High-Intensity Laser-Jet Photochemistry: Formation of Benzocyclobutenedione from 1,2,3-Indantrione via Transient Targeting

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The photochemistry of 1,2,3-indantrione (**1**) under high-intensity (laser-jet) conditions has been investigated. Irradiation of trione **1** in a benzene solution under laser-jet conditions produces a complex mixture in which benzocyclobutenedione (**2**) is observed to be the sole high-intensity product (ca. 11% yield, six cycles, 3.5 W MLUV argon ion laser) as compared to conventional irradiation (dispersed laser beam, 20 min, 3.5 W MLUV argon ion laser). Under similar conditions, dione **2** was not observed to undergo photolysis in the laser-jet (mass balance ca. 90%). Additionally, phthalic anhydride, (*E*)-1,1′-bis-isobenzofuranylidene-3,3′-dione ((*E*)-**4**), and 2-benzopyrano[4,3-*c*]-benzopyran-6,12-dione (**5**) were identified also in both the laser-jet and conventional irradiations of both trione **1** and dione **2**. In view of the previously reported product studies, it is proposed that the formation of dione **2** under laser-jet conditions occurs by a photochemical electrocyclization of the intermediary cyclohexadiene-1,2-bisketene (**B**). The decarbonylation of trione **1** to bisketene **B** and the electrocyclization of the transient bisketene **B** to dione **2** constitute an unprecedented sequential multiple-photon transformation of polyketones in solution, which has been uncovered through product studies by using the novel laser-jet technique.

Introduction

The convenience of obtaining high light intensities (pulsed laser techniques[1] and laser-jet photolysis[1-4]) has made possible the study of transient intermediate photochemistry, a field that has recently flourished. For example, the short-lived transient intermediates oxacarbene **A** and bisketene **B**, derived from 1,2,3-indantrione (**1**) or benzocyclobutenedione (**2**) in Scheme 1, have been investigated by several research groups over the last three decades.[5-14]

The intermediacy of **A** and **B** in the photolysis of **2** was first postulated by Brown and Solly to account for the formation of the dimeric products spirolactone **3** and (*E*)-1,1′-bis-isobenzofuranylidene-3,3′-dione or *trans*-biphthalyl [(*E*)-**4**].[5] A more extensive study of the photochemistry of dione **2** was accomplished by Staab and Ipaktschi.[6] In addition to the photodimer (*E*)-**4** (major), they also observed the *cis*-biphthalyl (*Z*)-**4** and the 2-benzopyrano-[4,3-*c*]benzopyran-6,12-dione or diisocoumarin (**5**) as photoproducts, but no spirolactone **3** was detected. Trapping studies by Staab and Ipaktschi[6] provided further evidence for the existence of the intermediates **A** and **B**. Thus, oxacarbene **A** was trapped by electron-rich olefins to yield spirolactone **6**, while bisketene **B** underwent effective Diels–Alder reaction with electron-deficient olefins such as maleic anhydride to produce the [4 + 2] cycloadduct **7**.

Kolc has observed the photochemical formation of benzyne from dione **2** under matrix isolation conditions (EPA matrix, 77 K), presumably by photochemical double-decarbonylation of bisketene **B**.[7] Upon warming of the matrix to room temperature, the benzyne yielded ultimately biphenylene. In another matrix study of dione **2**, Chapman and co-workers[8] characterized bisketene **B** by IR spectroscopy (2091 cm^{-1}) at 8 K. Upon extended irradiation in the matrix, bisketene **B** was observed to undergo stepwise decarbonylation to produce benzyne, which was characterized by IR spectroscopy. After warming of the argon matrix to room temperature, triphenylene was isolated. In yet another matrix study, bisketene **B** was found to absorb at 2064 and 2125 cm^{-1}.[10]

More recently, Mosandl and Wentrup[11] additionally characterized bisketene **B** in an argon matrix study at 11 K. In this case, bisketene **B** exhibited absorptions at 2077 and 2138 cm^{-1} and reverted photochemically ($\lambda >$ 320 nm) and thermally (120–140 K) to dione **2**. The photochemical formation of bisketene **B** and its photo-

