became light tan. Then the solid was extracted twice with hot 90–95% alcohol and, at the end, consisted of inorganic material only. From the absolute alcohol extracts, on evaporation, 7 g. of a very dark-colored substance was obtained, which was very soluble in water and strongly acidic. Its neutral equivalent was about 310, but from these data and the analyses, the substance could not be identified with any pure and simple compound known. From the 90–95% alcohol extracts, on cooling, a small amount (0.5 g.) of crystals separated, which was recrystallized from 90% alcohol and identified as potassium phenylsulfamate. The differential extraction was made possible by the fact that the latter compound is only sparingly soluble in absolute alcohol.

The identification of potassium phenylsulfamate was based on elementary analysis and on comparison with the following properties of an authentic specimen of the salt. (1) The salt is readily soluble in cold water and the resulting solution is neutral. (2) The aqueous neutral solution gives no test for the sulfate ion. If such a solution is made acid and heated up to boiling, addition of the barium chloride reagent yields an abundant precipitate of barium sulfate. (3) On making the aqueous solution of the salt alkaline with a sodium hydroxide solution, no hydrolysis occurs even after prolonged boiling. However, if the solution of the salt is first made acid with hydrochloric acid and boiled for a short time and, then, is made alkaline, aniline is liberated. (4) The compound crystallizes from ethanol or aqueous ethanol in the form of shiny plates. The solubility in hot absolute ethanol is very low.

Attempted Rearrangement in 60% Ethyl Alcohol in the Presence of Sulfur Dioxide.—A solution of 9 g. of potassium phenylsulfamate in 310 ml. of 60% aqueous alcohol, in the presence of 4.2 g. of 100% sulfuric acid, was made up by dissolving the sulfamate in water, adding a dilute sulfuric acid solution and, successively, the calculated amount of ethyl alcohol. Through this solution dry sulfur dioxide was passed at room temperature for 7 hr., then the reaction flask was stoppered and let stand overnight. On filtration the liquid was separated from some inorganic material, then made alkaline with potassium hydroxide and evaporated on a steam-bath. The residue was extracted with small portions of hot 90% alcohol and the extracts, on cooling, yielded 2.2 g. of unchanged phenylsulfamate. The residue left behind and the mother liquors were recombined, made acid, heated to boiling, then made alkaline and evaporated again. Any anilinesulfonic acid would be expected to be found in the residue as a salt, but such a residue proved to be inorganic material only. Any aniline formed during the reaction or further treatments of the reaction mixture was eliminated in the evaporations.

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LONDON, W.C. 1, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Molecular Association of Diarylformamidines. II. Effects of O- and P-Methyl Groups

BY ROYSTON M. ROBERTS

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Cryoscopic molecular weight determinations have been performed on benzene solutions of N,N′-di-*o*-tolylformamidine, N,N′-di-*p*-tolylformamidine, N-phenyl-N′-*o*-tolylformamidine and N-phenyl-N′-mesitylformamidine. All are associated except the first. The association factors of these compounds are compared with those of N,N′-diphenylformamidine, N,N′-di-*o*-chlorophenylformamidine and N,N′-di-*p*-chlorophenylformamidine. Steric and electronic effects of the substituents on the aromatic rings are discussed.

In an earlier paper[1] it was shown by cryoscopic measurements that molecules of N,N′-diphenylformamidine and N,N′-di-*p*-chlorophenylformamidine are associated in benzene solution, and that the degree of association is a function of the concentration of the solution. N,N′-Di-*o*-chlorophenylformamidine was found not to be associated under similar circumstances. The lack of association of this *o*-substituted compound was correlated with the fact that ethyl malonate reacts more slowly with N,N′-diarylformamidines which contain *o*-methyl and chloro substituents than with those which contain *meta*, *para* or no substituents.[1] Since both methyl and chloro substituents in the *o*-position decrease the rate of this reaction, it appears that the similar steric properties of the substituents are more important than the different electronic properties. It seemed interesting to investigate the effect of introducing *o*- and *p*-methyl groups into the N,N′-diphenylformamidine molecule upon the ability of these molecules to associate in benzene solution.

To this end the following compounds have been synthesized and their apparent molecular weights have been determined in benzene solution at the freezing point: N,N′-di-*o*-tolylformamidine, N,N′-di-*p*-tolylformamidine, N-phenyl-N′-*o*-tolylformamidine and N-phenyl-N′-mesitylformamidine. In Table I are given the apparent molecular weights of these four compounds at different concentrations. All but the first are associated, and the degree of association increases with the concentration of the solutions.

