Triphase Catalysis. Consideration of Catalyst and Experimental Conditions for Simple Nucleophilic Displacement Reactions[1]

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A series of 25 polymers has been examined as catalysts for cyanide, chloride, and acetate displacement on 1-bromooctane conducted as liquid/solid/liquid triphase catalysis (TC). Phosphonium-based polymers exhibited the highest activity and had a modest dependence on the nature of the organic solvent employed. Stirring improved yields only in one system investigated. Reusability of a phosphonium polymer was excellent.

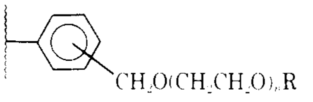
The use of insoluble polymers as catalysts in three-phase reactions (triphase catalysis, TC)[2] is receiving growing interest.[3] Several attractive synthetic procedures complementary to phase-transfer catalysis[4] have already been developed and show considerable promise for both laboratory as well as industrial applications.[5] In addition to the need for a better mechanistic understanding of these complex systems,[6,7] more empirical data are required to help guide synthetic efforts. In this paper we compare the efficacy of 25 polystyrene-based resins as catalysts for simple nucleophilic displacement reactions and examine the importance of the type of organic solvent and stirring conditions used. Specific systems investigated were cyanide, chloride, and acetate displacement on 1-bromooctane (reactions 1–3) employing resins **1–25**.

$$n\text{-}C_8H_{17}Br\ (org) + NaY(aq) \xrightarrow[\text{catalyst}]{\text{solid phase}} n\text{-}C_8H_{17}Y(org) + NaBr(aq) \quad (1\text{–}3)$$

$$1, Y = CN^-;\ 2, Y = Cl^-;\ 3, Y = OAc^-$$

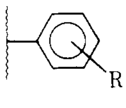
Results and Discussion

Catalyst Activity. Table I summarizes results obtained for triphase catalytic reactions 1–3 using polymers **1–25.** Polyether graft copolymers, previously found active in catalyzing the hydrolysis of 1-bromoadamantane and phenoxide ion displacement on primary organic bromides under triphase conditions, proved ineffective for reactions 1–3.[3,7,8] Replacement of sodium by potassium as the counterion did not improve results with resin **4**. Anion exchange polymers containing phosphonium groups (**18, 19**) proved to be most effective for these simple displacement reactions.[9] Interestingly, although **18** and **19** displayed similar activity per gram for reactions 1 and 2, the former catalyst was superior for reaction 3. Comparison of **18** with a phase-transfer catalyst, n-$C_{16}H_{33}P(n\text{-}C_4H_9)_3Br$,[10] revealed that the latter possessed greater activity per mole of phosphorus in all cases. Two ammonium-based polymers (**20, 21**) were also investigated. Similar to our previous finding,[11] only with a relatively low loading of methylenetrimethylammonium groups along the polymer backbone could significant triphase catalytic activity be found. A polymer-bound hexamethylphosphoramide, **24,** was less effective compared to **18** as a triphase catalyst for reactions 1 and 2 and completely ineffective for reaction 3.[12] Polymer **23,** which had a lower loading of phosphoramide groups, showed no measureable activity for all three displacement reactions. Cationic exchange type resins examined (**16, 17,** and **25**) were not active in catalyzing reactions 1–3.



microporous polystyrene–1% divinylbenzene[a]

1, 1; CH_3; 17
2, 2; CH_3; 17
3, 3; CH_3; 17
4, 16; CH_3; 17
5, 1; CH_3; 45
6, 2; CH_3; 45
7, 3; CH_3; 45
8, 1; CH_3; 92
9, 2; CH_3; 92
10, 3; CH_3; 92
11, 1; H; 17
12, 4; H; 17
13, 13; H; 17
14, 1; H; 92
15, 4; H; 92



microporous polystyrene–1% divinylbenzene[b]

16, $CO_2^-Na^+$; 6
17, $CO_2^-Na^+$; 17
18, $CH_2P^+(n\text{-}C_4H_9)_3Cl$; 17
19, $CH_2P^+(n\text{-}C_4H_9)_3Cl$; 92
20, $CH_2N^+(CH_3)_3Cl$; 17
21, $CH_2N^+(CH_3)_3Cl$; 92
22, H; 100
23, $CH_2N(CH_3)PO[N(CH_3)_2]_2$; 17
24, $CH_2N(CH_3)PO[N(CH_3)_2]_2$; 92
25, $SO_3^-Na^+$; 100

[a] *n*; R; % ring substitution. [b] R; % ring substitution.

