in 70% yield by treatment of diazoacetophenone with toluenesulfonic acid in benzene.[15,16] The photochemistry of α-sulfonyloxy ketones (including some α-tosyloxy analogues) has also been investigated.[16-19] The ease and moderate generality of the synthesis reported herein provides convenient access to α-tosyloxy ketones and should facilitate further investigations of their chemistry.

Experimental Section

General Methods. The ^1H NMR spectra reported herein were recorded on a Varian EM-360 spectrometer, tetramethylsilane being employed as an internal standard. Melting points and boiling points are uncorrected. Elemental compositions were determined at Galbraith Laboratories in Knoxville, TN. The NMR and IR spectral data were sometimes collected on samples from experimental runs other than the ones given in this section.

Detailed procedures for the direct α-tosyloxylation of 3-pentanone and cyclohexanone follow and serve as examples. However, workups vary from ketone to ketone. For anyone wishing full preparative information on those experiments not included herein, see the paragraph at the end of the paper about supplementary material.

2-(Tosyloxy)-3-pentanone. To a hot mixture of 3.92 g (10.0 mmol) of 1 and 25 mL of CH_3CN was added 10 mL of 3-pentanone. After 10 min at reflux, the reaction solution was concentrated in vacuo (H_2O aspirator), and the residual material was dissolved in 30 mL of CH_2Cl_2. The CH_2Cl_2 solution was washed with H_2O (2 × 100 mL), dried, and concentrated (at 0.2 mmHg) to give 2.40 g (93.6%) of 2-(tosyloxy)-3-pentanone as an oil: ^1H NMR ($CDCl_3$) δ 0.98 (t, 3.0 H, $J \simeq 6.5$ Hz), 1.33 (d, 2.9 H, $J \simeq 6.5$ Hz), 2.44 and 2.58 (overlapping s and q, 4.7 H, $J \simeq 7$ Hz for q), 4.81 (q, 0.9 H, $J \simeq 7$ Hz), 7.57 (AA'BB' m, 4.0 H).

Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.41; H, 6.49.

In another experiment, 2-(tosyloxy)-3-pentanone, obtained initially as an oil, gradually crystallized to a white, wet solid over a period of 5 days.

α-(Tosyloxy)cyclohexanone. To a solution of 1.2 mL of cyclohexanone in 30 mL of CH_2Cl_2 was added 3.93 g (10 mmol) of 1. After being stirred 3 h at room temperature, the reaction mixture was turbid and contained a floating light brown scum. It was then washed with H_2O (2 × 25 mL), dried over $MgSO_4$, and concentrated under aspirator vacuum to a clear yellow oil. The oil was taken up in 30 mL of warm diethyl ether and cooled for 19 h at −20 °C whereupon α-(tosyloxy)cyclohexanone crystallized from solution: yield 1.07 g (39.9%); mp 74–76 °C (unchanged after recrystallization from ether); ^1H NMR ($CDCl_3$) δ 1.30–2.70 (complex m overlapping with CH_3 singlet at 2.41, 11.2 H), 4.60–5.05 (complex m, 1.1 H); 7.51 (AA'BB' m, 4.0 H); IR (KBr) 1744 cm^{-1} (carbonyl).

Anal. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01. Found: C, 58.18; H, 6.02.

Phenyl(2-dimedonyl)iodonium Tosylate. To a hot solution of 1.07 g (7.63 mmol) of dimedone in 25 mL of CH_3CN was added a hot solution of 3.0 g (7.65 mmol) of 1 in 50 mL of CH_3CN. The reaction mixture was cooled first to room temperature and then at −20 °C for 5 h with the concomitant crystallization of white solid phenyl(2-dimedonyl)iodonium tosylate which was washed with a few milliliters of acetone and dried: yield 1.52 g; mp 119.5–120.5 °C. The filtrate was subsequently concentrated, and the residual liquid/solid was triturated with a few milliliters of hexanes to give an additional 0.62 g of product: mp 119–120 °C; combined yield 2.14 g (54.5%); ^1H NMR ($CDCl_3$) δ 0.90 (s, 6.0 H); 2.28 (s, 2.7 H), 2.48 (s, 3.9 H), 7–8.1 (m with 8 apparent s at δ 6.92, 7.05, 7.13, 7.27, 7.38, 7.52, 7.72, and 7.85, 9.0 H); IR (KBr) 1660 cm^{-1} (carbonyl, not calibrated).

Anal. Calcd for $C_{21}H_{23}O_5IS$: C, 49.03; H, 4.51; I, 24.67. Found: C, 49.00; H, 4.67; I, 24.80.

Thermolysis of Phenyl(2-dimedonyl)iodonium Tosylate. A mixture of phenyl(2-dimedonyl)iodonium tosylate (3.63 g, 7.06 mmol) and 50 mL of CH_3CN was brought to gentle reflux (ca. 72 °C) for a period of 1 h. The reaction solution was subsequently cooled to about 0 °C, 50 mL of Et_2O was added, and the solution was concentrated to a total volume of 50 mL whereupon α-(tosyloxy)dimedone began to crystallize out. After further cooling for 10 min at −20 °C, the product was isolated and washed with several milliliters of Et_2O: yield, 1.35 g (62%); mp 159–164 °C. The filtrate, upon concentration and washing with several milliliters of Et_2O, gave an additional crop (0.63 g) of product, combined yield 1.98 g (90.4%).

