the solid state for complexes III[33] and IV. There are two possible explanations for this discrepancy. The first is that the equation derived by Karplus does not apply and that the calculated solution pucker angles in Table XII are wrong. The second explanation is that the puckering angles are different in the solid state and in solution. We favor the latter explanation, especially in view of agreement between pucker angles in solution and in the solid state for V.[39]

How does one explain possible differences between solution and solid state? It seems unlikely that solvent coordination ($CDCl_3$ in this instance) is inducing puckering in solution. Rather, it seems more likely that puckering in solution is close to that of the hypothetical, unconstrained gaseous species and that the differences between solution and solid state are the results of packing effects in the solid state. Although this suggestion is hardly surprising, it is hard to substantiate. Some support results from the wide variation of pucker angles among the compounds of Table X, as we presume that the packing forces differ widely among the various compounds. It is interesting that compounds III and IV, though they crystallize in different space groups ($P2_1/c$ and $Pbca$), show similar pucker angles (1° and 5°) and show similar intermolecular interactions that could be indicative of similar packing forces.

Although the results are tentative, owing to the assumptions involved, we believe that the puckering differs in these metallacyclobutanes in solution and the solid state. Such a difference is important, since metallacycle puckering is often invoked in the mechanism of olefin metathesis reactions catalyzed in solution by transition–metal systems and except for rather specially tailored metallacycles, such as those synthesized here, information on the pucker angles is limited to results from solid-state studies.

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Registry No. I, 86854-27-5; II, 86854-28-6; III, 86854-29-7; IV, 86854-30-0; $[PtCl_2(C_2H_4)]_2$, 12073-36-8; cyclopropanemethanol, 2516-33-8; α-methylcyclopropanemethanol, 765-42-4; α,α-dimethylcyclopropanemethanol, 930-39-2; 1-methylcyclopropanemethanol, 2746-14-7.

Supplementary Material Available: Table III, thermal parameters for the non-hydrogen atoms, Table IV, positional and thermal parameters for the hydrogen atoms, Table V, root-mean-square amplitudes of vibration, Table VI, $10|F_o|$ vs. $10|F_c|$, Figure 1, δ vs. concentration of shift reagent, Figure 2, stereoview of the unit cell, Figure 5, ^1H spectrum of III, Figure 6, ^1H NMR spectra of I, and Figure 7, torsion angle vs. pucker angle (24 pages). Ordering information is given on any current masthead page.

Photoreactivity of (η^3-Allyl)palladium Complexes in the Presence of Organic Halides

Bertha De Poorter,[1] Jacques Muzart,* and Jean-Pierre Pete

Laboratoire de Photochimie, Equipe de Recherche Associée au CNRS No. 688, U.E.R. Sciences, B.P. 347, 51062 Reims Cedex, France

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Depending on the medium, bis(μ-chloro)bis(η^3-allyl)dipalladium complexes react photochemically with organic halides to yield either halogen-exchanged complexes or alkylated olefins.

Introduction

The reactivity of (η^3-allyl)palladium chloride complexes toward nucleophiles and even organometallics is well-known and has been applied frequently to alkylate olefinic compounds at the allylic position.[2] On the other hand, (η^3-allyl)nickel bromide complexes can be alkylated directly by organic halides.[3] These nickel complexes are generally prepared from allylic derivatives contrary to their palladium analogues that can be synthesized from olefins.[4]

In relation to a general study of the photoreactivity of (η^3-allyl)palladium complexes,[5,6] we have examined if these

Table I. Irradiation of 1 at λ = 366 nm in the Presence of Organic Halides

RX	RX/1 mole/mole	solv	conversn, %	yield of 2,[a] %
none[7]	0	CH_2Cl_2	0	
$BrCH(CO_2Et)_2$	10	CH_2Cl_2	30	28[b]
PhBr	used as solvent	PhBr	30	20
Cl_3CBr	100	CH_2Cl_2	76	40[c]
PhI	10	CH_2Cl_2	37	36
$PhCH_2Br$	25	CH_2Cl_2	80	79

[a] Isolated yield of 2 based on the amount of converted 1. [b] Also observed was a trace of 3. [c] Also isolated was 5 (15%) and a 1/2 mixture of 3 + 4 (15%).

