3 H), 3.70 (s, 3 H), 3.87 (d, 2 H), 4.53 (quintet, 1 H), 5.10 (s, 2 H), 6.00 (t, 1 H), 7.10 (d, 1 H), 7.30 (s, 5 H); IR ($CHCl_3$) 1510 (s), 1680 (s), 1720 (sh), 1740 (s) cm^{-1}.

L-Phenylalanine Hexafluoro-2-propyl Ester Hydrobromide. A 10-mL Erlenmeyer flask equipped with a Teflon-coated magnetic stirring bar and protected with a drying tube was charged with 0.225 g of (*Z*)-L-Phe-OHFP (0.5 mmol) and 3 mL of 33% hydrobromic acid in glacial acetic acid. This mixture was stirred for ca. 20 min, at which time evolution of CO_2 was no longer evident. The solution was concentrated under vacuum at room temperature, and the residue was triturated with dry ether to precipitate a white solid, H-Phe-OHFP·HBr, 163 mg (0.42 mmol, 83%): NMR (1:2 $CDCl_3$–Me_2SO-d_6) δ 3.30 (m, 2 H), 4.68 (m, 1 H), 6.80 (septet, 1 H, J = 6 Hz), 7.33 (s, 5 H); IR (KBr) 1785 (s) cm^{-1}. An analytical sample was recrystallized from HFP–ether, mp 215–225 °C dec.

Anal. Calcd for $C_{12}H_{12}BrF_6NO_2$: C, 36.38; H, 3.05; F, 28.78; Br, 20.17. Found: C, 36.39; H, 2.93; F, 28.96; Br, 20.38.

Hydrogenolysis of (*Z*)-L-Phe-OHFP. A 15-mL centrifuge tube equipped with a Teflon-coated magnetic stirring bar and sealed with a rubber septum was charged with 0.67 g of (*Z*)-L-Phe-OHFP, 0.07 g of 5% palladium-on-carbon, 4 mL of glacial acetic acid, and 0.2 mL of concentrated HCl. Hydrogen was bubbled through the stirred mixture for 5 h. After centrifugation, the supernatant was diluted with anhydrous ether and the precipitate was collected by filtration and triturated and washed further with ether. A 0.39-g (75%) yield of H-Phe-OHFP·HCl as a white powder which afforded a single, ninhydrin-positive spot on TLC was obtained. NMR and IR spectra were consistent with the structure of the expected product: NMR (Me_2SO-d_6) 3.30 (m, 2 H), 4.60 (m, 1 H), 6.93 (septet, 1 H, J = 6 Hz), 7.50 (s, 5 H); IR (KBr) 1780 cm^{-1}, no absorption near 1700 cm^{-1}.

Conclusions

Reactions of amino acid and peptide hexafluoro-2-propyl esters with carboxyl-protected amino acid derivatives in hexafluoro-2-propanol are considerably slower than might be desired. However, the system may be of use in special cases such as oligopeptide polymerization, where solubility is a more important consideration than time. Because there are no facile side reactions to destroy the active ester itself, the use of elevated temperatures (up to the boiling point of 59 °C) may be a feasible method for overcoming the intrinsic unreactivity so that the advantages of a powerful and volatile solvent and a volatile coupling coproduct may still be enjoyed. Racemization does occur with chiral α-acylamino HFP esters in the presence of amines.

Acknowledgment. The 360-MHz spectra obtained for racemization studies were obtained at the Purdue University Biochemical Magnetic Resonance Laboratory, supported by the Division of Research Resources, NIH (Grant RR 01077). We thank Mr. Vytautas Narutis for preparation of several analytical samples and Mr. Ralph Thomas for assistance with some of the rate studies.