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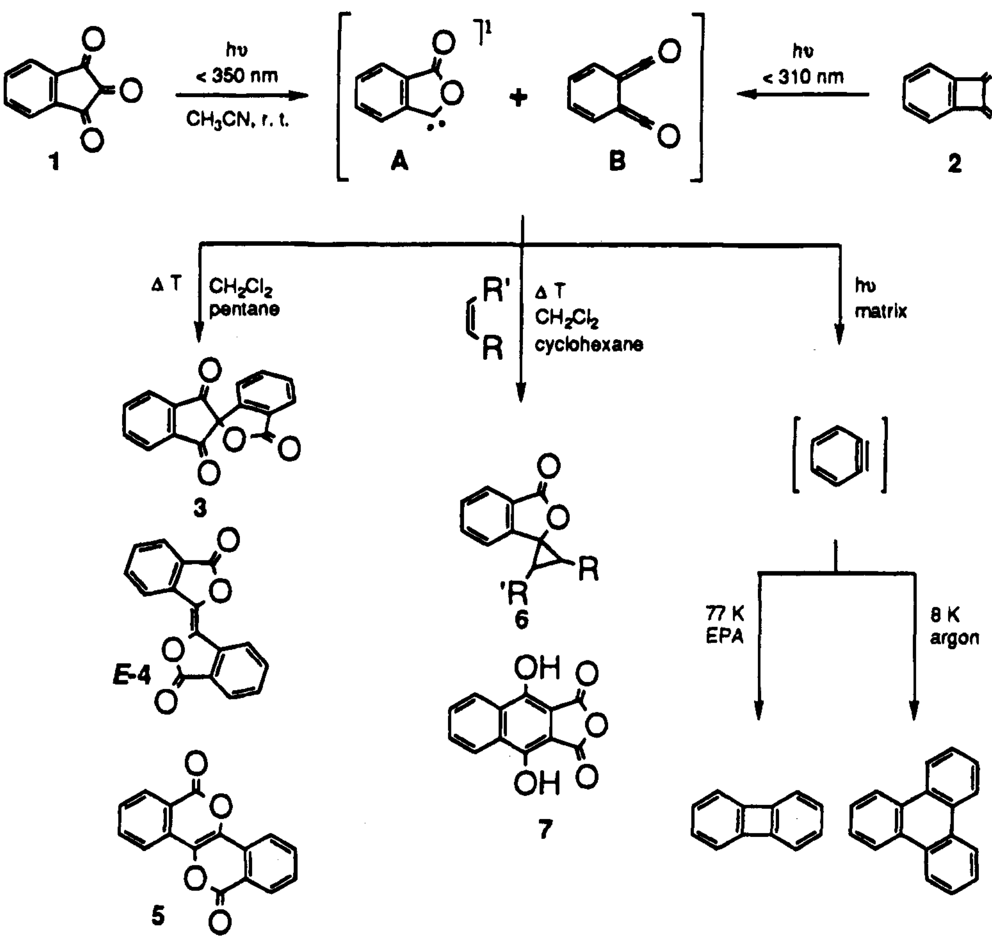
Scheme 1



reversion in the constrained medium could be recycled several times before ultimate decarbonylation to benzyne, as attested by IR spectroscopy.

Laser-flash studies of dione **2**, reported by Scaiano and co-workers,[13] indicate that two competing processes occur. One process produces the long-lived bisketene **B** ($\tau = 100$ μs, $\lambda_{max} = 380$ nm, toluene), the other the oxacarbene **A** ($\tau = 20$ μs, $\lambda_{max} < 300$ nm, toluene), which was indirectly detected by trapping with pyridine and adamantanethione.

Steady-state and laser-flash photolysis studies by Netto-Ferreira and Scaiano[14] have also implicated the intermediacy of **A** and **B** in the photochemistry of 1,2,3-indantrione (**1**). Irradiation of trione **1** in acetonitrile at 300 nm (250 h) produced (*E*)-**4** and **5** in a 1:7 ratio (GC analysis) with only 5% conversion. This relatively inefficient process was proposed to result by the slow loss of CO from an initially formed 1,5-diradical through α cleavage, which ultimately leads to oxacarbene **A** and bisketene **B**.