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Table II. Irradiation of 1 at λ = 366 nm in the Presence of Organic Halides and Coordinating Species

RX (equiv/1)	conditns solv + L (equiv/1)	alkylated products (yield, %)[a]	yield of 8,[a] %
none	CH_2Cl_2 + PPh_3 (2)		53[b]
$PhCH_2Br$ (25)	CH_2Cl_2 + PPh_3 (2)	6 (39)	29[c]
$PhCH_2Br$ (26)	CH_2Cl_2 + PPh_3 (4)	6 (47)	43
$PhCH_2Br$ (25)	CH_2Cl_2 + maleic acid anhydride (6)	(0)	0[d]
$PhCH_2Br$ (25)	CH_3CN	6 (5)	15[e]
$PhCH_2Br$ (25)	DMF	6 (42)	36[f]
CH_2=$CHCH_2Br$ (30)	CH_2Cl_2 + PPh_3 (2)	7 (35)	38[f]
PhBr (22)	CH_2Cl_2 + PPh_3 (2)	(0)	51[g]
n-PrBr (40)	CH_2Cl_2 + PPh_3 (2)	(0)	57[g]
n-BuI (22)	CH_2Cl_2 + PPh_3 (2)	(0)	43
Cl_3CBr (26)	CH_2Cl_2 + PPh_3 (2)	5 (46)	<5[h]

[a] Isolated yield based on introduced 1. [b] Also isolated was a 1/8 mixture of 1 + 9 (44%). [c] Also isolated were a 5/1 mixture of 3 + 4 (5%), 2a (10%), and a 8/1 mixture of 1 + 9 (9%). [d] 2a (25%) was the only isolated product. [e] Also isolated was 2a (15%). [f] Also isolated was 3 (<5%). [g] Also isolated was a mixture of 1 + 9 (30%). [h] Also isolated a 20/1 mixture 3 + 4 (35%).

Table III. Irradiation of 11a and 12a at λ = 366 nm in Methylene Chloride in the Presence of Benzyl Bromide and Triphenylphosphine

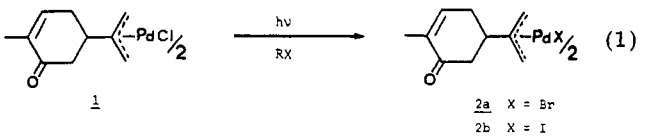
complex	benzylated olefins (yield, %)[a]	ratio of benzylated olefins[b]	1,5-dienes (yield, %)[a]	bromo complex (yield, %)[a]
11a	13 (22)	13a/13b = 2.5	14 (18)	11b (29)
12a	15 (22)	15a/15b = 3	16 (26)	12b (19)

[a] Isolated yields. [b] Ratio determined by NMR.

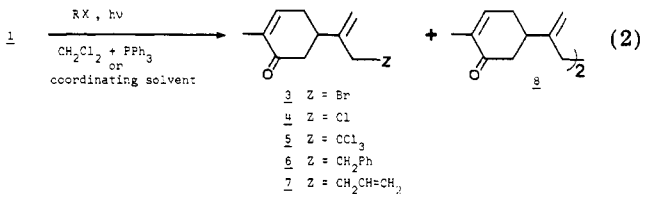
compounds, when irradiated, would be alkylated by organic halides. Such an alkylation would complement the methods described above.

Results

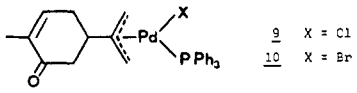
In methylene chloride, irradiation of the *l*-carvone complex 1 at 366 nm under an argon atmosphere in the presence of organic halides afforded complex 2 as the main isolated product ((1) and Table I). Without irradiation, no halide exchange was observed with diethyl bromomalonate, bromobenzene, or bromotrichloromethane. On the contrary, the yield of the bromo complex **2a** formed by reaction with benzyl bromide was higher in the dark (conversion 71%, yield 88%).



Addition of triphenylphosphine to the reaction mixture or the use of dimethylformamide as the solvent caused a change in the reactivity of 1, as alkylation products and the 1,5-diene 8 could be isolated ((2) and Table II).



