

mmoles) of bromine in 15 ml of acetic acid. The mixture was stirred 3 hr and treated with chloroform and with sodium bisulfite solution. A mixture of *cis*- and *trans*-dibromo ketones [mp 132–141° (hexane), 6.64 g, 15.8 mmoles, 83.0%] resulted.

Anal. Calcd for $C_{11}H_{10}Br_2Cl_2OS$: C, 31.58; H, 2.39. Found: C, 31.52; H, 2.60.

1,3-Dichloro-5,7-dimethyl-6H-cyclohepta[c]thiophen-6-one (6b) (Dichlorodimethyl-2-thiaazulen-6-one).—The above dibromo ketone (6.64 g, 15.8 mmoles), lithium chloride (2.0 g), calcium carbonate (4.0 g), and dimethylformamide (80 ml) were heated under nitrogen on a steam bath for 20 min. The mixture was treated with chloroform and dilute hydrochloric acid to give 3.59 g (13.9 mmoles, 87.8%) of pale yellow needles, mp 163–164° (hexane).

Anal. Calcd for $C_{11}H_8Cl_2OS$: C, 50.98; H, 3.11. Found: C, 50.81; H, 3.05.

1,3-Dichloro-5,7-dimethyl-6-phenyl-6H-cyclohepta[c]thiophen-6-ol (9b).—The reaction of the above thiaazulenone (520 mg, 2.00 mmoles) and phenyllithium (2.14 mmoles) was carried out as in the preparation of 9a to give 522 mg (1.55 mmoles, 77.5%) of colorless crystals, mp 155–157° (chloroform–heptane).

Anal. Calcd for $C_{17}H_{14}Cl_2OS$: C, 60.53; H, 4.18. Found: C, 61.08; H, 4.09.

Registry No.—2-Thiaazulen-6-one, 10095-83-7; **4a**, 10095-84-8; **4b**, 10095-92-8; **5**, 10095-85-9; **7**, 5368-72-9; **6a**, 10095-87-1; **6b**, 10095-95-1; **9a**, 10095-88-2; **9b**, 10095-96-2; **10a**, 10095-89-3; **3b**, 10095-90-6; 3-chloromethyl-2,5-dichlorothiophene, 10095-91-7; *cis* **4c**, 10095-93-9; *trans* **4c**, 10095-94-0.

Friedel-Crafts Isomerization. XV.¹

Aluminum Chloride Catalyzed Isomerization of Methylidiphenylmethanes

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No previous reports exist on the investigation of the Friedel-Crafts isomerization of methylidiphenylmethanes. Brown and Bolto² investigating the gallium bromide catalyzed benzylation of toluene with benzyl bromide suspected concurrent (or consecutive) isomerization and used short reactions times (in a flow system) to minimize this effect.

Olah, Kuhn, and Flood³ investigated the aluminum chloride catalyzed benzylation of toluene with benzyl chloride in nitromethane solution. They found that the isomer distribution of the formed methylidiphenylmethanes in this solvent was typically *ortho-para* (43.5% *ortho*, 4.5% *meta*, and 52.0% *para*) in sharp contrast with the observations of Brown and Bolto² (41% *ortho*, 19.5% *meta*, and 39.5% *para*), obtained in excess aromatic hydrocarbon as solvent. At the same time, the relative reactivity of the benzylation of toluene and benzene was found to be around 3.2 both from competitive³ and absolute⁴ rate determinations. The question, whether the Friedel-Crafts benzylation of toluene in hydrocarbon solvent gave isomer distribution affected by isomerization, thus obviously became an important one.

(1) Part XIV: G. A. Olah, J. C. Lapiere, and H. Schreier, *J. Org. Chem.*, **31**, 1268 (1966).

(2) H. C. Brown and B. A. Bolto, *J. Am. Chem. Soc.*, **81**, 3320 (1959).

(3) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1966).

(4) G. A. Olah and N. A. Overchuk, *ibid.*, **87**, 5786 (1965).

TABLE I
ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF
METHYLDIPHENYLMETHANES AT 0°