Herein, we report our laser-jet study of the relatively little explored photochemistry of the 1,2,3-indantrione (**1**), the purpose of which was to observe solution photochemistry of the transient intermediates involved. Trione **1** was chosen as a photochemical precursor due to its favorable absorption characteristics in the range of the available UV lines of the argon ion laser (333, 351, and 364 nm).

Results

Trione **1**, conveniently prepared in quantitative yield as dark purple needles from ninhydrin by vacuum pyrolysis (Scheme 2),[15] produces a pale green solution in benzene and pale blue solutions in acetone or acetonitrile. It exhibits absorption maxima at 330 nm as a shoulder of a stronger absorption below 300 nm and at 610 nm (very weak, $\epsilon = 29$) in benzene, acetone, and acetonitrile.[14,16]

Irradiation of the pale green solutions of trione **1** in benzene under high-intensity laser-jet (LJ) and conventional low-intensity photolysis conditions (dispersed laser beam) produced in both cases complex mixtures, as attested by thin layer chromatography. HPLC analysis of the benzene photolysate revealed the presence of one new high-intensity product, namely dione **2** (Scheme 2), in the laser-jet mixture but not in the conventional photolysis (Table 1, entries 1 and 2). Similarly, this high-intensity product was also obtained, but again in low yields, in the laser-jet photolysis of trione **1** in acetonitrile (Table 1, entries 3 and 4) and in acetone (Table 1, entries 5 and 6). The dione **2** was isolated in 11% absolute yield by means of preparative HPLC analysis and identified by comparison with the authentic material, which was synthesized pyrolytically from trione **1**[17a] or from anthranilic acid through benzocyclobutenone.[17b] Also from the preparative scale LJ reaction, phthalic anhydride was isolated in 5% yield as a low-intensity product, which again was identified by comparison with the authentic material.

In both laser-jet and conventional photolyses of trione **1**, *trans*-biphthalyl [(*E*)-**4**] and diisocoumarin (**5**) were

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Scheme 2

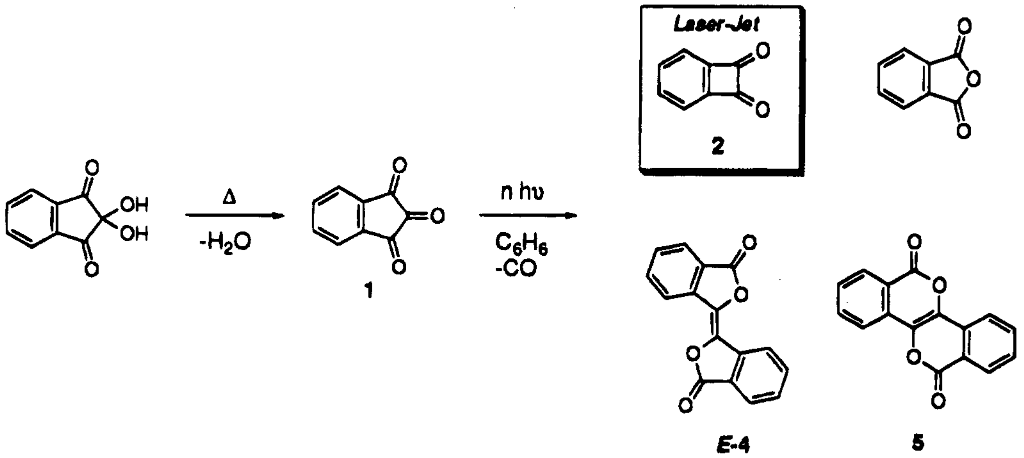

Table 1. Formation of Benzocyclobutenedione (2) from 1,2,3-Indantrione (1) in the Laser-Jet and Conventional Photolyses

	conditions[a]			mb[b]	convn[c]	% yield **2**[d]	
entry	mode	solv	time	(%)	(%)	abs[e]	corr[f]
1	LJ	C_6H_6	six cycles	93	58	4	6
2	conv	C_6H_6	20 min	100	42	*g*	
3	LJ	MeCN	six cycles	89	58	3	6
4	conv	MeCN	20 min	99	54	*g*	
5	LJ	Me_2CO	six cycles	100	55	2	3
6	conv	Me_2CO	20 min	99	62	*g*	

