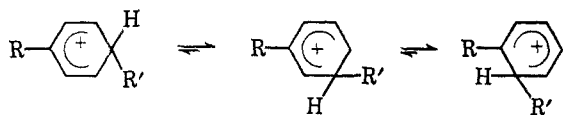


uct dialkylbenzenes. Any rearrangement affecting migrations of alkyl (or related substituents) from the conjugatively stabilized *ortho* and *para* positions of alkylbenzenonium ions into the *meta* positions must be considered thermodynamically and not kinetically controlled. Thus it is possible that in a system where no



apparent product isomerization takes place (for example, in the nitromethane solution of methyl-diphenylmethanes) there can be still rearrangement of the alkylation transition state favoring the formation of product compositions with higher *meta*-isomer contents than would be formed under purely kinetically controlled conditions.

#### Experimental Section

**2-Methyldiphenylmethane.**—A solution of phenylmagnesium bromide (100 ml of 3 *M* solution in ether) was placed in a 250-ml, three-neck, round-bottom flask equipped with a mechanical stirrer, drying tube, and dropping funnel. Cadmium chloride (1 g) and then  $\alpha$ -chloro-*o*-xylene (35 g) were added dropwise over a period of 15 min and the reaction mixture was refluxed for 1 hr. After usual work-up, a 38% yield of 2-methyldiphenylmethane [bp 138° (13 mm),  $n_D^{25}$  1.5775] was obtained.

**3-Methyldiphenylmethane.**—To benzene (40 g), 6.8 g of anhydrous zinc chloride was added in a three-neck, round-bottom flask equipped with stirrer, dropping funnel, and reflux condenser. Over a period of 1 hr, 28 g of  $\alpha$ -chloro-*m*-xylene was added to the stirred mixture. The mixture was stirred for 3 hr and then worked up in the usual way. A yield of 34% of 3-methyldiphenylmethane was obtained, bp 138° (14 mm),  $n_D^{25}$  1.5665.

**4-Methyldiphenylmethane.**—The reduction of 4-methylbenzophenone with palladium-hydrogen was carried out according to the procedure of Baltzly and Buck,<sup>10</sup> bp 138–139° (14 mm),  $n_D^{25}$  1.5651.

**General Procedure of Isomerization.**—The ratio of substrate and catalyst in all isomerizations was 0.2 mole of aluminum chloride/mole of methyldiphenylmethane. Water (0.05 mole) was added as a promoter and in order to keep the impurity moisture level constant. All isomerizations were carried out in capped reactions flasks, magnetically stirred, and thermostated at 0°. Samples were withdrawn periodically; the reaction was stopped by quenching with ice-water. The organic material was extracted with ether. The extracts were dried with anhydrous magnesium sulfate and analyzed by gas-liquid partition chromatography.

**Gas-Liquid Partition Chromatographic Analysis.**—All analyses were carried out on a Perkin-Elmer Model 226 fractometer equipped with a 150 ft length; 0.01-in. i.d. open tubular (Golay) column, coated with *m*-bis(*m*-phenoxyphenoxy)benzene modified with 20% Apiezon. A hydrogen flame-ionization detector with helium carrier gas of 30 psi was used, columns being operated at 125°, with detector temperature of 185–190° and injector block temperature of 310–320°. Peak areas were directly determined by use of a high-speed Infotronics Model CRS-1 electronic integrator. Characteristic retention times of the isomeric methyldiphenylmethanes follow: 2-methyl-, 111.3 min, 3-methyl-, 113.4 min, and 4-methyldiphenylmethane, 119.1 min. Good base-line separation was achieved.

**Registry No.**—Aluminum chloride, 7446-70-0; 2-methyldiphenylmethane, 713-36-0; 3-methyldiphenylmethane, 620-47-3; 4-methyldiphenylmethane, 620-83-7.

(10) R. Baltzly and J. S. Buck, *J. Am. Chem. Soc.*, **65**, 1984 (1943).

**Acknowledgment.**—The Petroleum Research Fund, administered by the American Chemical Society, is thanked for support of this work.