Registry No. (*Z*)-L-Phe-OHFP, 71785-36-9; (*Z*)-L-Phe-OH, 1161-13-3; HFP, 920-66-1; Boc-L-Val-OHFP, 71785-37-0; Boc-L-Val-OH, 13734-41-3; (*Z*)-Gly-OHFP, 71785-38-1; (*Z*)-Gly-OH, 1138-80-3; (*Z*)-L-Ala-OHFP, 71785-39-2; (*Z*)-L-Ala-L-Phe-OH, 2768-53-8; (*Z*)-Ala-L-Phe-OHFP, 71807-15-3; (*Z*)-L-Ala-D-OHFP, 71785-40-5; (*Z*)-L-Ala-D-Phe-OH, 17461-43-7; *N*,*N*′-dicyclohexyl-*O*-(1,1,1,3,3,3-hexafluoro-2-propyl)isourea, 71785-41-6; (*Z*)-L-Phe-L-Ala-OMe, 25422-44-0; L-Ala-OMe·HCl, 2491-20-5; (*Z*)-D-Phe-O-*N*-Su, 71785-36-9; (*Z*)-D-Phe-L-Ala-OMe, 3397-36-2; (*Z*)-Ala-L?-Phe-L-Phe-OMe, 71785-42-7; (*Z*)-Gly-OH *N*-hydroxysuccinimide ester, 2899-60-7; L-Ala-OMe, 10065-72-2; H-L-Phe-OHFP·HBr, 71785-43-8; H-L-Phe-OHFP·HCl, 71785-44-9; L-Phe-OMe·HCl, 7524-50-7; (*Z*)-L-Phe-OH *N*-hydroxysuccinimide ester, 3397-32-8; (*Z*)-D-Phe-D-Ala-OMe, 71785-45-0; (*Z*)-Gly-L-Ala-OMe, 16816-28-7.

Photolysis of Sodium Arenesulfonates in Aqueous Solution: Desulfonylation and Desulfonation[1,2]

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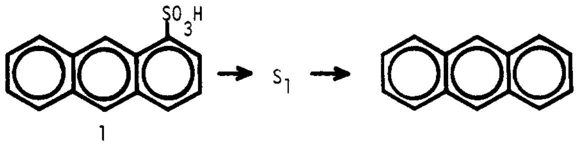
Received May 30, 1979

Photolysis of sodium anthracene-9-sulfonate (**3a**) gave 9,10-anthraquinone (**7a**) via the 9-anthranol anion (**6a**) by desulfonylation ($-SO_2$) and anthracene (**4a**) by desulfonation ($-SO_3$) in aqueous solution; in contrast, both sodium naphthalene-1- and mesitylenesulfonates (**3b** and **3c**) gave mainly desulfonation products with a trace of desulfonylation products.

Limited information is available on the relationship between the photochemical behavior and electronic configuration ($n-\pi^*$ or $\pi-\pi^*$) of the excited states of the arenesulfonates.[3-7] Studzinskii et al. photolyzed in acid aqueous media anthracene-1-sulfonic acid (1) and observed its desulfonation via the lower singlet state (S_1).[3] Properties of the S_1 state of reactive 1- and unreactive 2-anthracenesulfonic acids were compared.[3] They also investigated the photolysis of reduced anthraquinonesulfonic



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(ref 3)

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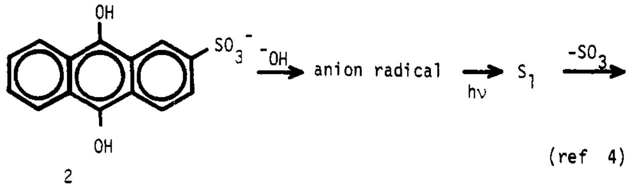
Table I. Photolyses of the Sodium Sulfonates (3a-c)

Ar-SO_3Na	concn, mM	solv	irrad time, min	conversion, %	recovery of 3, %	products − SO_2, % 7	products − SO_2, % 8	products − SO_3, % 4	products − SO_3, % 5
3a	2.9	H_2O	180	ca. 100		36.8		54.3	
3b	2.9	H_2O	180	ca. 20	ca. 80	trace	trace	1.5 (7.5)[a]	15.8 (79.0)[a]
3c	5.0	EtOH-H_2O (1:7)	150	ca. 100			0.8	78.2	