Organic Solvent. The nature of the organic solvent used for polymer-based triphase catalysts may influence the observed activity of the catalyst in several ways. First, it can be important in determining the absorption equilibria for the reactants on the polymer. Second, when a gelular resin is used it can control the extent of swelling, which in turn will determine the number of active sites available for catalysis. Third, it may be important in establishing the nature of the microenvironment at the active site and thus affect the free energy of activation. In Table II we summarize results obtained for reactions 1–3 catalyzed by **18, 20,** and **24** using *n*-heptane, toluene, and *o*-dichlorobenzene solvents. For each of these systems we find only a modest dependence of rate on the type of organic solvent used.[13]

Stirring. In principle, the rate-limiting step for TC using resin-based catalysts should be (a) diffusion of reactants across a thin layer surrounding the solid surface (Nernst or film diffusion), (b) chemical reaction at the particle surface, or (c) chemical reaction throughout the polymer matrix. If chemical reaction proceeds at a rate much higher than diffusion of reactants through the Nerst layer, (a) will control the rate. The observed catalysis should then be dependent on stirring speed. If, however, the rate is controlled by chemical reaction, stirring should not be an important factor. Since minimal stirring is needed to maintain the physical stability of the insoluble catalyst and is attractive for continuous flow methods, the question of stirring is an important one from a technological standpoint. All of the data presented in Tables I and II were derived from experiments conducted as unstirred systems. Table III summarizes the influence of stirring on reactions 1–3 using the two most active catalysts (**18** and **20**). Also included are results from control experiments performed

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Table I. Triphase-Catalyzed Nucleophilic Displacement[a]

reaction	catalyst	temp, °C	time, h	yield,[b], %
1	1-17[c]	110	24	0
	4[d]	110	24	0
	18	90	4	50
	18	110	8	90
	19	90	4	58
	20	90	4	23
	20	110	44	97
	21	90	24	0
	22	110	24	0
	23	90	24	0
	24	90	4	20
	24	110	44	92
	25	110	24	0
	$n\text{-}C_{16}H_{33}P^{+}(n\text{-}C_4H_9)_3{}^{-}Br$[e]	90	1	81
	none	110	24	0
2	1-17[c]	110	24	<1
	4[d]	110	24	<1
	18	110	4	43
	18	110	24	95
	19	110	4	35
	20	110	24	31
	20	110	72	75
	21	110	24	0
	22	110	24	0
	23	110	24	<1
	24	110	24	14
	24	110	96	66
	25	110	24	0
	$n\text{-}C_{16}H_{33}P^{+}(n\text{-}C_4H_9)_3{}^{-}Br$[e]	90	4	68
	none	110	24	<1
3	1-17[c]	90	24	0
	4[d]	90	24	0
	18	90	24	56
	18	110	48	88
	19	90	24	17
	20	90	24	10
	20	110	96	75
	21-25[c]	90	24	0
	$n\text{-}C_{16}H_{33}P^{+}(n\text{-}C_4H_9)_3{}^{-}Br$[e]	90	24	100
	none	90	24	0

[a] All reactions were carried out as unstirred systems in 8-mL culture tubes using 0.26 mmol of 1-bromooctane in 2 mL of toluene plus 8 mmol of NaCN, 4 mmol of NaCl, or 6 mmol of NaOAc dissolved in 2 mL of water. In all experiments, 0.05 g of polymer was used. [b] Yields were determined by GLC based on 1-bromooctane. [c] Each catalyst was tested individually. [d] Potassium salt was used. [e] A phase-transfer catalyst was (0.06 mmol) was used in place of the polymer catalyst.