[a] Laser-jet (LJ) irradiation: 3.5 W MLUV (unless otherwise specified), argon gas atmosphere, 50-μm capillary, flow rate 1.0 mL/min. Conventional (low-intensity) irradiations: 3.5 W MLUV dispersed laser beam, quartz lens (f = 10 mm), irradiation distance 100 mm, magnetic stirring, argon gas atmosphere, irradiation tube immersed in water bath at room temperature; a concentration of ca. 16.0 mM was used. [b] Mass balance (mb) represents the amount of recovered crude product. [c] Conversion represents the amount of recovered ninhydrin after workup by CH_2Cl_2/H_2O extraction. [d] As determined by HPLC analysis (SiO_2 LiChrosphere 100, 5-μm particle size, 250 × 4.5 mm, 3:1 CH_2Cl_2/hexane, flow rate = 1.5 mL/min, detected at 254 nm), calibrated for dione **2** for which y (μg) = mx (mV/min) [where m = 0.063 μg/(mV/min), r = 0.9998, reproducibility within ± 5% of stated values] served as a calibration curve. [e] Absolute yield. [f] Corrected yield based on amount trione converted. [g] Not observed.

detected also by analytical scale HPLC. These low-intensity products were identified by comparison of retention times and UV absorption spectra (obtained directly from the HPLC detector) with the authentic samples, the latter prepared according to literature procedures.[18,19] After attempted isolation of the photoproducts by extraction of the crude product mixtures with H_2O to remove unreacted trione **1** in form of ninhydrin and CH_2Cl_2 to solubilize the photoproducts (*E*)-**4** and **5**, these were, unfortunately, not observed by analytical scale HPLC in the resulting crude product mixture. In view of the low solubility of these compounds in common organic solvents, they were presumably lost during these workup operations.

In a series of control reactions, the persistence of dione **2** ($\lambda_{max} \leq 300$ nm, $\epsilon_{300} = 7500$) was probed under the photolysis conditions in benzene by HPLC analysis. Under the laser-jet conditions (3.5 W, six cycles, 16.2 mM), dione **2** was not consumed (mass balance ca. 87%); while under conventional irradiation (3.5 W, 20 min, 15.4 mM), it was converted ca. 17% (mass balance ca. 97%) to a mixture of unidentified polar photoproducts. Furthermore, the photocyclization of an independently generated bisketene **B** under the laser-jet conditions could not be conducted in solution in view of the labile nature of this sensitive substance.[7-11]

Discussion

The observation of dione **2** as a high-intensity product in the laser-jet photolysis of trione **1** constitutes one of the few examples of multiple-photon chemistry of polyketones in solution.[1,14,20] A related case is the photochemical conversion of tetramethylcyclopentanetrione to tetramethylcyclobutane-1,2-dione.[20]

On the basis of the detailed time-resolved laser-flash studies of trione **1**[14] and dione **2**[13] in solution, a reasonable mechanism for the formation of the high-intensity product dione **2** and the low-intensity products *trans*-biphthalyl [(*E*)-**4**], diisocoumarin (**5**), and phthalic anhydride is illustrated in Scheme 3. Thus, laser-flash photolysis of trione **1** at 308 nm in solution produces the relatively low-energy triplet (E_T = 42 kcal/mol) **1-T**, which exhibits absorption maxima at 360 and 570 nm with a lifetime of 6.5 μs in acetonitrile and 9 μs in benzene.[14] The excited trione **1-T** can either intersystem-cross or undergo α cleavage to the triplet 1,5-diradical **C**. This diradical **C** is believed to undergo slow decarbonylation as observed by the relatively low conversions under low-intensity conditions (5% in acetonitrile, 300 nm, 250 h).[14] On the basis of the complete conversion of trione **1** to phthalic anhydride in the presence of molecular oxygen and the absence of the benzyne-derived products biphenylene and triphenylene, it was concluded that **C** and not **D** was trapped by dioxygen to produce the cyclic peroxide **8**. The latter yields on decarboxylation presumably phthalic anhydride. Support for this mechanistic rationalization derives from the pyrolysis of trione **1** in the presence of dioxygen, which also yields phthalic anhydride.[15]