[a] Conversion yields.

acid (**2**) in basic aqueous ethanol and observed the desulfonation reaction to be two steps, proceeding via the S_1 state.[4] Mellier et al. observed photolysis (hydrolysis) of arenesulfonic acid esters of 3β(5α)-cholestanol to give corresponding alcohols via radical mechanisms.[6a] We previously reported that photolysis of methyl benzenesulfonate in methanol produced benzene, biphenyl, and anisole via radical fission of the S–Ph bond from the S_1 state.[6b] The reactions mentioned above all yield desulfonation products only.



2

$$ArSO_2OR \rightarrow ROH \quad \text{(ref 6a)}$$

Ar = Ph, tosyl, p-bromophenyl, etc.; R = cholestanyl

$$PhSO_3Me \xrightarrow[\text{MeOH}]{h\nu} PhH + PhPh + PhOMe + \text{others} \quad \text{(ref 6b)}$$

We have also described the photolysis of sodium arenesulfonates **3a–b** and **3d–g** in Me_2SO solutions to give

$$ArSO_3Na \xrightarrow[Me_2SO]{h\nu} ArH \quad \text{(ref 1)}$$

3a, Ar = 9-anthracene
3b, Ar = 1-naphthalene
3d, Ar = 2-naphthalene
3e, Ar = 2-toluene
3f, Ar = 4-toluene
3g, Ar = benzene

almost exclusively the corresponding desulfonation products with traces of desulfonylation products.[1] The reactions were proposed to proceed through the π–π* for the desulfonation.[1]

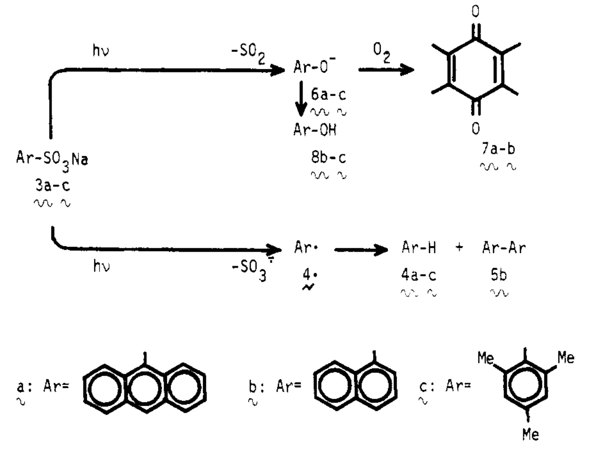
Ogata and his co-workers reported photolysis of benzenesulfonic acid in aqueous solution to give SO_2 and/or sulfuric acid,[6c] just after our preliminary communication.[2] They also detected benzene (16%) and biphenyl (<1%) but did not detect any organic desulfonylation products, e.g., phenol.[6c]

$$PhSO_3H \xrightarrow[H_3O^+ \text{ or } ^-OH/H_2O]{h\nu} PhH + PhPh + SO_2 \quad \text{(ref 6c)}$$

In this paper we describe a new photoelimination of SO_2 (desulfonylation) of sodium anthracene-9-, naphthalene-1-, and mesitylenesulfonates along with the corresponding photoelimination of SO_3 (desulfonation) at the same time (Scheme I). These are the first examples of photodesulfonylation of sulfonic acids to the best of our knowledge.

A solution of the anthracene-9-sulfonate **3a** in water containing 1 mL of 1 N NaOH was irradiated in air with an unfiltered (quartz) 300 W high-pressure mercury lamp for 3 h at ca. 30 °C. After irradiation, the precipitated products were filtered off and separated by silica gel preparative TLC to give anthracene (**4a**) and anthraquinone (**7a**). Photolysis of naphthalene-1-sulfonate (**3b**) gave mainly binaphthyl (**5b**) together with both traces of 1-naphthol (**8b**) and 1,4-naphthoquinone (**7b**) and naphthalene (**4b**). Most of the unchanged **3b** was recovered by TLC (ca. 80%). Photolysis of mesitylenesulfonate (**3c**) in aqueous ethanol (1:7) gave mesitylene (**4c**) and mesitol (**8c**). (See Table I.)