Reaction time	% Methylidiphenylmethane isomer distribution (normalized)		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
2-Methylidiphenylmethane			
0	>99.0		
30 sec	91.7	3.2	5.1
1 min	88.7	4.1	7.2
2	85.1	5.3	9.6
3	70.1	12.1	17.8
4	49.3	23.9	26.8
5	46.3	25.3	28.4
6	36.4	35.1	28.5
8	26.4	42.1	31.5
10	19.4	50.7	29.9
12	13.2	61.4	25.4
15	10.2	65.7	24.1
20	9.8	67.7	22.5
30	9.2	66.3	24.5
1 hr	10.4	65.5	25.1
24	9.7	65.5	24.8
3-Methylidiphenylmethane			
0	>99.0		
5 min	0.9	96.8	2.3
10	1.5	93.6	4.7
15	1.6	92.8	5.6
30	2.9	88.4	8.7
45	4.3	83.7	12.0
1 hr	5.5	80.7	13.9
1.5	7.4	73.7	18.9
2	7.7	70.3	22.0
6	8.3	68.5	23.2
24	9.7	66.1	24.2
4-Methylidiphenylmethane			
0	<0.1	<0.1	99.9
30 sec	2.1	2.4	95.5
1 min	4.5	8.5	87.0
2	7.8	12.0	80.2
3	11.5	21.7	66.8
5	12.5	36.3	51.2
7	12.7	45.4	41.9
10	11.3	57.7	31.0
15	10.2	62.7	27.1
30	9.9	65.5	24.6
24 hr	9.7	65.4	24.9

In the continued investigation of the Friedel-Crafts isomerization of disubstituted benzenes⁵ we now investigated the aluminum chloride catalyzed isomerization of the isomeric methylidiphenylmethanes.

Results and Discussion

The needed high purity isomeric methylidiphenylmethanes were prepared by standard methods, the best suited being the following.

2-Methylidiphenylmethane was prepared from α -chloro-*o*-xylene and phenylmagnesium bromide.

3-Methylidiphenylmethane was prepared by the $ZnCl_2$ -catalyzed Friedel-Crafts reaction of α -chloro-*m*-xylene with benzene.

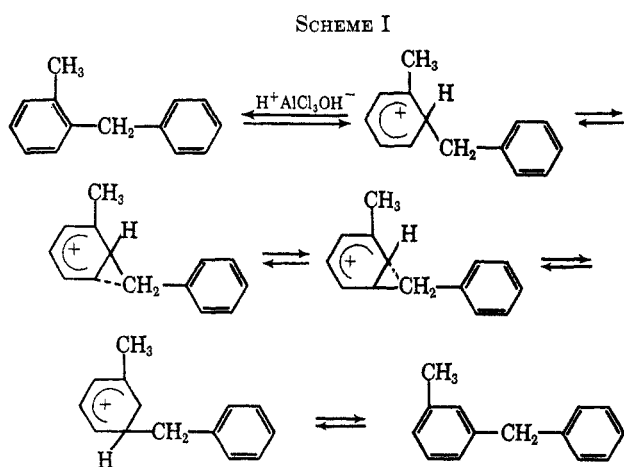
4-Methylidiphenylmethane was obtained by the catalytic (palladium on charcoal) hydrogenation of 4-methylbenzophenone.

The aluminum chloride catalyzed isomerization of the isomeric methylidiphenylmethanes was carried out

(5) Parts II and XIV of this series.

with water-promoted aluminum chloride at 0°. Time-composition data obtained are summarized in Table I.

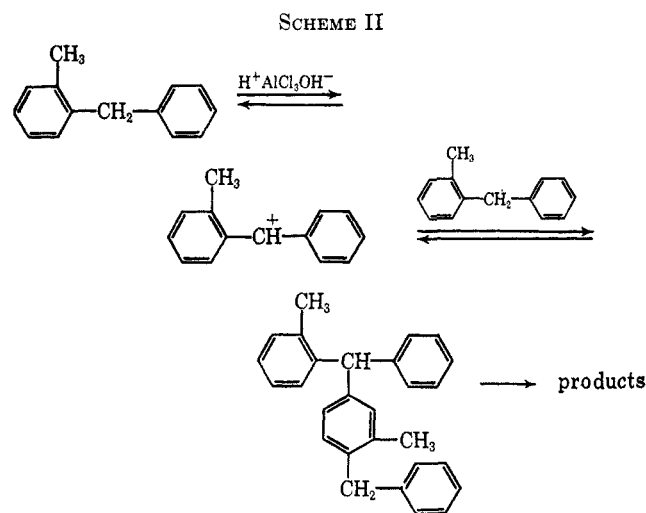
Isomerizations were fast, particularly in the case of the *ortho* and *para* isomers, and therefore were carried out at ice-bath temperature (0°). At room temperature they were practically completed in 1–2 min. All analyses were carried out with open tubular (capillary) gas chromatography, as described in the experimental part. Accuracy of the analysis of the isomer determination was estimated to be better than $\pm 3\%$, based on analysis of mixtures of known composition. Besides the isomeric methyl-diphenylmethanes, toluene, diphenylmethane, and dibenzyltoluenes (also unidentified higher molecular weight products) were also formed in the isomerizations, indicating disproportionation involving both benzyl and methyl group migration. The isomerization of xylenes⁶ was shown to involve predominant intramolecular 1,2 shifts. The experimental observation that the isomerization of 2-methyl-diphenylmethane goes through a fast maximum in the formation of the *para* isomer (and to a much lesser degree that of the *para* isomer through a maximum of the *ortho*), before giving the equilibrium concentration containing the usual high amount of *meta* isomer indicates, therefore, that the benzyl group must migrate, at least partially, through an intermolecular mechanism superimposed on the intramolecular migration of the methyl group. Transbenzylation, is also indicated by formation of toluene and dibenzyltoluenes. Formation of diphenylmethane at the same time indicates tendency of disproportionation involving the methyl group. These findings would indicate a mechanism based on protonation of methyl-diphenylmethanes to the corresponding σ complex, followed by isomerization involving either benzyl or methyl group migration (Scheme I).