Indeed, in the presence of triphenylphosphine, complex 1 could be benzylated or allylated by benzyl or allyl bromide in moderate yield; this reaction was accompanied by the dimerization of the η^3-allyl ligand which also took place in the absence of organic halide or when 1 was irradiated in acetonitrile.[5] Under dark conditions, the only products formed from 1, benzyl bromide, and triphenylphosphine were **2a** (17%) and the monomeric complexes **9** (38%) and **10** (38%). With maleic anhydride as an added coordinating species,[2k] no benzylated or dimerized product was observed. Although dimethylformamide appeared as effective as triphenylphosphine for the photolysis of 1 in the presence of benzyl bromide, the use of acetonitrile led only to low yields of 6 and 8.



Irradiation of 1 in methylene chloride solution containing bromotrichloromethane and triphenylphosphine led principally to the trichloromethylation product **5** and the allylic bromide **3**, while, with bromobenzene, *n*-propyl bromide, or *n*-butyl iodide as an organic halide, no alkylation was detected and 8 was the major product obtained. In similar conditions, irradiation of 1 and an excess of diethyl bromomalonate, methyl bromoacetate, or bromoacetophenone yielded complex mixtures; alkylation products and 8 were present in less than 5% yields. The yield of these products did not improve when **2a** was irradiated in the presence of diethyl bromomalonate or when 1 was photolyzed in dimethylformamide containing diethyl bromomalonate.

Irradiation of the dissymmetric complexes **11a** and **12a** in the presence of benzyl bromide and triphenylphosphine led to the regioselective benzylation of the less crowded side (Table III).

Discussion

Although irradiation of (η^3-allyl)palladium complexes in acetonitrile leads to 1,5-dienes in good yields,[5] no reaction was observed in methylene chloride[7] (Table I). The addition of an organic halide to the methylene chloride solution gives rise to an exchange of halogen atoms between the complex and the organic halide. Furthermore, in the presence of triphenylphosphine or in DMF, alkylation and dimerization of the allylic ligand becomes possible.

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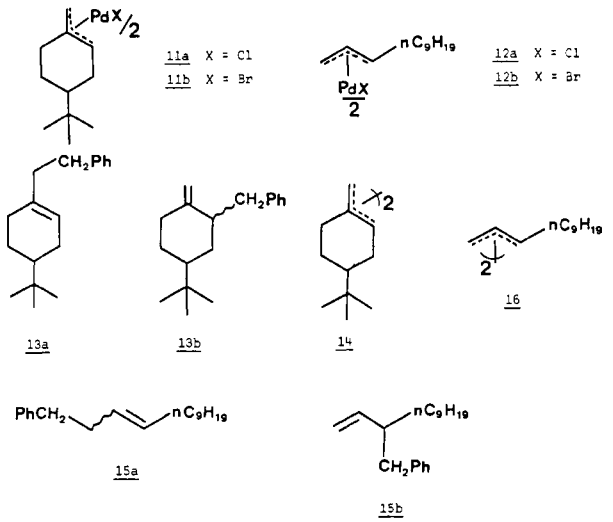
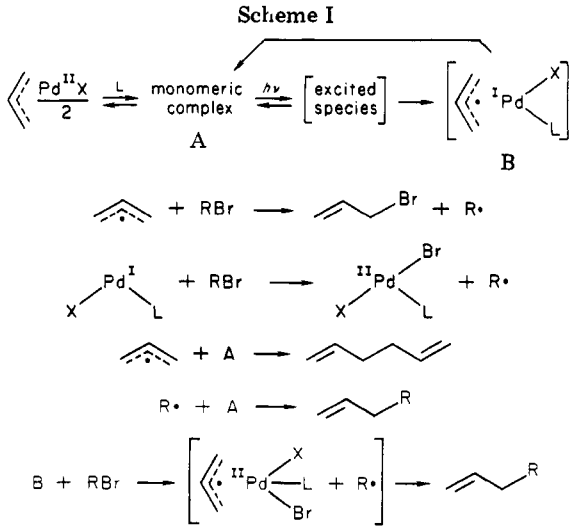


To our knowledge, halogen exchange in the dark with an organic halide has previously only been observed with methyl iodide and rationalized in terms of an "intermediate methyl iodide adduct".[8] A concerted halogen exchange between the complex and the organic halide via a pentacoordinated transition state could also be considered. Indeed, pentacoordinated palladium species have already been proposed.[9,10]