Scheme I



Detection of the Phenolate Anions (6a,b). To gain insight into the reaction pathways of desulfonylation, an aqueous KOH solution of **3a** was degassed (10^{-4} mmHg) and then irradiated at 15 °C in a quartz cell. After irradiation for 3 min, the UV spectrum of the solution showed a maximum at 435 nm due to the 9-anthranol anion **6a**.[8] However, when the solution was aerated, this maximum disappeared rapidly and a new maximum appeared at 324 nm due to anthraquinone (**7a**). In contrast, upon irradiation in air the spectrum showed only the new maximum at 324 nm. Similar spectroscopic results were obtained for **3b**; however, the extent of desulfonylation appears to be less than 1%.[9]

These results show the presence of a phenolate anion **6a** or **6b** as an intermediate which may be generated via an oxathiirane ring (**9**),[10] analogous to the oxirane **10** and oxazirane **11** intermediates proposed by Chapman and his co-workers in the photolyses of 9-anthroate (**12**)[8] and 9-nitroanthracene (**13**) (Scheme II).[11a] A similar interme-

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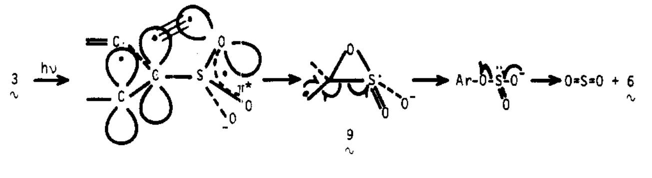
(8) A. W. Bradshaw and O. L. Chapman, *J. Am. Chem. Soc.*, **89**, 2372 (1967).

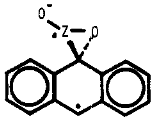
(9) The yield of **6b** was calculated to be ca. 0.2% from the extinction coefficient, ε (7600) of **6b** at 332.5 nm (for ε, M. J. Kamlet, "Organic Electronic Spectral Data", Vol. 1, Interscience, New York, 1960, p 304).

(10) Cf. L. Carlsen, N. Harrit, and A. Holm, *J. Chem. Soc., Perkin Trans. 1*, 1404 (1976).

(11) (a) O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thakarerry, *J. Am. Chem. Soc.*, **88**, 5550 (1966); (b) I. W. J. Still, P. C. Arora, M. S. Chauhan, M. H. Kwan, and M. T. Thomas, *Can. J. Chem.*, **54**, 455 (1976).

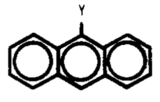
Scheme II





10: Z=C

11: Z=N



12: Y=CO$_2^-$

13: Y=NO$_2$

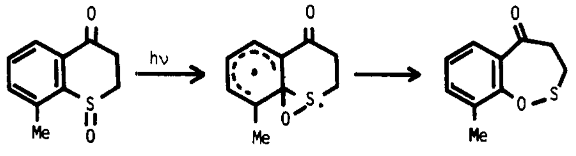
Table II. Quenching of Fluorescence and Photochemical Reactions of 3 with 1,3-Pentadiene at Room Temperature in Aqueous Solutions

Ar-SO$_3$H	fluorescence $k_q\tau_f$, M^{-1}	-SO$_3$ $k_q\tau$, M^{-1}	-SO$_2$ $k_q\tau$, M^{-1}
3a	0.5 × 10	4.8 × 10 (T$_2$)	1.4 × 10^2 (T$_1$) for 7a[a] 1.3 × 10^2 (T$_1$) for 6a[b]
3b	1.1 × 10	7.6 × 10^2 (T$_1$)	10 (S$_1$)[a]
3c	1.3 × 10	2.3 × 10^3 (T$_1$)	~10 (S$_1$)[a]

[a] In the air; analyzed by GLC. [b] In vacuo; analyzed by UV.

diate **6c** may exist in the photolysis of **3c**, though it could not be detected.

