the chiral diol (50 mg, 0.086 mmol), dissolved in absolute ethanol (25 ml), and Raney nickel (freshly prepared[41] from 0.5 g of W-1 nickel-aluminum alloy) was stirred and boiled under reflux while contained under nitrogen. The reaction was periodically monitored by tlc [hexane-benzene, 3:2 (v/v)], which showed only a progressive increase in the formation of benzylferrocene (R_f 0.80). After 24 hr benzylferrocene was the only detectable compound present. Identical results were obtained when the experiment was repeated using the achiral diol.

Registry No.—**1,** 1272-44-2; **3,** 1278-05-3; **4,** 1278-04-2; **5,** 12284-11-6; **6,** 12258-13-8; **7,** 12504-69-7; **8,** 12504-73-3; **9,** 12504-72-2; **10,** 12504-70-0; **11,** 12504-71-1.

Acknowledgments.—We wish to thank Dr. H. M. Fales of the National Heart Institute for mass spectra determined during the early stages of this work. Subsequent mass spectra were obtained with an instrument purchased in part with funds provided by a grant given by the National Science Foundation.

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[41] L. W. Convert and H. Adams, *J. Amer. Chem. Soc.*, **54**, 4116 (1932).

The Photochemistry of Aryl Alkyl Carbonates. I. The Chlorophenyl Ethyl Carbonates

EDWARD A. CARESS* AND IRA E. ROSENBERG[1]

Department of Chemistry, The George Washington University, Washington D. C. 20006

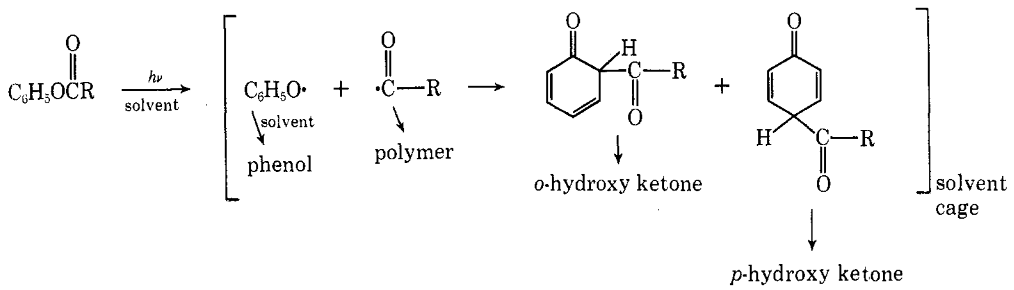
Received September 29, 1970

The photochemistry of the three chlorophenyl ethyl carbonates has been examined. The major process occurring is photodechlorination to give phenyl ethyl carbonate which subsequently undergoes a photo-Fries type of rearrangement. A minor process observed is the photosolvolysis of the chloride. The mechanisms of the reactions are discussed and the quantum yields are reported.

The Fries reaction is a well-known method for preparing aryl ketones from phenolic esters. The photo-Fries reaction is a less well-known but well-established method for effecting the same conversion.[2-7] The mechanism most often suggested for the reaction was proposed by Kobsa[4] and involves a homolytic cleavage of the carbonyl carbon-oxygen bond after the excitation of the ether molecule.

Pac and Tsutsumi[8] have reported that phenyl ethyl carbonate undergoes a photo-Fries type of reaction to give products analogous to those obtained in the photolysis of phenolic esters. Products that they identified were ethyl salicylate, ethyl *p*-hydroxybenzoate, and phenol. We have been investigating the photochemical reactions of a variety of aryl alkyl carbonates and can confirm Pac and Tsutsumi's results.

One way of investigating the mechanism of the photolysis of aryl alkyl carbonates is to examine the effect of placing various substituents on the aromatic ring. The type of substituent (electron attracting or electron repelling) and the position of the substituent relative to the reactive site have been shown to influence greatly the mode of photochemical reaction in aryl compounds.[9] Among the substituents chosen for this investigation was chlorine. In this paper we will discuss the observations that we made on the photochemical reaction of the chlorophenyl ethyl carbonates.