Some interesting observations can be made if the data on these compounds and those on the unsubstituted and chloro-substituted compounds described in the earlier paper are converted into units allowing direct comparison. This may be done by expressing the concentration of the solutions in molality and by dividing apparent molecular weight values by formula weights to give the association factor, α. The data on all seven compounds studied thus far are plotted in these units in Fig. 1.

It may be seen that the presence of two *p*-chlorine atoms does not greatly affect the degree of association; the curve for N,N′-di-*p*-chlorophenylformamidine (II) lies only slightly below that of N,N′-diphenylformamidine (I). However, replacement of the two *p*-hydrogens of N,N′-diphenylformamidine by methyl groups significantly increases the degree of association (III). These results are in

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[1] R. M. Roberts, THIS JOURNAL, **72**, 3608 (1950).

TABLE I

CRYOSCOPIC MOLECULAR WEIGHT DETERMINATIONS IN BENZENE

Concn. (g. solute per 100 g. solvent)	Apparent mol. wt.	Concn. (g. solute per 100 g. solvent)	Apparent mol. wt.
N,N'-Di-*o*-tolyl-formamidine (formula wt. 224)		N-Phenyl-N'-*o*-tolyl-formamidine (f.w. 210)	
1.01	210	0.57	227
1.43	212	1.08	245
		1.62	258
N,N'-Di-*p*-tolylformamidine (f.w. 224)		2.16	271
		2.86	283
0.56	293	3.87	296
1.10	308		
1.67	337	N-Phenyl-N'-mesityl-formamidine (f.w. 238)	
2.04	336		
2.48	344	0.42	262
3.04	348	1.12	298
3.55	354	2.13	327
4.38	359	3.10	342
5.25	366	3.99	348
6.02	370	4.88	351
7.35	374		
8.46	378		

the directions expected for the electronic effects of chloro and methyl groups operating from the *p*-position, on the basis of the theory that increasing electron density on nitrogen leads to stronger intermolecular hydrogen bonds.[2] When each aromatic ring contains one chlorine atom (IV) or one methyl group (V) in the *o*-position, the molecules are not associated because of the steric interference of the *o*-substituents with intermolecular hydrogen bonding. When only one of the aromatic rings contains an *o*-methyl group as in N-phenyl-N'-*o*-tolylformamidine (VI), association occurs, but to a smaller degree than in the unsubstituted compound. Since one methyl group on *each o*-position prevents association, this must mean that N-phenyl-N'-*o*-tolylformamidine forms hydrogen bonds only through the nitrogens adjacent to the unsubstituted ring.[3] It is not too surprising, then, to find that N-phenyl-N'-mesitylformamidine does associate (VII), since it too has one unsubstituted ring; and it is interesting to note that its degree of association is greater than that of N-phenyl-N'-*o*-tolylformamidine. In fact, the mesityl compound is almost as strongly associated as the unsubstituted compound, which must mean that the electronic effect of the three *o*- and *p*-methyl groups almost compensates for the steric interference which prevents hydrogen bonding at one end of the molecule.

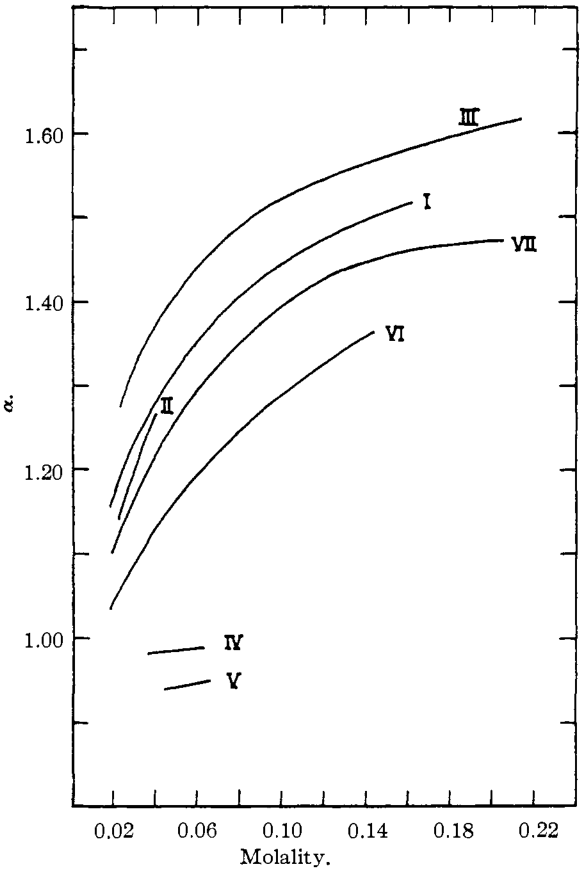

Fig. 1.—Association of N,N'-diarylformamidines in benzene solution: I, N,N'-diphenyl; II, N,N'-di-*p*-chlorophenyl; III, N,N'-di-*p*-tolyl; IV, N,N'-di-*o*-chlorophenyl; V, N,N'-di-*o*-tolyl; VI, N-*o*-tolyl-N'-phenyl; VII, N-mesityl-N'-phenyl.