Still et al. proposed a similar cyclic sulfenate (**15**) as an intermediate of photoreaction of a thiochromanone sulfoxide (**14**) to give **16**.[11b]

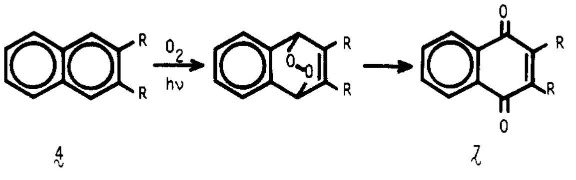


14 15 16

(ref 11a)

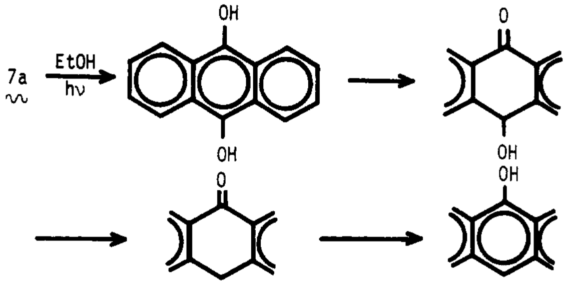
Desulfonation by the photolysis of the sulfonates **3a–c** may proceed via a radical pathway, which is supported by the generation of **5b** and **4**.

A number of papers can be found on photochemical oxygenation reactions of naphthalenes[12] and anthracenes[13] to give the corresponding quinones (**7a,b**). The photochemical reduction of 9,10-anthraquinone (**7a**) in ethanol to give 9-anthranol (**8a**) has also been reported.[14] However, both possibilities of oxygenation of the hydrocarbons **4** to give the corresponding quinones **7** and the reduction of the quinones **7** to give the corresponding phenols **8** were eliminated in the present reactions because of the behavior of **3** in vacuo.



4 7

(ref 12 and 13)



8a

(ref 14)

Detection of SO$_2$. The production of SO$_2$ was detected from each of the reaction mixtures, using [ZnFe(CN)$_5$(NO)] for gaseous SO$_2$ and [Na$_2$Fe(CN)$_5$(NO)] for sulfite anion.[15]

Quenching with 1,3-Pentadiene. Quenching of fluorescence and photolysis of the sulfonates **3a–c** shows that desulfonylation of **3b** and **3c** proceeds through the corresponding S$_1$ states and their desulfonation through a longer lived state, possibly T$_1$. In the case of **3a**, both desulfonylation and desulfonation appear to occur from states that are longer lived than S$_1$ from their quenching constants, $k_q\tau$[16] (see Table II). The $k_q\tau$ values for the production of anthraquinone (**7a**) in the air and 9-anthranol anion **6a** in vacuo are identical within experimental error.

Although it seems that the photochemical desulfonylation of **3** is very similar to photoelimination of NO[11] and CO[8] from 9-nitroanthracene (**11**) and 9-anthranoate (**10**), the stereochemical relation between O atoms of SO$_3$ and the aromatic nucleus plane is very different from the O atom of CO$_2$ or NO$_2$ of **10** and **11**. As if there is no steric hindrance to the SO$_3$ group like **10** and **11**, any one of the O atoms of SO$_3$ is perpendicular at any time to the nucleus plane, which is the different point from **10** and **11**. Therefore, the steric hindrance theory is not applicable to the present systems. Instead of that, we would mention electronical mixing of S$_1$ (or T$_2$) and T$_1$.