Results

The photolyses were performed by irradiating a solution of the chlorophenyl ethyl carbonate in isopropyl alcohol with a high-pressure mercury lamp using a Corex filter. The photolysis of the chlorophenyl ethyl carbonates (**1a–c**) gave phenyl ethyl carbonate (**2**) as the major product in each case. [The phenyl ethyl carbonate, as it was formed, was photolyzed to give phenol (**3**), ethyl salicylate (**4**), and ethyl *p*-hydroxybenzoate (**5**).] Two other products (**6** and **7**) were found; they appear to result from the interaction of the solvent with the chlorophenyl ethyl carbonate.

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[1] Abstracted from the Ph.D. Thesis of I. Rosenberg, The George Washington University, 1969.

[2] J. Anderson and C. Reese, *Proc. Chem. Soc.*, 216 (1960).

[3] J. Anderson and C. Reese, *J. Chem. Soc.*, 1781 (1963).

[4] H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962), and references therein.

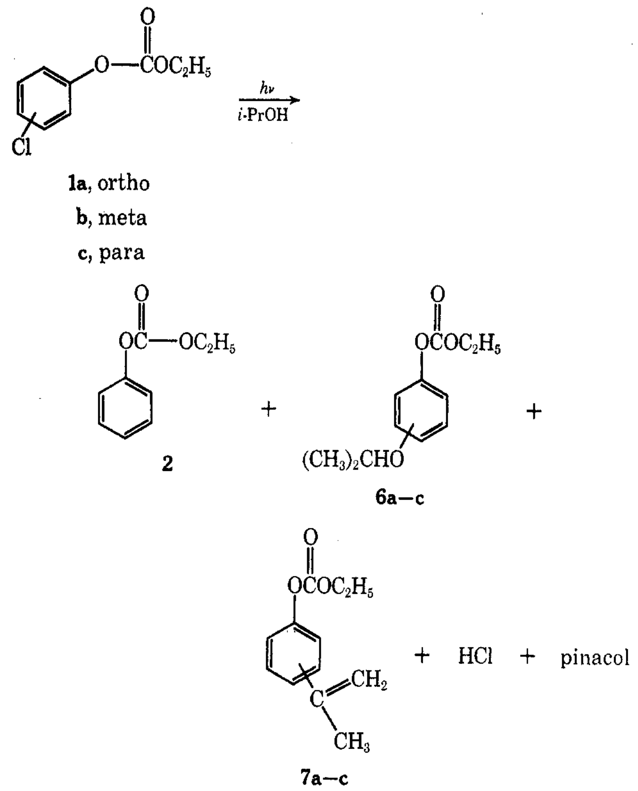
[5] H. Kobsa, Abstract of Papers, 148th National Meeting of the American Chemical Society, Chicago, Ill., 1964, 12E.

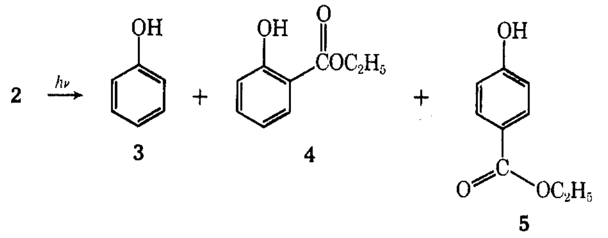
[6] V. Stenberg, "Organic Photochemistry," Vol. I, O. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 127–152.

[7] R. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **89**, 1970 (1967).

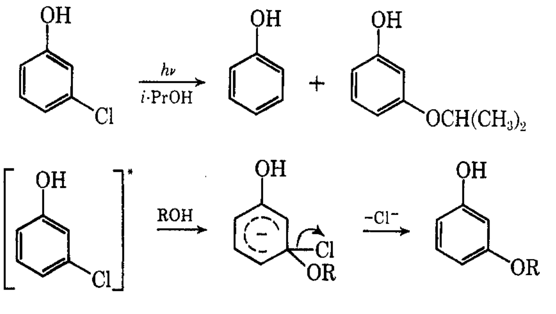
[8] C. Pac and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **37**, 1392 (1964).

[9] R. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966, pp 255–260.