The observed first-order decay of the triplet transient **1-T** represents decarbonylation of **C** to produce the triplet 1,4-diradical **D** as a very short-lived intermediate. Subsequently, the 1,4-diradical **D** intersystem-crosses to produce carbene **A** and bisketene **B**, which manifest themselves in the formation of *trans*-biphthalyl [(*E*)-**4**] and diisocoumarin (**5**), the low-intensity products isolated in the conventional irradiation of trione **1**, as reported by Scaiano.[14] The fact that these low-intensity products were also detected in the present laser-jet reactions of

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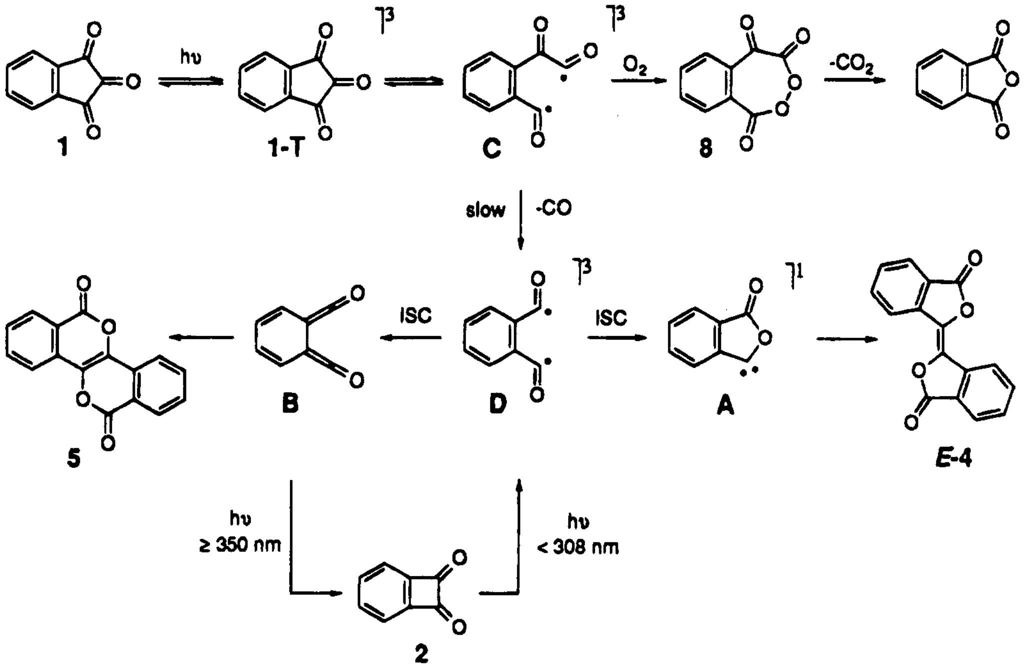
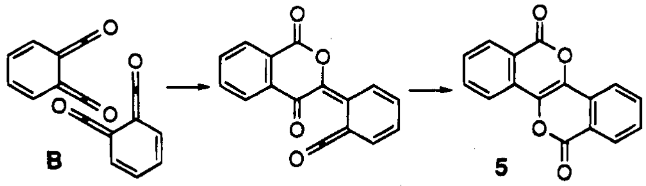
Scheme 3



Scheme 4



trione **1** implies the intermediacy of carbene **A** (Scheme 3) and bisketene **B** (Scheme 4) in these processes.

Diradical **D** has been also postulated by Scaiano[13] in the time-resolved laser-flash studies at 308 nm of dione **2**, in which it was concluded that the oxacarbene **A** (λ_{max} < 300 nm, τ = 20 μs) and bisketene **B** (λ_{max} = 380 nm, τ = 100 μs) were formed by independent processes from **D**. Additionally, the triplet-sensitized laser-flash studies of dione **2** with xanthone implies, but does not require, that bisketene **B** may also be formed from the triplet state of dione **2**. Since the irradiation of dione **2** in the presence of 1,3-cyclohexadiene as a triplet quencher did not effect the yield of bisketene **B**, Scaiano and coworkers[13] concluded that bisketene **B** derives either from a singlet-excited dione **2** or short-lived ($\tau \leq$ 5 ns) triplet 1,4-diradical.

