mechanistic understanding of both the retro-Bingel and the isomerization reactions.

The small amount of isomerization undergone by trisadducts **1**−**7** was also analyzed quantitatively and organized using two different criteria in an attempt to establish a pattern for stability. The first criterion is the reactivity of the dianions based on their tendency to induce isomerization and to undergo retro-Bingel. **1**−**7** follow the order (from least to most reactive)

6 (58) ≈
    4 (57) < **7** (31) < **3** (26) < **5** (17) < **1** (11) < **2** (8)
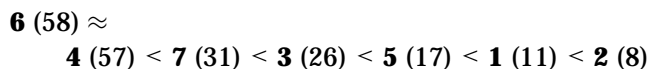
where the number in parentheses represents the percentage of material that remained unreacted after CPE. The second criterion used is the preferential formation of an isomer by electrolysis of other isomers. On the basis of this criterion **1**−**7** follow the order
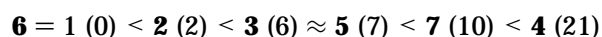
6 = 1 (0) < **2** (2) < **3** (6) ≈ **5** (7) < **7** (10) < **4** (21)

Table 3. Relative Distribution of Electrolysis Products at Room Temperature

starting material	monoadduct	bisadducts					trisadducts	retro-Bingel	shuffle	unr.	overall recovery
		e	t4	t3	t2	t1					
1 [e,e,e]	16	56	18	62 5	21	−	14 [e,e,e] = sm = 79 [e,t4,t2] = 21	78%	3%	11%	92%
2 [t3,t3,t3]	4	13	17	54 56	9	6	20 [t3,t3,t3] = sm = 40 [e,t3,t2] = 25 [t4,t3,t3] = 25 [e,t4,t2] = 10	58%	12%	8%	78%
3 [e,t3,t2]	3	44	7	45 13	33	2	42 [e,t3,t2] = sm = 62 [t4,t3,t3] = 24 [e,t3,t4] = 14	48%	16%	26%	90%
4 [t4,t3,t3]	5	5	35	20 50	5	5	61 [t4,t3,t3] = sm = 93 [e,t3,t2] = 2 [e,t4,t3] = 2 [e,t4,t2] = 3	25%	4%	57%	86%
5 [e,t4,t3]	7	17	17	30 60	3	3	27 [e,t4,t3] = sm = 63 [t4,t3,t3] = 7 [e,t4,t2] = 11 [t3,t3,t3] = 7 unknown = 7 unknown = 4	37%	10%	17%	64%
6 [t4,t4,t2]	2 (3% C_{60})	4	68	25 (*cis-3* = 8) 8	8	4	59 [t4,t4,t2] = sm = 98 unknown = 2	30%	1%	58%	89%
7 [e,t4,t2]	19 (2% C_{60})	50	21	34 6	15	9	35 [e,t4,t2] = sm = 89 [t4,t3,t3] = 11	55%	4%	31%	90%

where the numbers in parentheses represent sums of percentage yields relative to the total yield of the different reactions.

There is a clear correlation between the lack of reactivity of **4** and the favorable formation of this isomer by others. Also, the extent of reactivity of **1**−**3**, **5**, and **7** correlates well with their preferential formation by others. The only odd behavior is observed for [*t4,t4,t2*], **6**, which is not formed at all by others but is highly unreactive. We are currently investigating the possible reasons for this anomaly. Also, note that CPE of **5** and **6** produced two unknown tris-isomers, but their absolute yields are too small to warrant attempts at isolation.

