from Aldrich and used without purification. The 5% $H_2$/95% neon mixture was supplied by Matheson. Cyclotron irradiations were carried out on the BNL 60 in. cyclotron.

GLC analyses were carried out on a Hewlett-Packard HP 5830A chromatograph. GC/MS were run on a Hewlett-Packard HP 5985A by using the electron-impact mode with 70-eV electrons. Infrared spectra were taken with a Perkin-Elmer 735B infrared spectrophotometer and NMR spectra with a JEOL MH-100 NMR spectrometer. Radioactive measurements were carried out by using a Picker NaI (Tl) well counter (efficiency of 0.59) or a Capintec CRC-5R dose calibrator, depending on the amount of radioactivity being assayed.

**$H^{18}F$ Production.** No carrier added (NCA) $H^{18}F$ was produced in a flowing, heated, high-pressure Inconel target system containing 5% $H_2$/95% neon target gas by the $^{20}Ne(d,\alpha)^{18}F$ nuclear reaction.[10] The $^{18}F$ thus produced reacted with the hydrogen during deuteron irradiation, producing NCA $H^{18}F$. The flowing effluent from the target was passed through a Teflon loop (−78 °C) during irradiation which quantitatively trapped $H^{18}F$. Removal of the $H^{18}F$ was accomplished, by flushing the loop with an appropriate solvent or solvent/solute reagent system as shown below, in greater than 80% (often up to 95%) efficiency and in a soluble form. Typical flushing solutions were $CH_2Cl_2$, $CH_2Cl_2$/PhCOCl, PhCOCl, $CH_2Cl_2$/PhCOCl/1% MeOH, pyridine, benzene, or benzene containing 18-crown-6 (90 mM) saturated with either KF (0.17 mM), KI (2.5 mM), or $K_2CO_3$ (0.15 mM). This produced an anhydrous soluble source of $F^-$ (or HF) in one step.[11] Alternatively, the loop could be flushed with a stream of dry carrier gas (He or $N_2$) to remove $H^{18}F$. The targetry system employed is similar in design to the $F_2$/Ne target described by Casella et al.[10] Preliminary discussion can be found in the literature (see ref 10). A detailed report of the HF production system and recovery is described elsewhere.[12]

**Synthesis of $PhCO^{18}F$.** In a typical reaction, 1 mL of $CH_2Cl_2$ containing 20 μL of PhCOCl (to which was added 1% MeOH by volume to generate catalytic amounts of HCl) was used to flush the $H^{18}F$ from the Teflon $H^{18}F$ trapping loop. The reaction mixture was placed in a polyethylene test tube and stirred for 5–10 min. The reaction mixture was then subjected to radio gas chromatography (RGLC). Trapping of the effluent was accomplished by using charcoal traps, which were subsequently counted in a NaI (Tl) well counter. Typically 1-min fractions were collected for radioassay. The GLC system used was as follows: 10% DC-710, 12 ft × $^1/_8$ in. column 140 °C, 40 $cm^3$/min. PhCOF had $t_R = 6.3$ min, and PhCOCl had $t_R = 12.4$ min. Although yields were not optimized, analysis showed 40–85% of the injected amount was recovered from GLC, greater than 90% of which was recovered in the PhCOF peak.

**Reaction of $PhCO^{18}F$ with $(Ph_3P)_3RhCl$.** After formation of $PhCO^{18}F$ was complete, 180 mg of $(Ph_3P)_3RhCl$ was added to the reaction mixture and stirred for several minutes during which complete solubilization occurred, resulting in a dark brown solution. The complexes, a mixture of $(Ph_3P)_2Rh(COPh)FCl$ and $(Ph_3P)_2Rh(COPh)Cl_2$, were then precipitated by the addition of 25–50 mL of pentane.[13] The samples were centrifuged and decanted, and the precipitate was resuspended in pentane, centrifuged, and decanted a second time. The resulting precipitate was dried in vacuo, leaving a tan solid which contained 60–90% of the radioactivity.