Tosyloxylation of 2-Butanone. A mixture of 3.92 g (10.0 mmol) of [hydroxy(tosyloxy)iodo]benzene, 13.0 mL of 2-butanone, and 25 mL of CH_3CN was subjected to gentle reflux until a homogeneous solution resulted. The reaction mixture was then concentrated to an oil (4.07 g) shown by ^1H NMR analysis ($CDCl_3$) to consist of iodobenzene, 1-(tosyloxy)-2-butanone, and 3-(tosyloxy)-2-butanone. Integration of the methyl triplet at δ 1.0 for 1-(tosyloxy)-2-butanone and of the methyl doublet at δ 1.3 for 3-(tosyloxy)-2-butanone is consistent with a 1:1.57 mixture of these compounds.

Registry No. 1, 27126-76-7; 4, 88-15-3; 5, 81447-27-0; 6, 765-43-5; 7, 81447-28-1; 9, 126-81-8; 10, 81447-30-5; 11, 81447-31-6; 14, 80520-04-3; 15, 81447-32-7; 3-pentanone, 96-22-0; 2-(tosyloxy)-3-pentanone, 81447-33-8; α-(tosyloxy)cyclohexanone, 81447-34-9; cyclohexanone, 108-94-1; 2-butanone, 78-93-3; α-tosyloxyacetone, 1666-19-9; acetone, 67-64-1; α-tosyloxyacetophenone, 7257-94-5; acetophenone, 98-86-2; α-tosyloxydeoxybenzoin, 1678-43-9; deoxybenzoin, 451-40-1; 3-tosyloxy-2,4-pentanedione, 81447-35-0; 2,4-pentanedione, 123-54-6; tosyloxydibenzoylmethane, 81447-36-1; dibenzoylmethane, 120-46-7; ethyl tosyloxybenzoylacetate, 81447-37-2; ethyl benzoylacetate, 94-02-0.

Supplementary Material Available: Full experimental details on the α-tosyloxylations of 2-acetylthiophene, acetone, cyclopropyl methyl ketone, acetophenone, deoxybenzoin, 2,4-pentanedione, dibenzoylmethane, ethyl benzoylacetate, and dimedone with [hydroxy(tosyloxy)iodo]benzene (5 pages). Ordering information is given on any current masthead page.

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Decarbonylation of Aroyl Fluorides Using Wilkinson's Catalyst: A Reevaluation[1]

Richard E. Ehrenkaufer*

University of Michigan Medical Center, Division of Nuclear Medicine, Ann Arbor, Michigan 48109

Robert R. MacGregor and Alfred P. Wolf

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

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Synthetic methods for incorporating fluorine into aromatic molecules are quite limited.[2] New potentially useful methods are thus needed and are continuously being explored.

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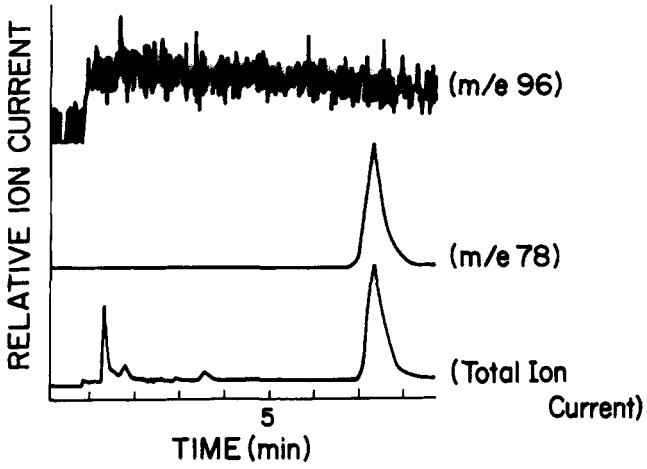

Figure 1. GC/MS of decarbonylation reaction carried out in refluxing toluene solution.

Reports by Olah and Kreienbühl[3] describe the synthesis of aryl fluorides from easily attainable aroyl fluorides[4] (ArCOF) by a catalytic decarbonylation reaction with Wilkinson's catalyst [$(Ph_3P)_3RhCl$]. The potential application of this reaction for the synthesis of ^{18}F-labeled aryl fluorides has been noted by several investigators.[5,6] However, since no further reference could be found to the application of this method to the synthesis of aryl fluorides, despite continued citation to its potential usefulness,[7] we attempted to investigate this reaction and its application in the synthesis of ^{18}F radiopharmaceuticals (^{18}F $T1/2$ = 110 m in). The speed of reaction and ease of preparation of the needed aroyl fluoride (ArCOF) precursors seemed ideally suited for synthesis utilizing short-lived isotopes.