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Experimental

Materials.—N,N'-Di-*p*-tolylformamidine (m.p. 139.5–140°) and N,N'-di-*o*-tolylformamidine (m.p. 151.5–152°) were prepared from ethyl *ortho*formate and the corresponding toluidines.

N-Phenyl-N'-*o*-tolylformamidine (m.p. 111–111.5°) and N-phenyl-N'-mesitylformamidine (m.p. 115–115.5°) were prepared from ethyl N-phenylformimidate and *o*-toluidine and mesidine, respectively. Care was taken to exclude all traces of acids in their preparation.[4] The latter formamidine is a new compound.

Anal.[5] Calcd. for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61. Found: C, 80.48; H, 7.67.

Mesidine was prepared from nitromesitylene by reduction with tin and hydrochloric acid.

Benzene was dried by distillation and protected from atmospheric moisture by a calcium chloride tube.

Apparatus and Procedure.—Essentially the same Beckmann-type apparatus described in the preceding paper was employed. In some experiments, excessive supercooling was prevented by removing the inner tube and placing its

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[2] Actually, the electronic effect of a substituent in a molecule which forms symmetrical intermolecular hydrogen bonds (such as the N–H···N bonds involved here) is difficult to predict, because increasing negative charge on a N atom should increase its electrostatic attraction for the H of another molecule, leading to a stronger bond; but it should also decrease the positive charge on H, leading to a weaker bond. L. Hunter and J. A. Marriott (*J. Chem. Soc.*, 777 (1941)) ascribed the greater association of benzimidazoles compared to N,N'-diarylacetamidines to the greater acidity of the former, but very different steric factors are involved in these two series which complicate the comparison.

[3] Amidines exhibit labile tautomerism, so that the hydrogen may be present on either of the two nitrogens as required in the associated molecules.

[4] R. M. Roberts, R. H. DeWolfe and J. H. Ross, THIS JOURNAL, **73**, 2277 (1951).

[5] Microanalysis by Drs. G. Weiler and F. B. Strauss, Oxford, England.

tip directly in the cooling bath until crystals formed. The molal freezing point constant used for benzene was 5.12°.

The low solubility of N,N′-di-*o*-tolylformamidine in benzene allowed determinations of freezing point depressions in only very dilute solutions where experimental errors were comparatively higher, but there is no doubt about the qualitative result.

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[Contribution from the Chemical Research Laboratory, Polaroid Corporation]

1,1-Difluoro-2-methylpropene, 3,3-Difluoro-2-methylpropene and 3,3-Difluoro-3-chloro-2-methylpropene[1]

By Richard S. Corley, Saul G. Cohen, Myron S. Simon and Henry T. Wolosinski

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The preparation and properties of $CF_2{=}C(CH_3)_2$, $CH_2{=}C(CH_3)CHF_2$, $CH_2{=}C(CH_3)CF_2Cl$ and a number of derivatives are described.

As part of a program on fluorinated monomers, it seemed to us to be of interest to prepare 1,1-difluoro-2-methylpropene, $CF_2{=}C(CH_3)_2$. During the course of this work, we prepared the isomeric 3,3-difluoro-2-methylpropene, $CH_2{=}C(CH_3)CHF_2$, the related 3,3-difluoro-3-chloro-2-methylpropene, $CH_2{=}C(CH_3)CF_2Cl$, and the known compounds 3,3,3-trifluoro-2-methylpropene, $CH_2{=}C(CH_3)CF_3$[2] and 1,1-dichloro-2-methylpropene, $CCl_2{=}C(CH_3)_2$.[3]

We were unable to prepare $CF_2{=}C(CH_3)_2$ by removal of fluorine and acetate from $CF_3C(CH_3)_2OCOCH_3$ or chlorine and acetate from $CF_2ClC(CH_3)_2OCOCH_3$ by treatment with zinc, although the related chloro compound, $CCl_2{=}C(CH_3)_2$, was readily prepared by this method[3] from $CCl_3C(CH_3)_2OCOCH_3$. The desired olefin, $CF_2{=}C(CH_3)_2$, was successfully prepared by (a) reaction of the phosphite, $(CF_2ClC(CH_3)_2O)_3P$, with zinc and by reduction of $CH_2{=}C(CH_3)CF_2Cl$ with (b) hydrogen with nickel catalyst or (c) lithium aluminum hydride. Method (c) was the only one of preparative significance. The olefin was completely free of isomers on careful 80-plate fractionation and was inert to silica defluorination, as would be expected of a vinylidene fluoride. Structural formulation as $CF_2{=}C(CH_3)_2$ was demonstrated by preparation of the dibromide, by permanganate oxidation to acetone and by the infrared spectrum ($C{=}CF_2$ absorption[4] at 1765 cm.$^{-1}$ and of very strong intensity due to heightened double bond polarity as compared to other vinylidene fluorides).