The UV spectra of (η^3-allyl)palladium chloride complexes show two large bands of absorption. The absorption observed at the longest wavelength has been assigned in part to a $d_{xz} \rightarrow d_{z^2}$ transition[11] whose activation leads to the labilization of metal–ligand bonds.[12] Addition of triphenylphosphine leads to a modification of the absorption[13] and to the formation of monomeric (η^3-allyl)- or (σ-allyl)palladium complexes.[14] The necessity of triphenylphosphine for the alkylation and/or dimerization to take place in methylene chloride solution suggests that these monomeric complexes are taking part in the photochemical reaction. As, moreover, allylic radicals have been trapped during the photolysis of (η^3-allyl)palladium chloride complexes[15] and are probably involved in the dimerization of the allyl group[5,16] and in the oxidation processes[6] previously observed, the results described above can be rationalized in part by the equations shown in Scheme I.

The first step following the absorption of a photon would be the production of a radical pair in which the allylic part can still be more or less bound to the palladium atom. Easy collapse of this radical pair to the starting material[16] and competition between processes b–f could explain the product distribution. Steps c and e are equivalent to those

Scheme I



proposed for the reaction of (σ-allyl)cobaloximes with polyhalomethanes[17] or diethyl bromomalonate.[18] When the reactivity of the organic halides with radicals[19] is low (*n*-PrBr, PhBr), the 1,5-diene is formed much faster than radical R· and no alkylation is detected. On the contrary, when RBr is a very reactive halide (e.g., $BrCCl_3$), reactions b and c can easily occur: the alkylation (eq e and/or f) and the bromination (eq b) can compete with diene formation. Apparently, in the case of benzyl or allyl bromide, R· is formed principally by reaction c and moderate yields of 1,5-diene and alkylation products are observed.

Conclusion

The results reported here demonstrate that allylic alkylation of olefins by organic halides is possible via the photolysis of the easily accessible (η^3-allyl)palladium complexes. Although the mechanism is not completely understood, we have shown that this reaction is strongly dependent on the nature of both the organic halide and the coordinating species.

Experimental Section

General Remarks. Irradiations were carried out with a Philips HPW 125-W lamp (λ = 366 nm). Preparative thin-layer purification was done on Merck silica gel 60 PF-254 plates.

Published procedures were used to prepare complexes **1**[4a], **11a**[4a], and **12a**.[20] The ^1H NMR spectra (δ) were recorded at 60 MHz in $CDCl_3$ with Me_4Si as internal reference, NMR spectra of **2a**, **2b**, **11b**, and **12b** were similar to those of the corresponding chloro complexes[4] except for a small downfield shift ($\Delta\delta$ <0.2) of the allylic protons. IR spectra were taken in $CHCl_3$ solution. Mass spectra were performed at the Faculty of Pharmacy of Reims.

Irradiation of Bis(μ-chloro)bis(η^3-allyl)dipalladium Complexes in the Presence of Organic Halides and Triphenylphosphine. In a typical experiment, **1** (43.2 mg, 0.074 mmol) and PPh_3 (42.3 mg, 0.161 mmol) were introduced in a two-necked Pyrex tube. After replacement of the atmosphere by argon, about 5 mL of freshly distilled dry CH_2Cl_2 was introduced with a syringe. After argon was bubbled into the solution for several minutes, allyl bromide (0.3 mL) was added with a syringe. Argon was then again passed through the solution for a few minutes. This mixture was irradiated at 366 nm during ca. 2 days. The orange solution was decanted from the crystals

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at the bottom (the IR spectrum showed these to be (triphenylphosphine)halopalladium complexes of unknown composition), evaporated, and chromatographed on preparative TLC (15% EtOAc in petroleum ether). This yielded **7** (9.9 mg, 0.052 mmol, 35%), **3** (~1.3 mg, 0.007 mmol, <5%), and **8** (8.4 mg, 0.028 mmol, 38%).