**Thermal Decomposition of Rhodium–Acid Halide Complexes.** The tan solid was transferred to a glass vessel and decomposed at 185 °C under vacuum. A glass coil at −78 °C acted as a product receiver vessel. During the heating, gas evolution could be observed, and the tan solid became a dark brown material.

The glass collection coil was designed such that it could be rinsed with an appropriate solvent and samples for GLC analysis could be taken.

GLC of PhF, PhCl, and PhH was carried out on a 10% DC 710 column (12 ft × $^1/_8$ in., 110 °C, 30 $cm^3$/min): PhH, PhF, 4 min; PhCl, 10.9 min. At 70 °C and 30 $cm^3$/min: PhH, 7.5 min; PhF, 8.1 min; PhCl, 31.3 min. For RGLC analysis samples were again collected in charcoal and counted as before.

**Reaction of "Cold" PhCOF with $(Ph_3P)_3RhCl$ and Thermal Decomposition. GC/MS and GLC Analyses.** For "cold" nonlabeled reactions the following conditions were used and were similar to those described in the literature[3] at 0.1 scale. $(Ph_3P)_3RhCl$ (50 mg) was reacted with 200 μL of PhCOF in 0.5 mL xylene (or toluene) at or near reflux temperatures. Aliquots were taken for GLC–GC/MS analyses.

Isolation of the precipitated complex of PhCOF for the unlabeled material was identical with the method discussed for the labeled compound. This sample was thermally decomposed in the direct-insertion probe of the GC/MS instrument; $T_{initial} = 30$ °C and was increased at 30 °C/min up to 285 °C.

**Registry No.** $(Ph_3P)_2Rh(COPh)^{18}FCl$, 81478-24-2; $(Ph_3P)_2Rh(COPh)Cl_2$, 52393-94-9; $(Ph_3P)_3ClRh(I)$, 14694-95-2; $PhCO^{18}F$, 63438-13-1; PhCOCl, 98-88-4.

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[10] V. Casella, et al., *J. Nucl. Med.*, **21**, 750–57 (1980); R. M. Lambrecht, R. Neirinckx, A. P. Wolf, *Int. J. Appl. Radiat. Isot.*, **29**, 175–83 (1979); R. L. Ehrenkaufer, et al. "Abstracts of Papers", Second Chemical Congress of the North American Continent, Las Vegas, NV Aug 24–29, 1980; American Chemical Society, Washington, DC, 1980.

[11] C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974); B. E. Gnade, G. P. Schwaiger, C. L. Liotta, and R. W. Fink, *Int. J. Appl. Radiat. Isot.*, **32**, 91–5 (1981).

[12] R. E. Ehrenkaufer, et al., submitted for publication in *Radiochim. Acta*.

[13] The structures of these complexes were assigned on the basis of their infrared carbonyl stretching frequencies. A frequency of 1660 $cm^{-1}$ was observed for the isolated complexes, indicating the presence of PhCO.

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# Palladium-Promoted Intramolecular Aromatic Nuclear Acyloxylation: Preparation of 2-Coumaranone

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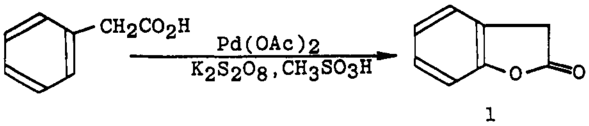
*Received August 11, 1981*

Lactones occur widely in nature and are found to exhibit various kinds of biological activities.[1] Although 2(3*H*)-benzofuranone (1), the five-membered benzolactone, is an important starting material for the synthesis of such biologically active substances, its direct synthesis via the intramolecular aromatic nuclear acyloxylation of phenylacetic acid has not been successful because of its ease of oxidation at the benzylic position and steric hindrance. This paper reports the successful intramolecular aromatic nuclear acyloxylation of phenylacetic acid.

Eberson and Joensson reported that phenyl acetate could be obtained from the direct acetoxylation of benzene in acetic acid by using $Pd(OAc)_2$, $K_2S_2O_8$, and 2,2′-bipyridine or pyridine.[2] So we first tried the reaction of phenylacetic acid under these reaction conditions, but only small amount of 1 was formed (Table I, runs 1 and 2).