Table II. Solvent Effects[a]

reaction	catalyst	organic solvent	temp, °C	time, h	yield, %
1	**18**	n-heptane	90	4	83
		toluene	90	4	76
		o-dichlorobenzene	90	4	65
	20	n-heptane	90	4	16
		toluene	90	4	19
		o-dichlorobenzene	90	4	21
	24	n-heptane	90	4	17
		toluene	90	4	21
		o-dichlorobenzene	90	4	20
	$n\text{-}C_{16}H_{33}P^{+}(n\text{-}C_4H_9)_3Br^{-}$	n-heptane	90	1	70
		toluene	90	1	81
		o-dichlorobenzene	90	1	86
2	**18**	n-heptane	90	4	30
		toluene	90	4	26
		o-dichlorobenzene	90	4	26
	20	n-heptane	110	24	38
		toluene	110	24	31
		o-dichlorobenzene	110	24	21
	24	n-heptane	110	24	22
		toluene	110	24	13
		o-dichlorobenzene	110	24	17
	$n\text{-}C_{16}H_{33}P^{+}(n\text{-}C_4H_9)_3Br^{-}$	n-heptane	90	4	52
		toluene	90	4	68
		o-dichlorobenzene	90	4	50
3	**18**	n-heptane	90	4	12
		toluene	90	4	20
		o-dichlorobenzene	90	4	18
	20	n-heptane	90	4	2
		toluene	90	4	2
		o-dichlorobenzene	90	4	2
	$n\text{-}C_{16}H_{33}P^{+}(n\text{-}C_4H_9)_3Br^{-}$	n-heptane	90	4	32
		toluene	90	4	41
		o-dichlorobenzene	90	4	27

[a] Reaction mixtures were similar to those described in footnote a of Table I, except that the organic solvent was varied.

in the absence of catalyst. For cyanide displacement on 1-bromooctane using **18**, a significantly faster rate was observed with the stirred (500 rpm) as compared to the unstirred reaction. When catalyst **20** was used, rates for stirred and unstirred processes were nearly identical. For reactions 2 and 3 catalyzed by **18**, rates were insensitive to stirring. Surprisingly, when **20** was used to carry out these same displacement reactions, a slight *reduction* in rate was noted when stirring was employed.[14]

Reuse of Catalyst. The ability to reuse **18** to catalyze reactions 1-3 was examined.[15] Pertinent data are listed in Table IV. For both cyanide and chloride ion displacement on 1-bromooctane no loss in activity was observed. The continuous decrease in activity of **18** for reaction 3 appears to be related to unfavorable ion exchange equilibria and not to catalyst decomposition.[16] Exposure of the resin (recovered after three runs) to an aqueous chloride solution regenerated the catalyst to its original activity.

Conclusions

Results obtained from this study indicate that for simple nucleophilic displacement reactions phosphonium-based polymers are most active as triphase catalysts. For reactions 1-3 catalyzed by **18** and **20**, the nature of the organic solvent had a modest influence on observed reaction rates. The fact that stirring improved yields only in one system investigated demonstrates that empirical testing is required in order to determine if stirring is necessary for optimal triphase catalytic procedures.

Experimental Section

General Methods. Unless stated otherwise, all reagents were obtained commercially and were used without further purification. Toluene was purified by distillation from sodium and benzophenone under a nitrogen atmosphere. Reagent grade o-dichlorobenzene and n-heptane were used directly. Deionized water was purified by distillation from $KMnO_4/Ba(OH)_2$. All ^1H NMR and IR spectra were

Table III. Influence of Stirring[a]

reaction	catalyst	temp, °C	time, h	stirring speed, rpm	yield,[b] %
1	none	115	1	1000	0
	18	90	2	0	62
		90	2	500	97
	20	90	5	0	20
		90	5	500	19
2	none	105	24	500	0
	18	105	4	0	61
		105	4	500	70
	20	105	24	0	36
		105	24	500	22
3	none	105	24	500	0
	18	105	6	0	58
		105	6	500	53
	20	105	30	0	31
		105	30	500	20

[a] Triphase reactions were performed in a three-neck round-bottom flask as described in the Experimental Section. [b] Yields were determined by GLC and are based on the starting organic halide.