Reaction of 1 with $PhCH_2Br$ in the Presence of PPh_3 under Dark Conditions. A solution of **1**, PPh_3, and $PhCH_2Br$, prepared as described above, was kept in the dark during 2 days. After evaporation of the solvent the mixture was chromatographed on preparative TLC (15% EtOAc in petroleum ether) to remove $PhCH_2Br$. No **6** or **8** was detected. The yellow band containing complexes was rechromatographed in 2% Et_2O/CH_2Cl_2, which yielded two fractions: (i) the fastest migrating fraction was a mixture of **2a** and **10**, as was clear from the ^1H NMR spectrum, where, besides the signals of **2a**, appeared aromatic protons and also three broad bands at ca. 4.6, 3.5, and 2.9 ppm, respectively (compare ref 14a); (ii) the second fraction was a mixture of **1** and **9** with new bands at ca. 4.6, 3.6, and 2.8 ppm. Yields: **1**, 8%; **9**, 38%; **2a**, 17%; **10**, 38%.

Characteristic Spectra of the Main Isolated Products. 10-Bromo-*p*-mentha-6,8(9)-dien-2-one (3). NMR similar to that described:[21] δ 6.6–6.9 (m, HC=CC=O), 5.27 (s) and 5.10 (d, J = 1.5 Hz, $=CH_2$), 4.03 (s, CH_2Br), 2.25–3.0 (m, aliphatic ring protons), 1.80 (d, J = 2 Hz, CH_3).

10-Chloro-*p*-mentha-6,8(9)-dien-2-one (4). NMR identical with that of a sample prepared following ref 22: only difference with that of **3** is δ (CH_2Cl) 4.11 (d, J = 1 Hz).

10-(Trichloromethyl)-*p*-mentha-6,8(9)-dien-2-one (5): NMR (difference with that of **3**) δ ($=CH_2$) 5.40 (s) and 5.30 (d, J = 1.5 Hz), δ (CH_2CCl_3) 3.45 (d, J = 1 Hz); IR 2990, 2950, 2920, 2840, 1660, 1440, 1425, 1370, 1100, 945, 910, 890, 825, 705 cm^{-1}; mass spectrum (monoisotopic, based on ^{35}Cl), m/e (relative intensity) 266 ($M^{+\cdot}$, 4), 224 (14), 107 (19), 105 (14), 93 (33), 82 (100), 54 (29); calcd for $C_{11}H_{13}OCl_3$ m/e 266.0031, measd m/e 265.9991.

10-Benzyl-*p*-mentha-6,8(9)-dien-2-one (6): NMR δ 7–7.5 (m, C_6H_5), 6.6–6.9 (m, HC=CC=O), 4.90 (deformed s, $=CH_2$), 2.0–3.0 (m, aliphatic protons), 1.80 (d, J = 2 Hz, CH_3); IR 3020, 2930, 1665, 1600, 1490, 1450, 1430, 1380, 1360, 1240, 1230, 1105, 1070, 1050, 900, 700 cm^{-1}; mass spectrum, m/e (relative intensity) 240 ($M^{+\cdot}$, 31), 149 (36), 136 (15), 135 (14), 107 (12), 91 (100), 82 (24); calcd for $C_{17}H_{20}O$ m/e 240.1514, measd m/e 240.1520.

10-Allyl-*p*-mentha-6,8(9)-dien-2-one (7): NMR δ 6.6–6.9 (m, HC=CC=O), 5.5–6.1 (m, HC=C), ca. 5 (m, high-field multiplets hidden under signal at 4.87 ppm, $J_{trans} \approx 15$ Hz and $J_{cis} \approx 10$ Hz, $=CH_2$), 4.87 (s, $=CH_2$), 2.2–2.6 (m, aliphatic protons), 1.80 (d, J = 2 Hz, CH_3); IR 3080, 3005, 2930, 2890, 2850, 1665, 1635, 1445, 1430, 1410, 1375, 1360, 1240, 1135, 1105, 1050, 995, 905, 895 cm^{-1}; mass spectrum, m/e (relative intensity) 190 ($M^{+\cdot}$, 3), 148 (12), 109 (40), 108 (26), 93 (24), 91 (19), 82 (100), 79 (23), 69 (16), 67 (15), 65 (16), 57 (18), 55 (22), 54 (31); calcd for $C_{13}H_{18}O$ m/e 190.1357, measd m/e 190.1362.

1,5-Diene 8. NMR identical with that of a sample obtained in ref 5: δ 6.6–6.9 (m, HC=CC=O), 4.85 (s, $=CH_2$), 2.25–2.75 (m, aliphatic ring protons), 2.20 (s, CH_2), 1.80 (d, J = 2 Hz, CH_3).