Experimental Section

Instrumentation. All melting points were taken with a microscope hot stage and are uncorrected. UV-vis spectra were recorded on a Shimadzu UV-200, fluorescence and phosphorescence spectra on a Hitachi MPF-2A, and GLC on a Yanagimoto Yanaco G-80.

Materials. Sodium anthracene-9-sulfonate (**3a**) was prepared by a method described in the literature from 9-nitroanthracene (**13**).[17] Both sodium naphthalene-1- and mesitylenesulfonates (**3b** and **3c**), 9,10-anthraquinone (**7a**), anthracene (**4a**), 1,4-naphthoquinone (**7b**), naphthalene (**4b**), 1,1′-binaphthyl (**5b**), 1-naphthol (**8b**), and mesitylene (**4c**) were purchased. Bimesitylene was prepared following the literature, mp 103–103.5 °C (lit.[18] mp 99.15 °C). Mesitol (**8c**) was prepared from mesitylene sulfonic acid,[19] mp 67–71 °C (lit.[20] mp 69 °C).

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[17] S. Yura and R. Oda, *Kogyo Kagaku Zasshi*, 44, 731 (1941) (*Chem. Abstr.*, **42**, 6792i (1948)).

[18] W. Moyer and R. Adams, *J. Am. Chem. Soc.*, **51**, 630 (1929).

[19] Seitaro Yamaguchi, "Experimental Organic Chemistry", 9th ed., Nankodo, Tokyo, 1944, p 645.

[20] C. W. Porter and F. H. Thuker, *J. Am. Chem. Soc.*, **43**, 1197 (1921).

General Method for Preparative Photolyses of 3a–c. A solution of **3** (2.9 or 5.0 mM) in water (180 mL) containing 1 mL of 1 N NaOH was irradiated internally in air with an unfiltered 300 W high-pressure mercury lamp (Eikosha P1H-300) for 180 or 150 min at ca. 30 °C. After irradiation, the precipitated products were filtered and separated by preparative TLC [silica gel PF_{254} (Merck), *n*-hexane] for the sulfonates **3a** and **3b**. For **3c**, the irradiated solution was extracted by $CHCl_3$ after acidification with dilute HCl, and the extract was analyzed on GLC [10% Silicone SE-GE-31 on Diasolid L (60–80 mesh) in a 2 m stainless steel column (inside diameter 2.5 mm), column temperature 212 °C, injection temperature 236 °C, carrier gas (N_2) 26.0 mL/min, sample 1 μL] and TLC [Silica gel PF_{254}-gilshaltig (Merck), 20 cm × 20 cm, thickness 2.2 mm, *n*-hexane] (see Table I).

Products were identified by comparisons of mp, IR, NMR, and/or retention times on GLC to those of the corresponding authentic samples (**4**, **5**, **7**, and **8**).

UV Spectra of the Irradiated Solutions: Detection of 6a and 6b in Vacuo. An aqueous solution of **3a** or **3b** (3.7 mM; 9 mL) containing 150 μL of 1 N KOH was degassed and then irradiated at 15 °C in a quartz cell. After 3 min of irradiation, the UV spectra of the solution were measured, λ_{max} (H_2O) for **3a** 435 nm (lit.[8] 435 nm). This maximum disappeared, and a maximum at 324 nm appeared on aeration, λ_{max} (H_2O) for **3b** 335 nm (sh) (authentic sample of **8b**, 335 nm).

Quenching with 1,3-Pentadiene. (a) Quenching of fluorescence of **3** in an aqueous solution (5.0 mM) with various concentrations of 1,3-pentadiene (distilled just before use) (1.3, 2.9, 5.2, 10.3, and 20.7 mM) was observed by the fluorometer at 25 °C. (b) Quenching of the products of desulfonylation and desulfonation from **3** in an aqueous solution (5.0 mM) with various concentrations of 1,3-pentadiene (1.3, 2.9, 5.2, 10.3, and 20.7 mM) in vacuo or in air was observed by UV and GLC. The $k_q\tau$ values were calculated from the slopes of the Stern–Volmer plots[16] (see Table II).