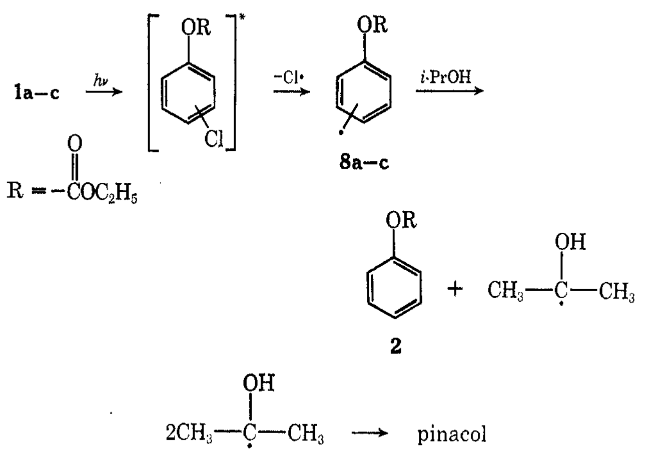




Pinhey and Rigby[10,11] have shown that *m*-chlorophenol on irradiation undergoes photoreduction and photosubstitution. They treat the substitution reaction as a solvolysis of the photoexcited chlorophenol.

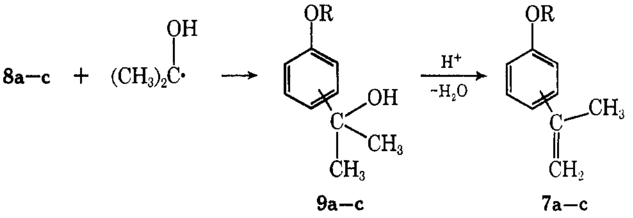


There appear to be two analogous processes occurring in the photochemical reaction of the chlorophenyl ethyl carbonates. The major process is the homolytic cleavage of the C–Cl bond to produce an aryl free radical and a Cl atom. The aryl radical then abstracts a H atom from the solvent to produce phenyl ethyl carbonate. The formation of substantial amounts of HCl and pinacol tend to substantiate the free-radical nature of this process.



The second process, and a minor one, is the displacement of chloride ion by a solvent molecule in a manner analogous to that shown above for *m*-chlorophenol. Thus we identified in each of the reaction mixtures a compound that has a molecular ion at *m/e* 224 which corresponds to the molecular weight of an isopropoxyphenyl ethyl carbonate, **6a–c**. The three compounds, in addition to having the same mass molecular ion, also had the same major peaks in their mass spectra. However, it is apparent from the relative abundance ratios of the peaks that these compounds are not identical but are most likely positional isomers. Pinhey and Rigby[10] have reported that the solvolysis occurs only with *m*-chlorophenol. We observed this reaction in all three chlorophenyl ethyl carbonates, although the percentage of the isopropoxyphenyl ethyl carbonate formed is larger in the meta isomer than it is in the other two isomers.

The isopropenylphenyl ethyl carbonates (**7**) probably form in the following manner.



The alcohol (**9a–c**) which we postulate to form initially, dehydrates in the reaction solution to give the observed product, **7a–c**. The presence of **7** was determined by gas chromatography–mass spectroscopy, and it is possible that the alcohol could have dehydrated in this procedure which would make **7a–c** an artifact. The authors consider this to be unlikely, however, since a molecular ion has been reported in the mass spectrum of 2-phenyl-2-propanol.[12]

Structure of 6 and 7.—The structures of these compounds were determined by mass spectroscopy. Using the meta isomer as an example, the mass spectrum of **6b** had a M^+ 224, a M − 42, which is loss of $(CH_3)_2C^+$, and a base peak of *m/e* 110 which corresponds to a dihydroxybenzene ion. This evidence establishes the presence of the isopropyl group and the attachment of two oxygens to the aryl ring. The mass spectrum of **7b** has a molecular ion at *m/e* 206 and a base peak at *m/e*

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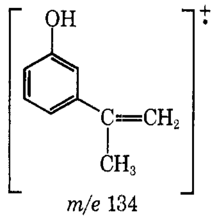
(10) J. Pinhey and R. Rigby, *Tetrahedron Lett.*, 1267 (1969).

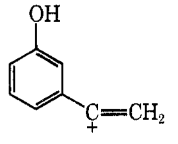
(11) J. Pinhey and R. Rigby, *ibid.*, 1271 (1969).