4-*tert*-Butyl-1-(2-phenylethyl)-1-cyclohexene and 2-benzyl-4-*tert*-butyl-1-methylenecyclohexane (13a,b): NMR δ, 7.2 (C_6H_5), 5.3–5.5 (m, HC=C of **13a**), 4.4–4.75 (m, $=CH_2$ of **13b**), 2.2–2.9 (m, $CHCH_2Ph$ and CH_2CH_2Ph), 1.5–2.5 (m, aliphatic ring protons), 0.9 (s, *t*-Bu); IR 3010, 2960, 2940, 2860, 1640, 1595, 1490, 1460, 1445, 1430, 1385, 1355, 1255, 1230, 1120, 1020, 910, 885, 700 cm^{-1}; mass spectrum, m/e (relative intensity) 242 ($M^{+\cdot}$, 19), 186 (21), 95 (37), 91 (35), 81 (23), 57 (100).

1,5-Dienes 14: NMR δ 5.3–5.5 (m, HC=C), 4.6 (m, $=CH_2$), 1.5–2.3 (m, aliphatic protons), 0.9 (s, *t*-Bu); IR, 3010, 2950, 2860, 1640, 1465, 1390, 1360, 1245, 1230, 910, 885, 805 cm^{-1}; mass spectrum, m/e (relative intensity) 302 ($M^{+\cdot}$, 6), 245 (19), 95 (31), 94 (25), 83 (13), 81 (25), 57 (100); calcd for $C_{22}H_{38}$ m/e 302.2973, measd m/e 302.2941.

1-Phenyl-3-tridecene and 3-benzyl-1-dodecene (15a,b): NMR δ 7.2 (C_6H_5), 5.5–5.9 (m, =CH of **15b**), 5.3–5.5 (m, HC=CH of **15a**), 4.7–5.0 (BC part of ABCX system, $=CH_2$ of **15b**), 1.5–2.8 (m, nonchain aliphatic protons), 1.3 (br s, CH_2 chain), 0.9 (deformed t, CH_3); IR 3060, 3010, 2950, 2930, 2850, 1640, 1600, 1490, 1460, 1450, 1435, 1370, 1260, 1075, 1025, 965, 910, 700 cm^{-1}; mass spectrum, m/e (relative intensity) 258 ($M^{+\cdot}$, 12), 131 (10), 104 (55), 97 (22), 91 (100), 83 (32), 69 (36), 57 (17), 55 (36); calcd for $C_{19}H_{30}$ m/e 258.2347, measd m/e 258.2324.

1,5-Dienes 16: NMR (identical with that of an authentic sample[5]) δ 5.5–6.0 (m, =CH), 5.3–5.5 (m, HC=CH), 4.8–5.2 (m, $=CH_2$), 1.5–2.2 (m) and 1.3 (br s, aliphatics), 0.9 (deformed t, CH_3); IR 3010, 2930, 2850, 1640, 1460, 1455, 1435, 1370, 1260, 1090, 965, 910, 810 cm^{-1} mass spectrum, m/e (relative intensity) 334 ($M^{+\cdot}$, 3), 207 (17), 193 (11), 166 (10), 138 (13), 123 (12), 111 (35), 97 (75), 83 (100), 69 (94), 57 (50), 55 (71).

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Registry No. **1**, 67719-68-0; **2a**, 86847-19-0; **3**, 75107-34-5; **4**, 86847-23-6; **5**, 86847-24-7; **6**, 86847-25-8; **7**, 86847-26-9; **8**, 75401-27-3; **9**, 86847-20-3; **10**, 86847-21-4; **11a**, 55940-14-2; **12a**, 86847-22-5; **13a**, 86847-27-0; **13b**, 86847-28-1; **15a**, 86847-29-2; **15b**, 86847-30-5; PPh_3, 603-35-0; $PhCH_2Br$, 100-39-0; PhI, 591-50-4; maleic anhydride, 108-31-6; dimethylformamide, 68-12-2; acetonitrile, 75-05-8; bromotrichloromethane, 75-62-7; bromobenzene, 108-86-1; *n*-propyl bromide, 106-94-5; *n*-butyl iodide, 542-69-8; bromomalonate, 685-87-0; bromoacetate, 96-32-2; bromoacetophenone, 57579-38-1; allyl bromide, 106-95-6.

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