In view of the previously reported results on the conventional irradiation of dione **2**[4,6,7] and trione **1**[14] the origin of the low-intensity products (*E*)-**4** and **5** from trione **1** is now clear also in the laser-jet photolysis. Dimerization of oxacarbene **A** leads to the *trans*-biphthalyl (*E*)-**4** and a *two-step dimerization* of bisketene **B** through [4 + 2] cycloaddition followed by electrocyclization (Scheme 4) yields diisocoumarin (**5**).[18] The observation of diisocoumarin (**5**) in the laser-jet and conventional photolyses of trione **1** *strongly* suggests the involvement of bisketene **B** in the photochemistry of trione **1** and dione **2** under high- as well as low-intensity conditions.

Since the formation of dione **2** in the laser-jet irradiation of trione **1** constitutes exclusively a high-intensity product, it is proposed herein that dione **2** is formed in the laser-jet from trione **1** by a multiple-photon, *transient targeting* mechanism involving the short-lived intermediate bisketene **B**. The first photon, or the *synthesis* photon, in this proposed mechanism produces the bisketene **B** intermediate through the slow decarbonylation step, as illustrated in Scheme 3. The second photon, or reaction photon, produces the observed high-intensity product, namely dione **2** by photoelectrocyclization of bisketene **B**. The favorable absorption characteristics of **B** (λ_{max} = 380 nm) near the available 364-nm UV laser line are particularly advantageous for such a transient targeting. Furthermore, the persistence of dione **2** during the laser-jet photolysis may be explained by unfavorable absorption of dione **2** ($\lambda_{max} \leq$ 300 nm) in the region of the argon ion laser. Indeed, a control experiment with dione **2** showed that under the laser-jet conditions this multiple-photon product is stable above 333 nm for the duration of the photolysis (six cycles).

Such a photoelectrocyclization of bisketene **B** to dione **2** is a reasonable mechanistic pathway; further, this two-step transformation of trione **1** to dione **2** by transient targeting of bisketene **B** represents a novel observation for solution photochemistry. In fact, Mosandl and Wentrup[11] have proposed, based on spectroscopic observations on the authentic bisketene **B**, that such a photoelectrocyclization occurs under matrix isolation conditions (λ > 320 nm). Matrix-isolated transient intermediates such as bisketene **B** persist long enough that conventional light sources can produce multiple-photon chemistry. Moreover, it is of interest to note that Mosandl and Wentrup[11] also reported, based on IR spectroscopic observations, the thermal reversion of bisketene **B** to dione **2** between 120 and 140 K. However, the fact remains that no dione **2** was observed in our conventional photolysis (dispersed laser-beam) of trione **1** through electrocyclization of the bisketene. The absence of dione **2** from the conventional (dispersed beam) photolysis of trione **1** may be explained by the transient nature of bisketene **B** (τ = 100 μs)[13] and the relatively low photon density of the dispersed beam experiments (in the laser-jet configuration it is estimated that effectively a *ca.* million-fold increase in light intensity prevails over that in the conventional laser-beam).[1-4] Additionally, if the dione **2** is formed in the conventional photolysis, it is more effectively consumed through the prolonged irradiation and, therefore, does not accumulate. Indeed, dione **2** still has sufficient absorption beyond 300 nm (ϵ_{300} ~7500) that photodecomposition during continuous irradiaton (20 min, 3.5 W) under the dispersed laser-beam conditions is rather likely. In contrast, despite the high intensities of the laser-jet irradiation, due to the short contact times (ca. 50 μs), the dione **2** persists. It must be emphasized that these laser-jet irradiations are at the threshold of the possibilities of this novel technique, as witnessed by the low yields of photoproducts even on multiple cycle laser-jet irradiations. Alternatively, some of the conventional photoproducts, namely the biphthalyl (*E*)-**4** and diisocoumarin (**5**), might photosensitize the decomposition of dione **2**. Unfortunately, solubility problems of (*E*)-**4** and **5** preclude such control experiments.

In conclusion, it must be stressed that the multiple-photon process

$$1 \xrightarrow{h\nu} \mathrm{B} \xrightarrow{h\nu} 2$$

in solution has been documented for the first time and constitutes an unprecedented observation for solution photochemistry of polyketones. The present study demonstrates the advantages of the novel laser-jet technique, in which the continuous output of the CW argon ion laser allows the monitoring of the solution photochemistry of photochemically generated short-lived intermediates such as the bisketene **B,** through product studies.

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Supporting Information Available: Experimental data (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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