(12) E. Stenhagen, *et al.*, Atlas of Mass Spectral Data, Vol. 1, Interscience, New York, N. Y., 1969, p 696.

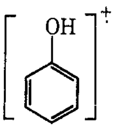
134. The latter peak corresponds to loss of carbon dioxide and ethylene which is always the major fragmentation pathway in aryl alkyl carbonates.[13] There are also major peaks at m/e 119 and 94 which are the loss of a methyl group from the m-isopropenylphenol ion and the phenol ion, respectively.



m/e 134



m/e 119



m/e 94

The ortho and para isomers of **6** and **7** give similar spectra except for variations in the intensity ratios of the peaks. This indicates that they are positional isomers and not the same compound nor are they in a mixture of constant composition such as might result from a photochemical process that permitted product isomerization.

Quantum Yields.—The quantum yields for the conversion of the chlorophenyl ethyl carbonates (**1a–c**) to phenyl ethyl carbonate (**2**) are as follows: **1a**, 0.83; **1b**, 0.68; **1c**, 0.33.[14] The decrease in quantum yield in going from the ortho to meta to para isomer is in keeping with the proposed mechanism for the formation of phenyl ethyl carbonate. The initial reaction step after activation is the loss of a chlorine atom to form the intermediate **8a–c**. An inductive effect appears to be adequate to explain the stabilization of the ortho isomer over the meta isomer over the para isomer.

Conclusion

The major photo process which takes place with the chlorophenyl ethyl carbonates is photodechlorination to form phenyl ethyl carbonate which subsequently undergoes a photo-Fries type of rearrangement. The evidence indicates that a homolytic cleavage of the chlorine–carbon bond to give an aryl radical is the major primary process. Abstraction of a hydrogen atom by the aryl radical from the solvent produces the phenyl ethyl carbonate, while reaction of the aryl radical with the solvent radical followed by dehydration produces the observed isopropenylphenyl ethyl carbonate. A minor primary process is believed to be a solvolytic displacement of chloride ion to produce the observed isopropoxyphenyl ethyl carbonate. The quantum yield measurements are consistent with this mechanistic hypothesis. The multiplicity of the excited state is not known but it is under active investigation.

Experimental Section

The gas chromatography (gc) was carried out on a Hewlett-Packard Model 700 gas chromatograph, equipped with a Model 240 temperature programming unit. The chromatograms were recorded on a Honeywell recorder equipped with a Disc integrator. The gc analytical measurements were made with a 6 ft by $^1/_8$ in. column packed with 10% UC-W98 on Chromosorb A. The gc collections were made using a 3 ft by 0.25 in. column packed with 20% SE-52 on Chromosorb A. The detector and the injection port temperatures were 250° and the gas-flow rate was 30 ml/min. The mass spectra were obtained using a Perkin-Elmer Model 270 GC-DF mass spectrometer. This instrument has a gas chromatograph interfaced with the mass spectrometer.

TABLE I

PHOTOLYSIS OF o-CHLOROPHENYL ETHYL CARBONATE

Compd	Gc retention, time, sec	Column temp, °C	%	Deviation, ±
Pinacol[a]	120	100	21	1.0
Phenol (**3**)	66	150	5	1.0
Phenyl ethyl carbonate (**2**)	216	150	66	1.3
Ethyl salicylate (**4**)	264	150	1.3	0.4
o-Chlorophenyl ethyl carbonate (**1a**)[b]	408	150	1.5	0.2
o-Isopropenylphenyl ethyl carbonate (**7a**)	474	150	3.2	0.1
o-Isopropoxyphenyl ethyl carbonate (**6a**)	686	150	1.4	0.2

[a] Separate run. [b] An unknown peak follows this one very closely. It represents 0.6 ± 0.1% of the mixture and is believed to be ethyl p-hydroxybenzoate (**5**).

TABLE II

PHOTOLYSIS OF m-CHLOROPHENYL ETHYL CARBONATE

Compd	Gc retention time, sec	Column temp, °C	%	Deviation, ±
Pinacol[a]	120	100	24.5	0.4
Phenol (**3**)	48	160	2.8	0.1
Phenyl ethyl carbonate (**2**)	180	160	62.0	1.3
Ethyl salicylate (**4**)	216	160	2.5	0.03
m-Chlorophenyl ethyl carbonate (**1b**)	336	160	3.2	0.3
Ethyl p-hydroxybenzoate	588	160	0.5	0.1
m-Isopropenylphenyl ethyl carbonate (**7b**)	654	160	3.5	0.4
m-Isopropoxyphenyl ethyl carbonate (**6b**)	1128	160	2.6	0.2

[a] Separate run.