The fact that the isomerization and retro-Bingel reactions of **1**−**7** and also those of bisadducts[26] proceed easily at room temperature and below implies thermodynamic control. It is reasonable to assume that the chemical reactivity of a given regioisomer observed experimentally correlates with the relative stability of its dianion to which the neutral species was converted prior to the follow up reactions. To prove this assumption we carried out a series of semiemirical PM3- and AM1-calculations using the program package Hyperchem.[31] The PM3 heats of formation of the sterically allowed[4,8] bisadducts C_{62}-$(COOEt)_4$ and $C_{62}(COOEt)_4{}^{2-}$ are presented in Figure 4. As reported earlier,[4,8] the most stable isomer of the neutral bisadducts is the *e* isomer. However, the *trans* adducts are almost isoenergetic. Only the *cis-3* and *cis-2* adducts are somewhat less stable, whereas the *cis-1* isomer is sterically forbidden. These results clearly show that the product distribution of the 2-fold addition of
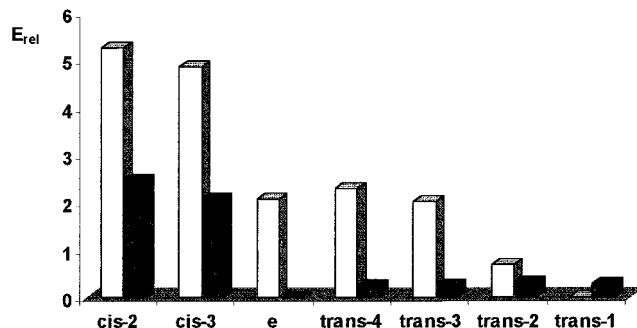
(31) HYPERCHEM 4.5; Hypercube, 1995, 419 Phillip Street, Waterloo, Ontario, N2L3X2 (Canada).

Figure 4. Relative PM3 heats of formation (kcal/mol) of bisadducts ($C_{62}H_4$ as models): white, dianions; black, neutral species.

bromo diethlymalonate shown cannot be a consequence of mere thermodynamic control. Significantly, the differences of the relative stabilities are much more pronounced in the dianions (Figure 4), with the *cis* adducts being even more destabilized. This fits very well with the observation that shuffling of the bisadduct dianions did not cause the formation of any *cis* bisadduct at all.[26] But even more importantly, the most stable dianion is now the *trans-1* adduct followed by the *trans-2* isomer (Figure 4). This is in perfect accordance with the experimentally observed product ratios shown in Figure 1. Obviously, charging a bisadduct with two electrons causes a thermodynamically controlled product distribution involving Umpolung of regioselectivity. It is reasonable to correlate the 0 K gas phase energy with that in solution at higher temperatures, since fullerenes exhibit extremely small reorganization energies.[32] A similar situation is found for the trisadducts (Figure 5). The differences of the relative energies of the dianions is much more pronounced than
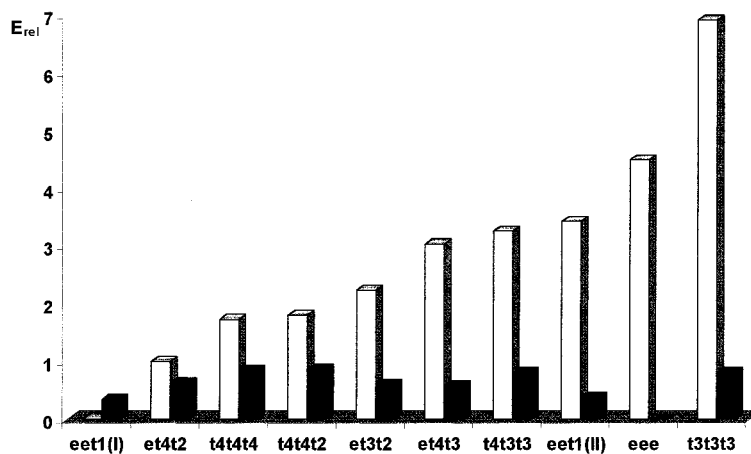
Figure 5. Relative PM3 heats of formation (kcal/mol) of trisadducts ($C_{63}H_6$ as models): white, dianions; black, neutral species.

Table 4.   Relative Distribution of Electrolysis Products as a Function of Temperature

starting material	monoadduct	bisadducts					trisadducts	retro-Bingel	shuffle	unr.	overall recovery
		e	*t4*	*t3*	*t2*	*t1*					
2 [*t3,t3,t3*] at RT	4	13	17	54 / 56	9	6	20 [*t3,t3,t3*] = sm = 40 [*e,t3,t2*] = 25 [*t4,t3,t3*] = 25 [*e,t4,t2*] = 10	58%	12%	8%	78%
2 [*t3,t3,t3*] at 0 °C	2	7	16	56 / 64	5	7	22 [*t3,t3,t3*] = sm = 77 [*e,t3,t2*] = 9 [*t4,t3,t3*] = 9 [*e,t4,t2*] = 5	58%	5%	17%	80%
1 [*e,e,e*] at RT	16	56	18	62 / 5	21	–	14 [*e,e,e*] = sm = 79 [*e,t4,t2*] = 21	78%	3%	11%	92%
1 [*e,e,e*] at −40 °C	7	55	5	20 / 10	5	20	21 [*e,e,e*] = sm = 62 [*e,t4,t2*] = 19 [*e,t4,t3*] = neglig. [*e,t3,t2*] = 5 [*t3,t3,t3*] = neglig. unknown = 14[a]	27%	8%	13%	48%