The observed acid-catalyzed disproportionation above can be viewed as an electrophilic transalkylation which involves nucleophilic displacement on the intermediate complex by another molecule of benzyltoluene. Thus the disproportionation (transalkylation) reaction is not considered to involve the cleavage of relatively unstable primary carbonium ions ($C_6H_5-CH_2^+$ or CH_3^+) in any "free" state.

An alternate mechanism, based on analogy with suggestions of Pines,⁷ Schmerling,⁸ and Streitwieser,⁹ for

the acid-catalyzed isomerization of di- and trialkylbenzenes, would involve hydride abstraction to form a methylbenzhydryl cation (tolylphenylcarbonium ion) which would react with a second molecule of methyl-diphenylmethane to form a benzhydryldiphenylmethane type of intermediate, cleaving to the isomeric methyl-diphenylmethane and other observed cleavage products (toluene, diphenylmethane, etc.) (Scheme II).



Although benzydryldiphenylmethane derivatives may be formed, no attempt was made to identify them in the high-boiling residues of the isomerizations. No clear decision at this point is possible between the two possible mechanistic pathways based on present data. They could operate simultaneously, yielding the complex reaction mixtures.

The observation, that methyl-diphenylmethanes undergo facile isomerization under the catalytic effect of aluminum chloride (and presumably other Lewis acid, halide catalysts) in hydrocarbon media, would explain the discrepancy between the benzylation data of Brown and Bolto² and those of Olah, *et al.*^{3,4}

The isomerization of 2- and 4-methyl-diphenylmethane in hydrocarbon media is quite fast, particularly when the reactions are run at room temperature ($\sim 25^\circ$). The use of nitromethane as solvent, on the other hand, slows down isomerization to such an extent that when pure 2- or 4-methyl-diphenylmethane was stirred at 25° for 2 hr with aluminum chloride, no trace of isomerization was detectable.

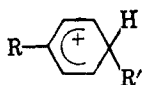
It must, however, also be remembered that isomerization affecting isomer distributions in Friedel-Crafts-type alkylations are by no means limited to product isomerizations. It was pointed out³ that isomerization of the benzenonium ion type transition state of an alkylation reaction (prior to proton elimination) can take place even under conditions which do not favor product isomerization (*e.g.*, protonation of or hydride ion abstractions from the products). The fact that alkylation takes place clearly indicates that along the reaction pathway a benzenonium ion type of transition state must be formed even when the medium is otherwise unsuited to formation of these ions from the prod-

(6) R. H. Allen and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 5289 (1959).

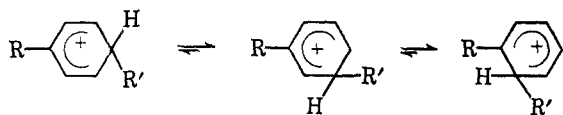
(7) H. Pines and J. T. Arrigio, *ibid.*, **80**, 4369 (1958).

(8) L. Schmerling, J. P. Luvisti, and R. W. Welch, *ibid.*, **81**, 2719 (1959).

(9) A. Streitwieser, Jr., and L. Reif, *ibid.*, **82**, 5003 (1960).



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 α -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 α -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,¹⁰ 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.^{1a}

XXX. Formation of Aryl Fluorides via Decarbonylation of Aroyl Fluorides

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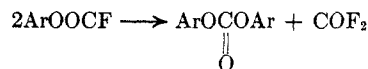
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The preparation of aryl fluorides cannot be accomplished by the same simple direct halogenation methods which are used to prepare aryl chlorides, bromides, and iodides. The inability of fluorine to form a cation of even positively polarized complex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



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,⁶ this method would provide easy access to aryl fluorides.

The thermal decarbonylation of benzoyl chloride to give low yields of chlorobenzene was reported.^{7,8} 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 catalyzed⁹ 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).