#### Organic Fluorine Compounds.<sup>1a</sup>

#### XXX. Formation of Aryl Fluorides via Decarbonylation of Aroyl Fluorides

GEORGE A. OLAH AND PAUL KREIENBÜHL<sup>1b</sup>

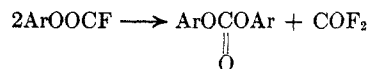
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Received November 21, 1966

The preparation of aryl fluorides cannot be accomplished by the same simple direct halogenation methods which are used to prepare aryl chlorides, bromides, and iodides. The inability of fluorine to form a cation of even positively polarized complex prevents electrophilic fluorination. Aryl fluorides are prepared *via* the diazotization of aryl amines,<sup>2</sup> through nucleophilic displacement of suitable substituted other halides,<sup>3</sup> and by certain indirect routes like thermal or catalytic decomposition of aryl thiofluoromates.<sup>4,5</sup>



Attempted decarboxylation of aryl fluoroformates resulted in preferential formation of diaryl carbonates (in a bimolecular elimination reaction).



We have now investigated the possibility of preparing aryl fluorides by the decarbonylation of aroyl fluorides.



As aroyl fluorides are readily available,<sup>6</sup> this method would provide easy access to aryl fluorides.

The thermal decarbonylation of benzoyl chloride to give low yields of chlorobenzene was reported.<sup>7,8</sup> Attempts to affect the thermal decarbonylation of benzoyl fluoride and other aroyl fluorides in our hands proved unsuccessful.

No decarbonylation was observed in nitrogen atmosphere up to 700° (in a heated tube reactor). If atmospheric moisture was present, benzoic anhydride was formed.

Palladium chloride or palladium-charcoal catalyzed<sup>9</sup> decarbonylation attempts of aroyl fluorides were also unsuccessful.

(1) (a) Part XXIX: G. A. Olah, S. J. Kuhn, and R. E. A. Dear, *J. Org. Chem.*, **30**, 1317 (1965). (b) Postdoctoral research investigator, 1966–1967.

(2) G. Balz and G. Schiemann, *Ber.*, **60**, 1186 (1927); R. L. Ferm and C. A. VanderWerf, *J. Am. Chem. Soc.*, **72**, 4809 (1950).

(3) H. B. Gottlieb, *ibid.*, **58**, 532 (1936); G. C. Finger and C. W. Kruse, *ibid.*, **78**, 6034 (1956).

(4) G. A. Olah (to the Dow Chemical Co.), U. S. Patents 3,219,680 and 3,270,089 (1966).

(5) K. O. Christie and A. E. Pavlath, *J. Org. Chem.*, **30**, 3170 (1965); **31**, 559 (1966).

(6) G. A. Olah and S. J. Kuhn, *ibid.*, **26**, 237 (1961); *Org. Syn.*, **45**, 3 (1965).

(7) A. Mailhe, *Compt. Rend.*, **180**, 1111 (1925); A. Mailhe and F. deGodon, *Bull. Soc. Chim. France*, [4] **19**, 449 (1916).

(8) L. Erlenmeyer, *Helv. Chim. Acta*, **16**, 903 (1933).

(9) These catalysts decarbonylate alkanoyl chlorides: J. Tsuji, K. Ohno, and J. Kajimoto, *Tetrahedron Letters*, 456S (1965).

Blum<sup>10</sup> and Tsuji and Ohno<sup>11</sup> recently reported the decarbonylation of acyl chlorides and bromides by tris(triphenylphosphine)rhodium chloride.

We wish now to report our observation on the decarbonylation of aroyl fluorides and in particular, observations relating to catalytic decarbonylation.

Decarbonylation of benzoyl fluoride by tris(triphenylphosphine)rhodium chloride was observed in reactions carried out either in excess, neat benzoyl fluoride, or using solvents like benzene, toluene, *o*-xylene, and  $\alpha$ -methylnaphthalene. Best results were obtained either in reactions in neat benzoyl fluoride or in *o*-xylene as solvent. Reactions were carried at 80–120° heating the reaction mixture for 1 hr, then distilling off products and analyzing by glpc, infrared, and nmr spectroscopy. Decarbonylation of aroyl fluorides is a fairly general reaction. Besides benzoyl fluoride, *p*-toluoyl fluoride, *m*-chloro-, *p*-chloro-, and *p*-fluorobenzoyl fluoride yielded the corresponding substituted fluorobenzenes. The decarbonylations are quantitative, based on the amount of aryl fluorides formed and tris(triphenylphosphine)rhodium chloride used.

It was also found that the reactions are catalytic to the degree that 280–580% mole equiv of fluoroaromatic compounds can be formed (Table I) before the activity of the rhodium chloride "catalyst" is lost.