[a] The polarity of this unknown is between that of [*e,e,e*] and [*e,t4,t3*].

those of the neutral species. In some cases Umpolung of regioselectivity is observed. For example, neutral *e,e,e*-**1** is the most stable isomer, whereas the corresponding dianion is considerably destabilized. Only the dianion of *trans-3,trans-3,trans-3,*-**2** is less stable. These computational results fit very well with the experimental findings from above that **1**[2−] and **2**[2−] are the most reactive isomers. They are also in line with the observed stability of **7**. However, the experimentally observed stability of **4** is not in good agreement with the computations.

To pursue the possibility of making new trisadducts by electrolytically shuffling other trisadducts, different experimental conditions were tried using the only samples in relatively large supply, namely isomers **1** and **2**. The results of these attempts are presented in Table 4.

A CPE of **2** at 0 °C was first attempted in the hope that the retro-Bingel reaction could be inhibited to some extent at a lower temperature. It was presumed that rearrangement of the cyclopropane ring over the fullerene surface occurs one leg at a time, with one leg detaching and subsequently reattaching at a different (kinetically

more favorable) position. It was also presumed that simultaneous (or consecutive) detachment of the two legs (retro-Bingel) requires more energy, but that the final product is thermodynamically favored. Consequently, lowering the temperature would inhibit the retro-Bingel reaction. The results obtained for **2** under these conditions were thus surprising (see Table 4). The overall reaction process was slowed (17% of the starting material remained unreacted compared to only 8% at RT) and the proportion of isomerization vs retro-Bingel decreased by a factor of 2.

On the basis of its voltammetric results at low temperature, and since more of isomer **1** was available compared to **2**, a drastic attempt was made by conducting electrolysis at −40 °C using the former. A total of 4 electron equivalents were passed at the second reduction potential before interrupting the electrolysis process. Although 13% of the starting material was recovered unreacted, the proportion of isomerization vs retro-Bingel increased dramatically by a factor of 8 with respect to the RT reaction. Five trisadduct peaks (other than that for [*e,e,e*]) were observed by HPLC as compared to only one at RT. Furthermore, one of these five peaks is very significant because it corresponds to 14% of all trisad-

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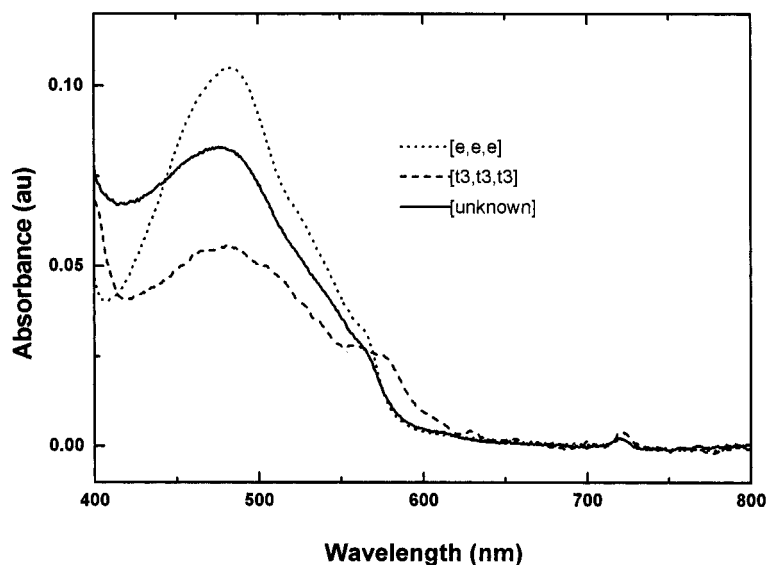
Figure 6. UV–vis spectra (400–800 nm) of unknown trisadduct (solid line). The spectra of **1** (dotted line) and **2** (dashed line) are also shown for comparison.