We have found that the $Pd(OAc)_2$–$K_2S_2O_8$–$CH_3SO_3H$ system causes the cyclization to give 1 (Table I, runs 5–7)



(1)

1

together with small amounts of benzaldehyde, benzyl phenylacetate, and benzyl acetate as byproducts. The data

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[1] Devon, T. K. "Handbook of Naturally Occurring Compounds"; Academic Press: New York, 1972; Vol. 1 and 2.

[2] Eberson, L.; Joensson, L. *J. Chem. Soc., Chem. Commun.* **1974**, 885.

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Table I. Preparation of Benzofuranone by Intramolecular Acetoxylation of Phenylacetic Acid[a]

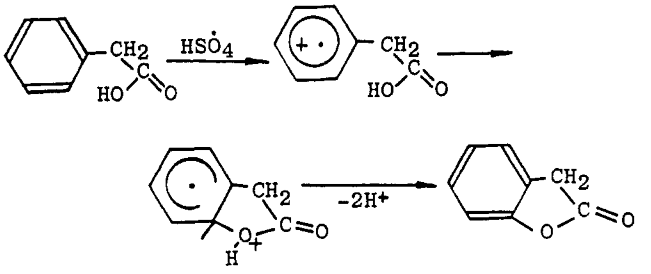
| run | $K_2S_2O_8$, mmol | $CH_3SO_3H$, mL | others (amt) | product yield,[b] % |
|---|---|---|---|---|
| 1 | 4 | | 2,2′-bipyridine (0.5 mmol) | c |
| 2 | 4 | | pyridine (0.9 mmol) | 5[c] |
| 3 | 4 | | | |
| 4 | 1 | 0.63 | | 1[d] |
| 5 | 4 | 1 | | 15[d] |
| 6 | 8 | 1.5 | | 17[d] |
| 7 | 12 | 2 | | 13[d] |
| 8 | 16 | 2.5 | | 4[d] |
| 9 | 20 | 3 | | 1[d] |
| 10 | 4 | 1 | HMPA[e] (2 mL) | |
| 11 | 4 | 1 | $CH_2ClCH_2Cl$[f] | 1[d] |
| 12 | 12 | 2 | $Cu(OAc)_2$[g] (10 mmol) | |
| 13 | | 1 | | |

[a] Reactions were carried out at 100 °C with stirring for 8 h in a 50-mL centrifuge tube sealed with a NO-Air stopper by using $Pd(OAc)_2$ (0.5 mmol), dioxane (10 mL), and phenylacetic acid (5 mmol) unless otherwise noted. [b] Yields are based on $Pd(OAc)_2$ and determined by GLC using an internal standard. [c] Small amounts of benzaldehyde and much smaller amounts of benzyl acetate were also formed. [d] Small amounts of benzaldehyde and benzyl phenylacetate and much smaller amounts of benzyl acetate were also formed. [e] Dioxane (8 mL) and 2 mL of hexamethylphosphoramide (HMPA) were used. [f] 1,2-Dichloroethane (10 mL) was used instead of dioxane. [g] $CuCl_2$ also resulted in no reaction.

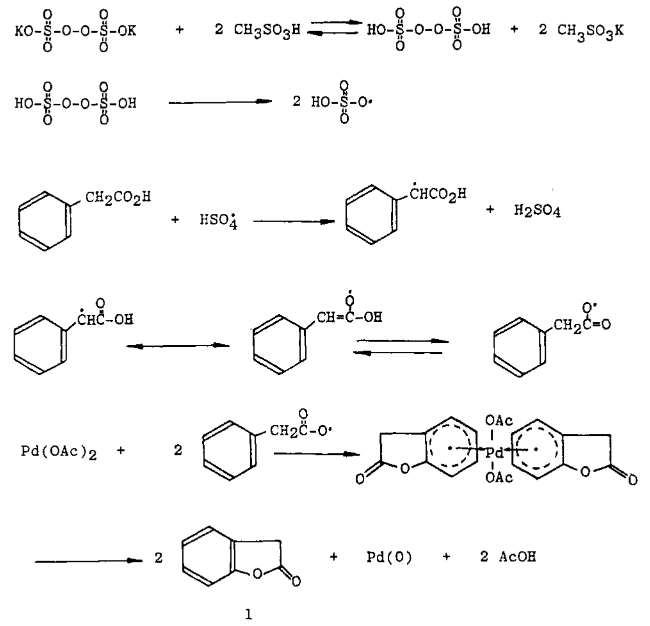
in Table I show that the presence of both $K_2S_2O_8$ and $CH_3SO_3H$ is essential for the reaction, that their molar ratios are very important, and that dioxane is the best solvent. $Pd(NO_3)_2$ was found to be ineffective for catalysis of the reaction,[3] and other oxidants such as $Pb(OAc)_4$ and $K_2Cr_2O_7$ did not work.