Chlorophenyl Ethyl Carbonates (1a–c).—The chlorophenyl ethyl carbonates were prepared by the method of Smith and Kosters.[15] It was found that by allowing the reaction mixtures to stand for 24–48 hr longer than indicated, the yields could be increased over those reported. The boiling points, yields, and uv maxima are as follows: **1a** (ortho) {bp 77–78° (0.1 Torr) [(lit.[13] 130–131° (15 Torr)]; 91%; 264 mμ (ϵ 9.37 × 10^2), 273 (8.18 × 10^2)}; **1b** (meta) {bp 72° (0.01 Torr) [(lit.[13] 90–91° (1.6 Torr)]; 83%; 255 mμ (ϵ 3.24 × 10^2), 263 (2.66 × 10^2)}; **1c** (para) {bp 75° (0.1 Torr) [(lit.[13] 149–151° (33 Torr)]; 84%; 267 mμ (ϵ 5.55 × 10^2), 275 (4.64 × 10^2)}.

Photolysis Conditions.—The chlorophenyl ethyl carbonate (5 ml, 5.8 g, 0.029 mol) was dissolved in 250 ml of Spectrograde isopropyl alcohol, and the solution was placed in a standard immersion-well type photochemical apparatus. The solution was stirred with a magnetic stirrer and purged with nitrogen for 15 min. The solution was then irradiated with a 450-W Hanovia[16] high-pressure mercury lamp through a Corex filter sleeve. The photolyses were carried out under a positive nitrogen pressure for the following lengths of time: **1a**, 24 hr; **1b**, 28 hr; **1c**, 26 hr. The composition of the reaction mixtures can be found in Tables I–III.

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[13] H. Budzikiewitcz, *et al.*, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 484–493.

[14] The determination of the quantum yields was made by P. A. Tatem as part of her M.S. Thesis. The apparatus used was a Rayonet photochemical reactor equipped with a merry-go-round (The Southern New England Ultraviolet Co., Middletown, Conn.), and a benzophenone actinometer was used.

[15] G. Smith and B. Kosters, *Chem. Ber.*, **93**, 2403 (1960).

[16] Engelhard Hanovia, Inc., Newark, N. J.

TABLE III

PHOTOLYSIS OF *p*-CHLOROPHENYL ETHYL CARBONATE

Compd	Gc retention time, sec	Column temp, °C	%	Deviation ±
Pinacol[a]	120	100	10.3	0.5
Phenol (**3**)	65	150	1.2	0.1
Phenyl ethyl carbonate (**2**)	216	150	29.0	0.2
Ethyl salicylate (**4**)	264	150	1.3	0.1
p-Chlorophenyl ethyl carbonate (**1c**)[b]	360	150	55.9	0.1
p-Isopropenylphenyl ethyl carbonate (**7c**)[c]	900	150	1.2	0.2

[a] Separate run. [b] An unknown peak follows this peak very closely. It represents 1.1% (±0.1) of the mixture and is believed to be ethyl *p*-hydroxybenzoate (**5**). [c] Using gas chromatography-mass spectroscopy an additional peak was observed after this peak and was identified as *p*-isopropoxyphenyl ethyl carbonate (**6c**) from its mass spectrum.

A control reaction was carried out for each of the chlorophenyl ethyl carbonates and gc analysis showed that no dark reaction had occurred. The photolyses were monitored by gc and were stopped when it appeared that new products were not being formed. When the photolysis was ended, the solvent was evaporated under vacuum and the remaining solution analyzed by gc and by gc-mass spectroscopy. The principle products of the photolysis were collected as they eluted from the gas chromatograph and analyzed further by nuclear magnetic resonance (nmr) and by infrared (ir) spectroscopy.

Product Identification.—Pinacol was identified by comparing its retention time with that of an authentic sample.