Table IV. Reuse of 18 in TC[a]

reaction	run no.	time, h	yield, %[b,c]
1	1	4	42 (42)
	2	4	45 (44)
	3	4	55 (53)
2	1	5	27 (26)
	2	5	20 (18)
	3	5	20 (23)
3	1	24	51 (53)
	2	24	29 (30)
	3	24	22 (23)
	4[d]	24	55 (49)

[a] Reaction temperature in all cases was 90 °C. Conditions used are described in the Experimental Section. [b] Yields (GLC) were based on 1-bromooctane. [c] Numbers in parentheses refer to a duplicate experiment carried out simultaneously. [d] Reaction was carried out with recovered resin which was first treated with an aqueous sodium chloride solution (see Experimental Section).

recorded using Varian A-60 and Beckman Acculab 7 spectrometers, respectively. Product mixtures were analyzed by GLC on a Hewlett Packard Model 5830 A flame ionization instrument using either a 1.7 ft × 0.125 in. UCW-982 on Chromosorb W column or a 1.7 ft × 0.125 in. Carbowax on Chromosorb P column. Appropriate response factors relative to an internal standard were determined for each different substance analyzed. Mass balance in all cases was >95%. Culture tubes when used as reaction vessels were 8-mL Corning no. 9826 tubes equipped with a Teflon-lined screw cap. Oil bath temperatures were controlled with the aid of a THERM-O-WATCH electronic controller Model L6-1000 (I^2R Co., Cheltenham, Pa.) attached to a thermometer and were accurate to ±0.5 °C.

Polymer Catalysts. Resins **1–21** and **23–25** were prepared employing procedures previously described.[12,17–21] Cross-linked polystyrene, **22,** was obtained from commercial sources (Bio Rad Laboratories) and was used as obtained.

General Procedure for Determination of Triphase Catalytic Activity. Procedures similar to that described for the conversion of 1-bromooctane to 1-cyanooctane were followed in obtaining all of the data reported in Tables I and II. To a Corning no. 9826 culture tube containing 0.05 g of **18** was added a solution of 0.39 g (8.0 mmol) of sodium cyanide dissolved in 2.0 mL of water followed by 0.05 g (0.26 mmol) of 1-bromooctane plus 2.0 mL of toluene. An internal standard (*n*-dodecane) was added to the reaction mixture, and the tube was shaken vigorously for 2 min, placed in an oil bath maintained at 90 °C for 4 h, withdrawn, and cooled to room temperature. Analysis of the organic phase by GLC indicated a 50% yield of 1-cyanooctane. In all cases where *o*-dichlorobenzene was employed, the aqueous layer was the upper liquid phase in the reaction mixture. For chloride and acetate ion displacement reactions, 0.24 (4.0 mmol) and 0.8 g (6.0 mmol) of the corresponding sodium salts were dissolved in 2 mL of water.

Stirred Triphase Reactions. The apparatus used for stirred reactions consisted of a 100-mL, three-neck, round-bottom flask equipped with a reflux condenser, sampling port, and Teflon stirring paddle attached to a stirring rod. The rod was connected to a Cole-Parmer Stir-Pak stirrer having a tachometer accessory. A standard triphase reaction was carried out as follows. An aqueous solution of sodium cyanide (8.0 g (0.16 mol) in 20 mL of distilled water), 20 mL of a toluene solution containing an internal standard and catalyst **18** (0.5 g, 20 mol% based on phosphonium groups) were added to the reaction vessel thermostated at 90 °C. The stirring rod was positioned so that the upper edge of the paddle rested at the aqueous/organic interface along with the insoluble polymer. After the mixture was stirred at 500 rpm for 30 min, 1-bromooctane (0.58 g, 3.0 mmol) was added via syringe. For unstirred experiments, no additional stirring was performed. For chloride and acetate ion displacement reactions, 6.0 (0.1 mol) and 10.0 g (73.5 mmol) of the corresponding sodium salts were dissolved in 20 mL of water, respectively.

Reuse of Catalyst. Procedures similar to that described for the conversion of 1-bromooctane to 1-cyanooctane were followed in obtaining all of the data reported in Table IV. To a Corning no. 9826 culture tube containing 0.05 g of **18** was added a solution of 0.70 g (14.3 mmol) of sodium cyanide dissolved in 3.5 mL of water followed by 0.09 g (0.45 mmol) of 1-bromooctane plus 3.5 mL of toluene. An internal standard (*n*-dodecane) was added to the reaction mixture, and the tube was shaken vigorously for 2 min, placed in an oil bath maintained at 90 °C for 4 h, withdrawn, and cooled to room temperature. Special care was taken at the end of the shaking period to ensure that nearly all of the polymer was located at the liquid/liquid interface. Analysis of the organic phase by GLC indicated a 42% yield of 1-cyanooctane. In order to determine the reusability of the catalyst, 1-bromooctane was added to this same tube to return the organic layer to 0.13 M in organic halide. Further heating at 90 °C for 4 h led to a 45% yield of 1-cyanooctane. For acetate displacement reactions, after three consecutive reactions were performed the polymer was filtered, washed with water and toluene, and subjected to further heating with 4 mL of saturated sodium chloride solution plus 4 mL of toluene for 12 h at 90 °C. The resulting resin was then filtered, washed with toluene and water, dried [110 °C, 4 h (0.05 mm)], and tested again for triphase catalytic activity.