It is well-known that $K_2S_2O_8$ evolves a $SO_4^{-}\cdot$ species.[4] However, $K_2S_2O_8$ plus $CH_3SO_3H$ would produce $H_2S_2O_8$ which would yield $HOSO_3\cdot$ radicals. Joensson and Wistrand reported that the $K_2S_2O_8$–$Pd(OAc)_2$–$CF_3COOH$ system evolves $SO_4^{-}\cdot$ radical anions which react with alkylbenzenes to give the benzyl radical via α-H abstraction.[5] The radical nature of the reaction is shown by the formation of byproducts such as benzaldehyde, benzyl phenylacetate, and benzyl acetate.

### Scheme I



### Scheme II



There are a number of reports and reviews dealing with reactions of aryl carboxylic acids with various oxidant systems including peroxydisulfate.[6] Basically it appears from the literature that aryl carboxylic acids can undergo oxidation at three sites: (a) carboxyl group, (b) aromatic ring, (c) α-C–H bond. Of the three possibilities, oxidation at site a, the carboxyl group, to produce a carboxy radical $RCO_2\cdot$ is favored in cases where the aromatic ring is not electron-rich and when the carboxylate ion concentration is reasonable. But in the present case, the use of $CH_3SO_3H$ should keep the carboxylate ion concentration very low, so as to disfavor a. Oxidation at site b, the aromatic ring, to produce radical cation $\cdot^{+}PhCH_2CO_2H$ could be occurring (Scheme I). This mechanism needs no palladium. In fact, in the separate experiment with $K_2S_2O_8$ and $CH_3SO_3H$ and without $Pd(OAc)_2$, a small amount of 1 was formed. However, that addition of $Pd(OAc)_2$ increases the yield of 1 and decreases those of byproducts suggests that $Pd(OAc)_2$ plays an important role for the reaction. Finally, oxidation at site c, the α-C–H bond to produce a benzylic radical $Ph\dot{C}HCO_2H$ which rearranges to an acyloxy radical (Scheme II) may also be occurring. The reaction of acyloxy radicals with $Pd(OAc)_2$ might lead to a $Pd(OAc)_2$–aryl complex which decomposes into 1 and Pd(0). The acyloxy radicals in the Scheme II partially undergo decarboxylation to give byproducts such as benzaldehyde, benzyl phenylacetate, and benzyl acetate. But the use of both $CH_3SO_3H$ and $Pd(OAc)_2$ might repress the usual decarboxylation and allow a cyclization to occur. Joensson and Wistrand used $CF_3CO_2H$ instead of $CH_3SO_3H$ to change action of the persulfate on the carboxylic acid from $RCO_2^-$ oxidation to aromatic oxidation.[5] On these bases we tentatively propose a mechanism outlined in Scheme II.

Although the yield is low, this is the first example of the preparation of 1 via an intramolecular aromatic nuclear acyloxylation of phenylacetic acid.

## Experimental Section

**General Methods.** NMR spectra were obtained with a Hitachi R-24S spectrometer using $Me_4Si$ as an internal standard. Palladium acetate was prepared from palladium sponge and glacial

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[3] Ichikawa, K.; Uemura, S.; Okada, T. *Nippon Kagaku Zasshi*, **1969**, *90*, 212.

[4] (a) Tanner, D. D.; Osman, S. A. A. *J. Am. Chem. Soc.* **1968**, *90*, 6572. (b) Eberhardt, M. K. *Ibid.* **1981**, *103*, 3878.