ducts isolated in this reaction, and most importantly, it is not any of the seven tris-isomer samples that we had at hand. From its position in the HPLC chromatogram it is clear that this unknown is more polar than [*t4,t3,e*] and less polar than [*e,e,e*]. On the basis of this, we speculate that the unknown is the [*t4,t4,t4*] isomer (**8**), whose synthetic formation is not preferred.[30] The calculation on the dianions (Figure 5) corroborate this suggestion, since **8**$^{2-}$ is among the most stable isomers. The only other possible isomers which would exhibit the polarity observed would have to have one of the addends at a *cis* position. However, the formation of dianions involving *cis* positions is a very unfavorable process,[26] a fact that is also theoretically supported by semiempirical calculations (Figure 4). The unknown material has been isolated, and its UV–vis spectrum is shown in Figure 6. However, the small amount obtained has made it difficult to obtain an NMR spectrum.

Conclusions

A two-electron bulk reduction of tris[di(ethoxycarbonyl)-methano][60]fullerenes **1**–**7** at controlled potential results in competing retro-Bingel and isomerization reactions. A mixture of mono-, bis-, and trisadducts is obtained in all cases with preferential loss of one or two of the addends. These results are in contrast with those for the bis[di(ethoxycarbonyl)methano][60]fullerenes obtained in a previous study,[25] where a two-electron CPE resulted in much more isomerization than retro-Bingel. The experimental finding that the regioselectivity of malonate additions to neutral precursors is different from rearrangements of dianions can be explained with an Umpolung of reactivity and introduction of thermodynamic control caused by charging of the neutral species with two electrons. Conducting the electrolysis reactions at a lower temperature increases the proportion of isomerization vs retro-Bingel products but reduces the overall reactivity of the starting material. This variation in reaction rates with temperature indicates that the mechanism controlling these two reactions are different and very complex. Isolation of the removed addend(s) is currently underway in order to help describe clearly the mechanism involved in the retro-Bingel reaction. Also,

a new tris-isomer which may have the structure [*t4,t4,t4*] has been isolated, and its UV–vis spectrum has been obtained. Experiments to fully identify this isomer are currently underway.

Experimental Section

General. The synthesis of all compounds used in this study has been reported elsewhere.[4,9,30] Toluene and ethyl acetate for HPLC and column chromatography were purchased HPLC grade and used without further purification. Column chromatography (CC): SiO$_2$ 60 (230–400 mesh, 0.040–0.063 mm) from E. Merck. HPLC analysis of electrolysis products was obtained using a Si 60 (5 μm) (250 × 4 mm) column with toluene as eluent solvent pumped at a rate of 1 mL min^{-1}.

Elecrochemistry. For CV, dried, degassed, vapor-transferred CH$_2$Cl$_2$ (Aldrich, HPLC grade) was used to prepare a solution of **1**–**7** (3.5 × 10^{-4} mol dm^{-3}) containing Bu$_4$NPF$_6$ (Fluka, recrystallized twice from ethanol) (0.1 mol dm^{-3}) and Ferrocene (sublimed) (Aldrich) (3.5 × 10^{-4} mol dm^{-3}). A three-electrode configuration consisting of a Pt disk (3 mm) working electrode, a Pt wire counter electrode, and a Ag wire pseudoreference electrode was used. All potentials reported are referenced vs the Fc/Fc$^+$ couple. All solutions were magnetically stirred and bubbled with argon prior to each voltammetric measurement.

For electrolysis, fullerene trisadducts **1**–**7** (2–3 mg) and supporting electrolyte, Bu$_4$NPF$_6$ (0.6 g), were placed into a home-built two-compartment electrolysis cell (for full description, see ref 33) The cell was degassed and evacuated to 10^{-6} mmHg. The solvent, CH$_2$Cl$_2$ (14 mL), which had also been degassed and evacuated to the same pressure, was then vapor-transferred into the cell, directly from P$_2$O$_5$. Prior to CPE, cyclic voltammetry was performed using a Pt disk (3 mm) working electrode to obtain the reduction potentials vs a Ag wire pseudoreference electrode. The latter was separated from the bulk solution using a Vycor tip. Unless otherwise specified, exhaustive CPE was conducted at 293 K on a Pt grid (100 mesh, 6.5 cm^2) working electrode at 100 mV more negative than the second reduction peak potential. The solution was then exhaustively reoxidized at 0 V. The electrolyte was removed by passing the product mixture through a short column of SiO$_2$ and eluted with toluene. TLC, HPLC, and/or UV–vis spectroscopy were used to identify the products.