Our preliminary attempts to repeat the work of Olah and Kreienbühl (as analyzed by GLC) *apparently* resulted in the formation of fluorobenzene. However, when the synthesis was carried out by using benzoyl fluoride-^{18}F under a variety of conditions, no labeled fluorobenzene-^{18}F could be detected. Again, under conditions where carrier amounts of "cold" unlabeled PhCOF was added to labeled $PhCO^{18}F$ an *apparent* peak for Ph–F was observed (by GLC), but no ^{18}F was associated with it. We thus became suspicious that the presumed Ph–F peak was incorrectly identified under the GLC conditions used. Modification of GLC conditions by lowering the temperature for analysis from 110 to 70 °C allowed the separation of benzene and fluorobenzene, thus tentatively identifying the actual (and only) product as benzene.

Realizing the possible ambiguity of product identification through GLC retention times, the reactions were repeated under catalytic conditions as described by Olah, and the reaction mixture was submitted to GC/MS for positive identification. The stoichiometric complex $(Ph_3P)_2Rh(COPh)FCl$ was also isolated and subjected to pyrolysis in the direct-insertion probe in the GC/MS as well. Standards were run to identify the parent mass peaks for benzene (m/e 78) and fluorobenzene (m/e 96) as well as the electron-impact cracking patterns for the pure compounds. Fluorobenzene does exhibit a strong parent at m/e 96 with approximately 50% the intensity of the base peak at m/e 63 ($P - CH_2F$).

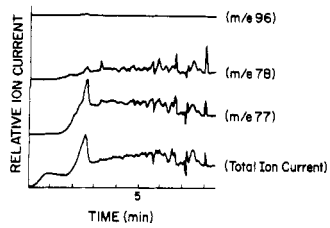

Figure 2. Mass spectral analysis of the high-temperature pyrolysis of the isolated stoichiometric complex $(Ph_3P)_2Rh(COPh)FCl$.

Table I. High-Temperature Pyrolysis of the Stoichiometric Complex $(Ph_3P)_2Rh(COPh)FCl$[13]

m/e	77	78	96	152	183	199	277
rel intens	100	33.6	not detected	15.8	7.0	14.0	13.2

GC/MS analysis of the catalytic reaction mixtures in refluxing toluene or xylene showed no significant product mass peaks above m/e 78 and had a cracking pattern identical with that of the benzene standard. Monitoring of m/e 78 and 96 as a function of time (elution from GLC) and comparison with the total ion current as a function of time indicated that the m/e 78 peak was coincident with the total ionization mass peak from GLC. Even at increased sensitivity (×10), no contribution from m/e 96 (fluorobenzene) was observed (see Figure 1).

Since it was observed that high-temperature pyrolysis of the $(Ph_3P)_2Rh(COPh)Cl_2$ does in fact produce a little chlorobenzene,[8] the solid, stoichiometric complex $[(Ph_3P)_2Rh(COPh)FCl]$ was subjected to pyrolysis in the direct-insertion probe of the mass spectrometer and heated from 30 to 285 °C at 30 °C/min. Results, shown in Figure 2, indicate that the major contribution is from phenyl radical cleavage (m/e 77) and to a lesser from benzene (m/e 78). Essentially no fluorobenzene is observed although other higher molecular weight peaks were also observed (Table I).

It thus appears that under all of the conditions that were tried, with either catalytic or stoichiometric amounts of the Wilkinson's catalyst in solution or in high-temperature pyrolyses, none produced the desired and reported fluorobenzene. The initial reports of Olah and Kreienbühl are therefore in error.[9]

In fact, recent studies by Kampmeier et al.[8] in which they were unable to reproduce earlier reports of decarbonylation of benzoyl chloride at low temperature (30–100 °C) with the Wilkinson's catalyst cast further doubt on these reactions and the proposed mechanism and intermediates. These reactions appear to be more complex and less understood than once supposed, and a complete reevaluation of these systems is now in order.

Experimental Section

Benzoyl fluoride (Aldrich) and benzoyl chloride (Aldrich) were distilled prior to use. NMR and IR of these materials showed them to be pure. Xylene and toluene were distilled from Na/benzophenone and were stored over molecular sieves (5A) to ensure dryness. $(Ph_3P)_3RhCl$ and 18-crown-6 were also purchased

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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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(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.

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

Toshihiro Fukagawa, Yuzo Fujiwara,* and Hiroshi Taniguchi

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

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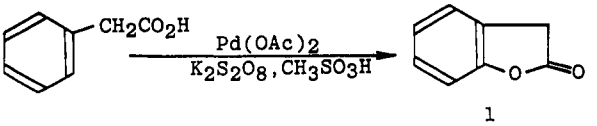
Lactones occur widely in nature and are found to exhibit various kinds of biological activities.[1] Although 2(3*H*)-benzofuranone (1), the five-membered benzolactone, is an important starting material for the synthesis of such biologically active substances, its direct synthesis via the intramolecular 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)



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

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