Registry No.—n-$C_8H_{17}Br$, 111-83-1; n-$C_8H_{17}CN$, 2243-27-8; n-$C_8H_{17}Cl$, 111-85-3; n-$C_8H_{17}OAc$, 112-14-1; NaCN, 143-33-9; NaCl, 7647-14-5; NaOAc, 127-09-3.

References and Notes

(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446) and the Army Research Office (Contract DAAG-29-76-G-0330).

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(14) Observed adhesion of some of the polymer to the inside walls of the reaction vessel physically removes catalyst from the liquid/liquid interface and may account for at least a portion of this phenomenon.

(15) Reuse of **18** in a preparative-scale conversion of 1-bromooctane to 1-cyanooctane was also examined. In this case, the procedure used was similar to that described for stirred TC (see Experimental Section) except that no internal standard was added, and the following quantities of aqueous cyanide, catalyst **18**, and toluene solution of organic halide were used: 40 g (0.8 mol) of sodium cyanide in 100 mL of water; 2.5 g of **18;** 5.8 g (0.03 mol) of 1-bromooctane in 100 mL of toluene. Stirring (500 rpm) was stopped after 4.5 h at 90 °C; GLC analysis indicated no detectable starting halide. The product mixture was cooled to room temperature and filtered. The insoluble resin was washed with 50 mL of toluene, the combined organic

phase was dried (Na_2SO_4) and concentrated, and the residue was distilled under nitrogen to yield 3.6 g (89%) of 1-cyanooctane having ^1H NMR and IR spectra indistinguishable from those of an authentic sample. Reuse of recovered **18** in an identical experiment led to an 84% yield of 1-cyanooctane.

(16) Bromide ion liberated in the reaction may compete effectively with acetate for phosphonium sites on the polymer and act as a catalyst poison.

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Free-Radical Addition of Iodo-*F*-alkanes to Isomeric 5-Norbornene-2,3-dicarboxylic Acid Derivatives

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Free-radical addition of linear iodo-*F*-alkanes (R_FI) to isomeric 5-norbornene-2,3-dicarboxylic acids and derivatives occurred stereoselectively. The anhydrides gave trans addition of R_FI exclusively, while exo-cis addition was the principal mode of reaction of *endo*-2,3-dicarboxylic esters. Nonstereoselective addition of the branched 2-*F*-propyl iodide took place as the result of steric crowding in the intermediate radical. Azonitrile, peroxide, or ultraviolet initiation was used as required. Chemical transformation of the resulting adducts was profoundly affected by their structure, particularly by the position of the iodine atom. Heating of *exo*-6-iodo-*exo*-*F*-alkyl-2,3-norbornanedicarboxylic esters gave a lactone, with loss of alkyl iodide; the *endo*-6-iodo compounds remain unchanged. Similarly, base-induced cyclization of the *exo*-6-iodo derivatives to a nortricyclene product took place and the *endo*-6-iodo isomer again was unaffected. This stereospecificity sheds new light on these reactions. Spectroscopic properties of these *F*-containing compounds were extensively studied, and a new area of derivative chemistry was opened.