[5] Joensson, L.; Wistrand, L. G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 669.

[6] (a) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 995. (b) Dessau, R. M.; Heiba, E. I. *J. Org. Chem.* **1975**, *40*, 3647. (c) Steenken, S.; O'Neill, P.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1977**, *81*, 26. (d) Ashworth, B.; Gilbert, B. C.; Holmes, R. G. G.; Norman, R. O. C. *J. Chem.Soc., Perkin Trans. 2* **1978**, 951. (e) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; pp 99–106. (f) Kochi, J. K., Ed. "Free Radicals"; Wiley: 1973; Vol. I, pp 651–656.

acetic acid by the method of Wilkinson et al.[7] Dioxane was refluxed with sodium metal and distilled. Other starting materials were commercial grade.

**Intramolecular Aromatic Nuclear Acyloxylation Reaction of Phenylacetic Acid (Run 6).** Into a 50-mL centrifuge tube containing a magnetic stirring bar were added phenylacetic acid (5 mmol), $K_2S_2O_8$ (8 mmol), $Pd(OAc)_2$ (0.5 mmol), dioxane (10 mL), and $CH_3SO_3H$ (1.5 mL), and the tube was sealed under air with a No-Air stopper. Then the mixture was heated with stirring for 8 h at 100 °C. The reaction mixture was filtered to remove Pd metal and $K_2S_2O_8$, was neutralized with saturated aqueous sodium bicarbonate, and was extracted with ether. After evaporation of the ether, the products were analyzed by GLC and, in some cases, separated by column chromatography (silica gel). Yields were determined by GLC directly with the use of an internal standard (Table I). The identities of the products were proved by IR, NMR, and retention time comparison with authentic samples.

**Registry No.** 1, 553-86-6; phenylacetic acid, 103-82-2.

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(7) Stephenson, T. A.; Morehouse, S. M.; Powel, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

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# *Communications*

## Poly(ethylene glycols) Are Extraordinary Catalysts in Liquid–Liquid Two-Phase Dehydrohalogenation[1]

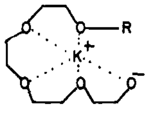
*Summary:* Poly(ethylene glycols) [$HO(CH_2CH_2O)_nH$, where $n > 3$] are highly active and selective in catalyzing dehydrohalogenation in organic–aqueous hydroxide two-phase systems.

*Sir:* We have discovered that simple poly(ethylene glycols) [$HO(CH_2CH_2O)_nH$, where $n > 3$] are highly active and selective in catalyzing dehydrohalogenation in organic–aqueous hydroxide two-phase systems.[2] In this communication we document our findings and provide data which suggest that novel polymeric alkoxides and/or hydroxides are involved.

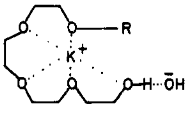
Reaction of 0.5 mL of 2.0 M 2-bromooctane in benzene with 0.5 mL of 60% aqueous potassium hydroxide in the presence of conventional phase-transfer catalysts (10 mol % of tetrabutylammonium hydrogen sulfate or 18-crown-6) at 80 °C for 2 h produced only a modest extent of dehydrohalogenation (Table I).[3] In the absence of catalyst or in the presence of ethylene glycol, diethylene glycol, or triethylene glycol, no detectable reaction was observed. In sharp contrast, tetraethylene glycol exhibited activity comparable to that of the ammonium salt and crown ether. Pentaethylene glycol and poly(ethylene glycols) having average molecular weights of 600 and 3400 (PEG 600 and PEG 3400, respectively) all had high activity. Poly(ethylene glycol) monomethyl ether (average molecular weight 750) having half the hydroxyl content of PEG 600, converted approximately half as much organic bromide in the same time period. Replacement of both terminal hydroxyl groups with ether functionalities [PEG 600–$(n\text{-}C_4H_9)_2$] rendered the polymer essentially inactive.[4] Combination of 18-crown-6 and PEG 600 had only slightly greater activity than PEG 600 used alone. Finally, upon extended reaction with tetrabutylammonium hydrogen sulfate or 18-crown-6, 2-octanol appeared in significant yields;[5] PEG 600 and PEG 600 + 18-crown-6 afforded alkenes, exclusively.