TABLE I

DECARBONYLATION OF AROYL FLUORIDES TO ARYL FLUORIDES BY TRIS(TRIPHENYLPHOSPHINE)RHODIUM CHLORIDE

Aroyl fluoride	Product aryl fluoride	% conversion before deactivation of catalyst
Benzoyl	Fluorobenzene	580
<i>p</i> -Toluoyl	<i>p</i> -Fluorotoluene	470
<i>m</i> -Toluoyl	<i>m</i> -Fluorotoluene	530
<i>p</i> -Chlorobenzoyl	<i>p</i> -Chlorofluorobenzene	350
<i>m</i> -Chlorobenzoyl	<i>m</i> -Chlorofluorobenzene	280
<i>p</i> -Fluorobenzoyl	<i>p</i> -Difluorobenzene	340

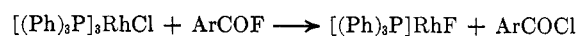
In a typical experiment, a mixture of 2.5 ml of *m*-toluoyl fluoride, 0.5 g of tris(triphenylphosphine)rhodium chloride, and 0.1 g of *o*-xylene (as internal reference standard) were heated for 3 hr at reflux temperature in 10 ml of toluene. The red color of the original reaction mixture changes to yellow and a precipitate forms. After filtration the solution was analyzed by glpc (using a Perkin-Elmer Model F-11 vapor fractometer equipped with a 12-ft Carbowax M-20 filled column). From the ratio of the *m*-fluorotoluene/*o*-xylene peaks the yield of *m*-fluorotoluene found was 0.37 g (530%), based on the amount of catalyst used. Product identification was also achieved by collecting, under semipreparative conditions, gc samples and obtaining their infrared and nmr spectra which were identical with those of pure *m*-fluorotoluene. Longer reaction times and higher temperatures did not further increase yield and catalyst was found to become inactive. Blum<sup>10</sup> was able to show that decarbonylation of aroyl chlorides and bromides is catalytic, according to the reversibility of the reaction of the rhodium carbonyl compound with triphenylphosphine liberating CO and regenerating the active catalyst.



(10) J. Blum, *Tetrahedron Letters*, 1605, 3041 (1966).

(11) J. Tsuji and K. Ohno, *ibid.*, 4731 (1966).

The fast deactivation of the same catalyst in the reactions with aroyl fluorides in our view is a consequence of a halogen exchange reaction producing tris(triphenylphosphine)rhodium fluoride, which itself is inactive in decarbonylation reactions.



Aroyl chlorides were identified in the reaction mixtures proving the halogen exchange.

Whereas our work demonstrated the feasibility of the decarbonylation of aroyl fluorides to aryl fluorides, so far the reaction was achieved only by using tris(triphenylphosphine)rhodium chloride as decarbonylating agent. Because rapid chlorine-fluorine exchange deactivates the catalyst, the method is limited at the present time. We are continuing efforts to find a decarbonylating catalyst which would not be deactivated by aroyl fluorides.

**Acknowledgment.**—Support of this work by a grant of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

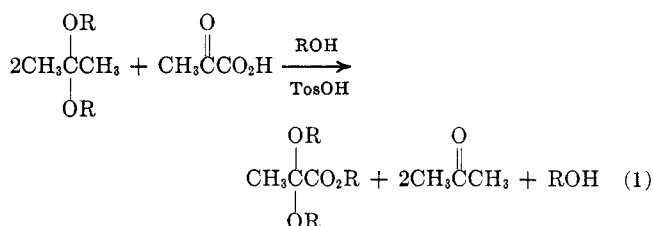
### Preparation of Alkyl 2,2-Dialkoxypropanoates<sup>1</sup>

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Alkyl 2,2-dialkoxypropanoates have been prepared in one step by treatment of pyruvic acid with dialkoxypropanes in alcohols as shown in eq 1.



R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, allyl, *n*-C<sub>4</sub>H<sub>9</sub>, *i*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>5</sub>H<sub>11</sub>, *i*-C<sub>5</sub>H<sub>11</sub>

The required dialkoxypropanes were readily made from 2,2-dimethoxypropane and the proper alcohol by the method of Lorette and Howard.<sup>2</sup>

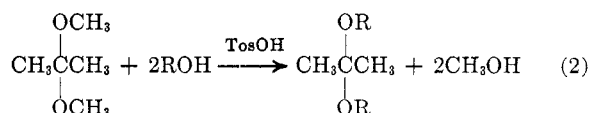


Table I summarizes the yields obtained in the preparation of the ketal esters. In general the yields were

(1) (a) This investigation was supported by Public Health Service Grant GM12399 from the National Institute of General Medical Sciences. (b) Presented at the Great Lakes Regional Meeting of the American Chemical Society, Chicago, Ill., June 16–17, 1966.

(2) N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960).