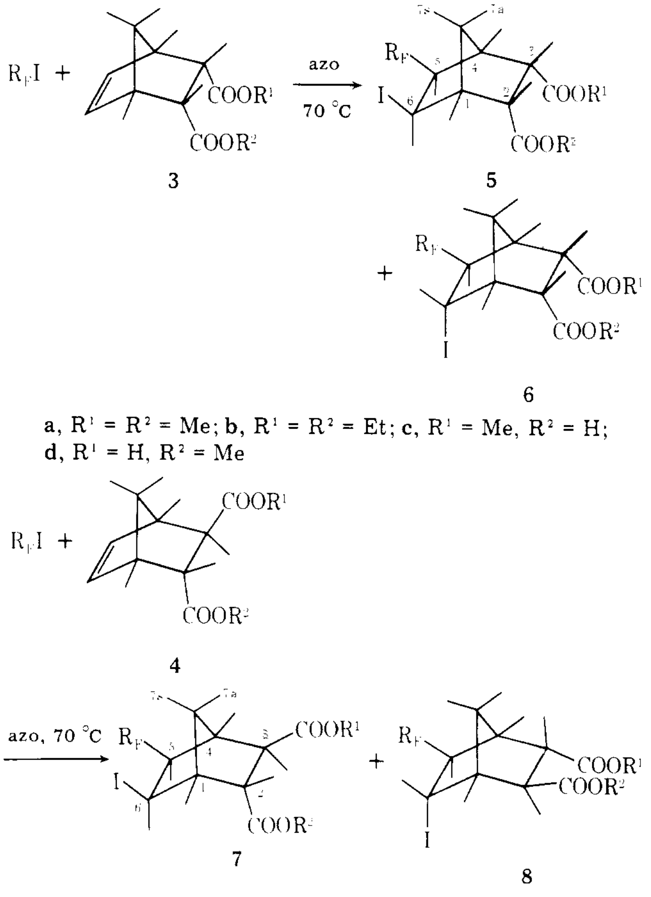
Historical Background. Reaction of norbornene with various addenda has been frequently reported. My early work[1] showed that trans addition of iodo-*F*-alkanes (R_FI) occurred, the *F*-alkyl group taking an exo position and the iodine atom exclusively adding in an endo position. Ludwick and Martin[2] explored radical additions of polyhalomethanes to *endo*-norbornene anhydride (bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride) (**1**) and discovered temperature dependent rotation of the dibromofluoromethyl group in the exo-cis adduct from tribromofluoromethane. Smart[3] examined radical addition of halogens and 1-iodo-*F*-propane to 5,5,6,6-tetrafluoro-2-norbornene, and Osborn, Van Auken, and Trecker[4] studied the effects of steric factors on the addition of carbon tetrachloride to norbornene derivatives. From a theoretical standpoint, radical addition of R_FI to *endo*- and *exo*-norbornene anhydrides (**1** and **2**) was of great interest since steric and electronic factors should have a pronounced effect. Additionally, a rich derivative chemistry of the products could be envisioned. The starting 5-norbornene anhydrides were readily available as the *endo*-anhydride is isomerized into the *exo*-anhydride by simple heating.[5] A convenient preparative procedure was recently reported.[6]

It is the purpose of this paper to describe the free-radical addition of R_FI to **1** and **2** and their derivatives and to report some significant new reactions of the adducts.

Results

Free-radical addition of R_FI ($R_F = CF_3(CF_2)_n$, n = 3, 5, 7) to dimethyl 5-norbornene-*endo*-2,*endo*-3-dicarboxylate (**3a**) occurred smoothly at 70 °C using an azonitrile initiator and afforded chiefly (90–97%) the *exo*-6-iodo isomer **5a** and only 3–10% of *endo*-6-iodo adduct **6a**.[7] The R_F group added exclusively in the exo position, as observed previously.[1] By contrast, the branched 2-iodo-*F*-propane did not react stereoselectively, but gave both *exo*- and *endo*-iodo products in about equal amounts. These reactants and products, together with the analogous reaction of the diethyl ester **3b**, the stereoisomeric *trans*-diesters **4a** and **4b**, and the diacid **4c**, are summarized in Scheme I. The half-esters **3c** and **3d** behaved similarly to the diesters **3a** and **3b**. Esterification of the adducts **5c** and **5d** gave principally the same diester **5a** as was isolated from addition of R_FI to **3a**. The *trans*-diester **4a** gave

Scheme I. Stereoselective Free-Radical Addition of 1-Iodo-*F*-alkanes to Isomeric 5-Norbornene-2,3-dicarboxylic Acids and Esters



a, $R^1 = R^2 = Me$; b, $R^1 = R^2 = Et$; c, $R^1 = Me$, $R^2 = H$; d, $R^1 = H$, $R^2 = Me$

a, $R^1 = R^2 = Me$; b, $R^1 = R^2 = Et$; c, $R^1 = R^2 = H$

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