The isomeric olefin, $CH_2{=}C(CH_3)CHF_2$, was formed in good yield by (a) dehydration of $CHF_2C(CH_3)_2OH$ by treatment with phosphorus pentachloride and (b) pyrolysis of the acetate ester of this carbinol. Careful fractionation on a 60-plate column gave no indication of the presence of the other isomer, $CF_2{=}C(CH_3)_2$, and showed a single boiling point plateau. The structure of $CH_2{=}C(CH_3)CHF_2$ was confirmed by its infrared absorption spectrum ($C{=}CH_2$ absorption of medium intensity at 1665 and 1850 cm.$^{-1}$),[4] preparation of the dibromide and pyrolytic defluorination over silica[5] to yield methacrolein, $CH_2{=}C(CH_3)CHO$. It may be noted that difluoromethyldimethylcarbinol was not dehydrated by (a) drastic treatment with phosphorus pentoxide, (b) the Chugaev reaction, (c) the boric ester method[6] or (d) the Grignard alcoholate pyrolysis method.[7]

The known 3,3,3-trifluoro-2-methylpropene, $CH_2{=}C(CH_3)CF_3$, and the new 3,3-difluoro-3-chloro-2-methylpropene, $CH_2{=}C(CH_3)CF_2Cl$, were prepared by modification of an established method[2] *via* dehydration of the appropriate trihalomethyldimethylcarbinol with phosphorus pentachloride.

$$CX_3COCl + 2CH_3MgBr \longrightarrow CX_3C(CH_3)_2OH \longrightarrow CH_2{=}C(CH_3)CX_3$$

The compound $CH_2{=}C(CH_3)CF_2Cl$ was shown to contain no other isomer on careful fractionation and the structure confirmed by the infrared spectrum ($CH_2{=}C$ absorption of medium intensity at 1665 and 1860 cm.$^{-1}$; no trace of $CF_2{=}C$ absorption at 1765 cm.$^{-1}$). The reduction of $CH_2{=}C(CH_3)CF_2Cl$ to $CF_2{=}C(CH_3)_2$ is therefore formulated as hydrogenolysis of the allylic chlorine atom accompanied or preceded by allylic rearrangement.[8]

The three similar isobutylenes, $CH_2{=}C(CH_3)CF_3$, $CH_2{=}C(CH_3)CF_2Cl$ and $CH_2{=}C(CH_3)CHF_2$, failed to polymerize under a wide variety of conditions.

Acknowledgments.—The authors are glad [illegible] knowledge their indebtedness to Miss Adelaide Sutton for infrared spectroscopy, to Mr. Marshall W. Kane for much preparative help, to Drs. Daniel I. Livingston and Pandurang Kamath for polymerization studies and to Dr. Elkan R. Blout for many helpful discussions.

Experimental[9]

CF_3COCl.—The acid chloride (b.p. −27°) was prepared in 85–92% average yield. Treatment of a sample in ether

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[1] This work was sponsored by the Signal Corps, Department of the Army.

[2] (a) E. Swarts, *Bull. Soc. chim. Belg.*, **1927**, 195; **1929**, 108. (b) A. L. Henne, J. W. Shepard and E. J. Young, This Journal, **72**, 3577 (1950).

[3] Z. Jocitsch and Al. Faworsky, *Chem. Zentr.*, **70, I,** 778 (1899).

[4] See, *e.g.*, L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, pp. 33, 37.

[5] *Cf.*, W. E. Hanford and G. W. Rigby (to du Pont), U. S. Patent 2,409,274 (October 15, 1946).

[6] W. Brandenberg and A. Galat, This Journal, **72**, 3275 (1950).

[7] F. C. Whitmore and H. S. Rothrock, *ibid.*, **55**, 1106 (1933).

[8] *Cf.* D. G. Kundiger and H. N. Haney, *ibid.*, **76**, 615 (1954); Maurice Prober, *ibid.*, **76**, 4189 (1954).

[9] All m.p.'s are corrected. Combustion analyses are by the Clark Microanalytical Laboratory, Urbana, Illinois, and Dr. Carol K. Fitz, Needham, Massachusetts.