Registry No. 3a, 17213-01-3; **3b**, 85-47-2; **3c**, 65090-17-7; **4a**, 120-12-7; **4b**, 130-14-3; **4c**, 108-67-8; **5b**, 604-53-5; **7a**, 84-65-1; **7b**, 130-15-4; **8b**, 90-15-3; **8c**, 527-60-6; 9-nitroanthracene, 602-60-8; bimesitylene, 4482-03-5; mesitylenesulfonic acid, 3453-83-6.

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Cationic Cyclizations. Cation Generation through Magnesium Alkoxide Thermolysis. Regioselective Indene Formation

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Received June 4, 1979

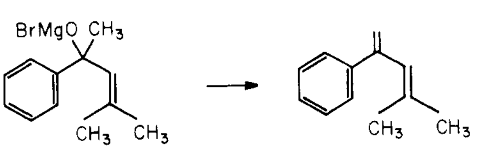
In contrast to the behavior of sodium or potassium alkoxides, magnesium alkoxides undergo heterolytic α cleavage to generate carbocations. Products resulting from such carbonium ions are mediated by their generation in strong base and exhibit remarkable purity and regioselectivity. Thus solid state thermolysis of magnesium salts of substituted 1-phenylallyl alcohols leads to efficient indene formation without the subsequent double bond migration characteristic of acid-mediated cyclizations. Compounds produced by such methods include 1-phenyl-3-methylindene, 1,3-diphenylindene, 1-phenyl-2-methylindene, and 1,1,3-trimethylindene. Similarly produced was 9-phenylfluorene. Magnesium alkoxide pyrolysis thus provides a method for trapping the kinetic product of rearrangement.

Alkali metal alkoxides of certain tertiary alcohols readily undergo heterolytic β scission to generate ketones and carbanion derivatives in a reaction which is the reverse of the corresponding carbanion addition reaction (eq 1).[1]

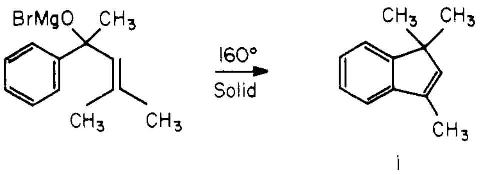
$$R_3C\text{-}O^- M^+ \rightarrow R^-M^+ + R_2C{=}O \qquad (1)$$

This reaction has been used in extensive mechanistic studies of carbanions. Until recently, the corresponding thermolyses of magnesium alkoxides have not been carried out.[2] We anticipated that the stronger magnesium–oxygen bond would have a pronounced effect upon the reactivity of such alkoxides, and we were intrigued by a report that the alkoxide generated by addition of phenylmagnesium bromide to 4-methyl-3-propen-2-one underwent facile 1,2 elimination to the olefin (Scheme I).[3] In the course of repeating that work, we observed the precipitation of the alkoxide from ether solution as a fluffy white solid and proceeded to investigate its chemistry directly by isolation of the precipitate under inert atmosphere. When the dried powder was pyrolyzed at 160 °C under vacuum, a single liquid product was produced in high yield, 1,1,3-trimethylindene (Scheme II). The remarkable facility for indene formation prompted us to a further investigation of this reaction, not only with the anticipation that this would provide us with a single-step high-yield indene synthesis, but also with the expectation that mechanistic investigations would disclose the intermediates involved

Scheme I



Scheme II



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[1] H. D. Zook, J. March, and D. F. Smith, *J. Am. Chem. Soc.*, 81, 1617 (1959).

[2] (a) During the preparation of this manuscript, the pyrolysis of magnesium alkoxides leading to elimination to olefins was reported. (b) E. C. Ashby, G. F. Willard, and Anil B. Goel, *J. Org. Chem.*, **44**, 1221 (1979).

[3] V. I. Esafov, *Zh. Obsch. Khim.* **27**, 2711 (1957).

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