Phenol (3) was identified by comparing its retention time and mass spectrum with those of an authentic sample.

Phenyl Ethyl Carbonate (2).—The retention time and mass spectrum of this compound were identical with those of an authentic sample. A pure sample of the material was obtained using preparative gc. The ir and nmr spectra of the material confirmed its identity as phenyl ethyl carbonate.

Ethyl Salicylate (4).—This compound was identified by comparing its retention time and mass spectrum with those of an authentic sample.

Ethyl *p*-hydroxybenzoate (5) was identified by its retention time. The identification is certain in the *m*-chlorophenyl ethyl carbonate reaction mixture and its reasonably certain in the other two reaction mixtures.

Isopropenylphenyl Ethyl Carbonate (7).—Identification was made from the mass spectra obtained by gc-mass spectroscopy. The mass spectral data in the case of the meta isomer are given in Table IV.

TABLE IV

m/e	% of base	*m/e*	% of base
m-Isopropenyl Ethyl Carbonate			
207	2.5	162	7.5
206	11.0	135	11.8
134	100.0	115	14.2
133	32.0	94	58.0
119	24.0	91	34.2
117	14.2		
m-Isopropoxyphenyl Ethyl Carbonate			
225	1.8	138	6.0
224	7.5	137	2.5
183	1.0	110	100.0
182	3.5	109	9.5
152	3.5		

Isopropoxyphenyl Ethyl Carbonate (6).—Identification was made from mass spectra obtained by means of gc-mass spectroscopy. The mass spectral data are given in Table IV in the case of the meta isomer.

Registry No.—**1a**, 1847-88-7; **1b**, 1847-87-6; **1c**, 22719-87-5.

Acknowledgments.—The authors thank the National Science Foundation (Grant P7 2164 E) for matching funds for the purchase of the nmr spectrometer and the mass spectrometer. The authors also wish to express their appreciation to the University Committee on Research for support of this work during the summers of 1968 and 1969.

The Reaction of Organometallic Reagents with Pyridinium Ions[1]

ROBERT E. LYLE* AND EDWARD WHITE V[2]

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

Received February 11, 1970

The products of the reactions of methyl Grignard reagent with 1-methyl- and 1-benzyl-3-cyanopyridinium ions were shown to be mixtures of 1,2- and 1,6-dihydropyridines[3] resulting from nucleophilic addition at the ring carbons. From the reaction of these salts with aryl Grignards, only 6-aryl-1,6-dihydropyridines were detected. Comparable results were obtained from the reaction of methyl- and phenylcadmium reagents with 1-methyl- and 1-benzyl-3-methoxycarbonylpyridinium ions except that the phenylcadmium reagent with the 1-benzyl salt gave a mixture of products. The product of the reaction of 1-triphenylmethylpyridinium tetrafluoroborate with phenylmagnesium bromide gave 4-phenylpyridine on thermal decomposition. The structures of the products were based on spectral data.

The reactions of nucleophiles with pyridines occur to give 2- or 6-substituted pyridines presumably *via* 1,2- or 1,6-dihydropyridines[3] as intermediates.[4] The generality of this conclusion has been supported by the recent characterization of the organolithium adduct to pyridine.[5] In a few isolated examples, organometallic

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[1] This research was presented in part before the Organic Division at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970. The research was supported in part by a grant from the National Cancer Institute of the National Institutes of Health, CA-04143.

[2] The research was abstracted from the thesis of E. White V presented to the Graduate Faculty of the University of New Hampshire in partial fulfillment of the requirements of the Ph.D. Degree.

[3] The correct numbering system for these dihydropyridines would require that they both be 1,2-dihydropyridine; however, to facilitate the understanding of the results and to be in keeping with earlier papers, the 1,2- and 1,6-dihydropyridine convention will be used throughout this paper.

[4] R. A. Abramovitch and J. G. Saha, *Advan. Heterocycl. Chem.*, **6**, 229 (1966).

[5] (a) R. A. Abramovitch and G. A. Poulton, *J. Chem. Soc. B*, 901 (1969); (b) C. S. Giam and J. L. Strout, *Chem. Commun.*, 142 (1969); (c) G. Fraenkel and J. C. Cooper, *Tetrahedron Lett.*, 1825 (1968).