Further evidence for the efficacy of poly(ethylene glycols) in promoting dehydrohalogenation is provided in Table II. Vicinal dibromides were smoothly converted to the corresponding alkynes by using 10 mol % of PEG 600. This is in marked contrast to tetrabutylammonium hydrogen sulfate where *stoichiometric* amounts of the salt are required.[6,7] Remarkably, $\beta$-bromoethyl phenyl ether, which has been reported to undergo phase-transfer-catalyzed dehydrohalogenation (benzyltriethylamminium chloride) at elevated temperatures (150 °C),[8] proceeds rapidly and quantitatively to the corresponding alkene with PEG 600 at 50 °C. Preliminary carbene generation experiments also demonstrate the synthetic potential of poly(ethylene glycols) in organic–aqueous hydroxide systems. Thus, whereas benzyltriethylammonium chloride fails to catalyze the formation of 1,1-dibromo-2-hexylcyclopropane when a benzene solution of 1-octene plus bromoform is heated with 50% aqueous sodium hydroxide at 50 °C for 20 h, PEG 600 affords a 61% isolated yield of the dibromide after 3 h at room temperature.

In addition to their synthetic value, the above results suggest that novel polymeric alkoxides 1 and/or hydroxides 2 are involved. Self-solvation is inferred by the abrupt



**1**



**2**

R = H, $(CH_2CH_2O)_{n-4}H$, $(CH_2CH_2O)_{n-4}X$ (X = alkyl)

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(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-02-4446).

(2) For recent applications of poly(ethylene glycols) in two-phase organic syntheses, see: Stott, P. E.; Bradshaw, J. S.; Parish, W. W. *J. Am. Chem. Soc.* **1980**, *102*, 4810. Lee, D. G.; Chang, V. S. *J. Org. Chem.* **1978**, *43*, 1532. Sukata, K. *Yuki Gosei Kagaku* **1981**, *39*, 443. Lehmkuhl, H.; Fabet, F.; Hauschild, K. *Synthesis* **1977**, 184. Zupancic, B.; Kokalj, M. *Ibid.* **1981**, 913. Balasubramanian, D.; Sukumar, P.; Chandani, B. *Tetrahedron Lett.* **1979**, 3543. For use of poly(ethylene glycols) as *solvents* in elimination and displacement reactions, see: Lehmkuhl, H.; Rabet, F.; Hauschild, K. *Synthesis* **1977**, 184. Brandstrom, A. *Acta Chem. Scand.* **1959**, *13*, 610, 611. Brandstrom, A. *Ibid.* **1956**, *10*, 1197.

(3) Reviews of phase-transfer catalysis: (a) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis"; Academic Press; New York, 1978. (b) Weber, W.P.; Gokel, G. W. "Phase-Transfer Catalysis in Organic Synthesis"; Springer-Verlag: New York, 1977. (c) Brandstrom, A. *Adv. Phys. Org. Chem.* **1977**, *15*, 267. (d) Dehmlow, E. V. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 493.

(4) Alkylation of PEG 600 with $n\text{-}C_4H_9Cl$ was carried out by using procedures similar to those previously described: Gibson, T. *J. Org. Chem.* **1980**, *45*, 1095. The final polyether product was purified by column chromatography (silica gel/$CHCl_3$).

(5) Similar results have previously been reported elsewhere: Herriott, A.; Picker, D. *Tetrahedron Lett.* **1972**, 4521.

(6) Gorques, A.; LeCoq, A. *Tetrahedron Lett.* **1976**, 4723.

(7) In solid–liquid two-phase dehydrohalogenations, catalytic quantities of ammonium salts have been successfully employed: Dehmlow, E. V.; Lissel, M. *Tetrahedron* **1981**, *37*, 1653.

(8) Shostakovski, S. M.; Kozyrev, V. G.; Il'ina, G. I.; Bannikova, U. B. *Zh. Prikl. Khim.* **1977**, *50*, 463.

0022-3263/82/1947-2493$01.25/0