2. The substitution of groups in the *ortho* positions in the aromatic nuclei of dibenzoylethylene lowers the apparent reduction potential. The substitution of the α-hydrogen atom in the same compound by a variety of atoms or groups has the same effect.

3. Dibenzoylcyclopropane and dibenzoylcyclobutane have been synthesized. Neither compound is reduced by chromous chloride, but the former is reduced by boiling with zinc and acetic acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

THE REACTION BETWEEN DICHLORO-ACETIC ACID AND AROMATIC AMINES

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In 1923 one of us[1] published a paper in which we stated that not only did dichloro-acetic acid react with aniline and similar amines to form salts, but also that salts of trichloro-acetic acid were formed if the amount of acid was increased and the temperature of the reaction allowed to rise. The trichloro-acetates of aniline, *o*-toluidine, *p*-toluidine, α-naphthylamine and *m*-nitro-aniline, were described as having been obtained from dichloro-acetic acid. These results were checked up by preparing the trichloro-acetates from trichloro-acetic acid. We supposed that two molecules of dichloro-acetic acid shifted to one molecule of monochloro-acetic acid and one of trichloro-acetic acid. To show that this could happen we treated *p*-nitro-aniline with dichloro-acetic acid in the presence of phosphorus pentoxide and obtained a solid product which was found to consist of *p*-nitro-monochloro-acetanilide and *p*-nitrotrichloro-acetanilide. In 1925 Doughty[2] repeated our experiments but was unable to obtain the trichloro-acetates from dichloro-acetic acid. We thereupon repeated our own experiments and were also unable to obtain the trichloro-acetates. This has greatly puzzled us because in carrying out our original work we felt we had taken every care to check up our observations. We purified our dichloro-acetic acid by redistillation, using that portion boiling at 191°. We also carefully examined the trichloro-acetate (1) by decomposing it with sodium hydroxide and obtaining aniline and (2) by treating an alcoholic solution with sulfuric acid, obtaining the ethyl ester of trichloro-acetic acid which was converted into the amide; m. p., 141°. Also, the analysis for chlorine gave excellent figures for three atoms: calculated, 41.52%; found, 41.44%. The conversion into a trichloro-acetate seemed to us to be proved in a thorough manner. Unfortunately, new samples of

[1] Wheeler and Smith, THIS JOURNAL, **45**, 1994 (1923).

[2] Doughty, *ibid.*, **47**, 1095 (1925).

dichloro-acetic acid had to be used since none of the acid used in 1923 was left. This led us to examine a variety of preparations, testing the dichloro-acetic acid with very pure aniline. These experiments revealed considerable variation in the quality of the acids, all of which were water white and labeled C. P. In no case, however, did any transformation take place.

In connection with this reëxamination we prepared the dichloro-acetates and trichloro-acetates of methylaniline, *o*-chloro-aniline, 2,4-dichloro-aniline, *o*-anisidine, benzidine and *p*-aminophenol. These reactions were tried out in various ways. One mole of acid was tried with one of amine, and also two of acid. The constituents were mixed direct and also in benzene solution. They were tried cold and also hot. In no case did the transformation into a trichloro-acetate occur.

Experimental Part

The amine salts of dichloro-acetic acid and of trichloro-acetic acid were prepared by mixing together one mole of each compound, except in the case of benzidine, where two moles of the acid were used. Heat usually developed and crystals began to form while the solution was still hot. The solid amines were first dissolved in alcohol before the addition of the acid.

The crystals were colorless needles, except the following: the two benzidine salts, leaves; 2,4-dichloro-aniline trichloro-acetate, octahedrons; *o*-chloro-aniline trichloro-acetate, plates. Alcohol was used for recrystallizing except in the following cases: chloroform for the dichloro-aniline trichloro-acetate and carbon tetrachloride for the methylaniline salts. The results are condensed into Table I.

TABLE I

AMINE SALTS OF DICHLORO- AND TRICHLORO-ACETIC ACIDS

	Dichloro-acetate			Trichloro-acetate		
		Cl, %			Cl, %	
	M. p., °C.	Calcd.	Found	M. p., °C.	Calcd.	Found
Methylaniline	96	30.04	30.49	97	39.37	39.45
o-Chloro-aniline	69–70	41.48	41.32	120	48.80	48.68
2,4-Dichloro-aniline	132–138	48.79	48.81	123–124	54.55	54.63
o-Anisidine	96	28.13	28.09	141	37.12	37.03
Benzidine	203	31.92	31.93	166	41.62	41.42
p-Aminophenol	148	29.79	29.66	166	39.03	38.71

Commercial Dichloro-acetic Acids.—Samples of dichloro-acetic acid, all labeled C. P., were obtained from Kahlbaum, Merck, Eastman and Coleman-Bell. These were treated with pure aniline, both direct and in benzene solution. Mixtures of 1 mole to 1 mole were used and also 1 mole to 2 moles of acid. In all cases but one the salt produced was mixed with a yellow by-product which made itself very evident, owing to its strong yellow color and sparing solubility even in hot solution. Various melting points were obtained, ranging from 140° to 165°. In this examination no attempt was made to purify the products. While no transformation to a trichloro-acetate was noted, we believe this offers a very quick method of determining qualitatively the purity of dichloro-acetic acid.

TABLE II

BEHAVIOR OF DICHLORO-ACETIC ACIDS WITH ANILINE

Source	Ppt.	M. p., °C.	Recryst.	M. p., °C.	By-product
Coleman-Bell	Pale yellow	115–118	Yellow	122	Yellow
Merck	Pink	95–102	Yellow	118–122	Yellow
Eastman	Yellow	114–117	Orange	118–121	Orange
Kahlbaum	White	122	White	122	None

We wish to thank Mr. R. D. Norton for his assistance in testing the commercial preparations of dichloro-acetic acid and for reëxamination of some of the salts.

Summary

1. The dichloro-acetates and trichloro-acetates of methylaniline, *o*-chloro-aniline, 2,4-dichloro-aniline, benzidine, *o*-anisidine and *p*-amino-phenol were prepared.

2. Identical products were obtained in cold and hot solutions and also when two moles of acid were used instead of one.

3. No salt formation occurred with dimethylaniline.

4. The purity of dichloro-acetic acid was quickly noted by its reaction with pure aniline. In the samples examined, one made from chloral gave a pure white salt at once; other acids gave a yellow compound in addition to the white salt.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE REDUCTION OF AROMATIC NITRO COMPOUNDS TO AMINES WITH HYDROGEN AND PLATINUM-OXIDE PLATINUM BLACK AS A CATALYST. XIV[1]

BY ROGER ADAMS, F. L. COHEN AND O. W. REES[2]

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Though the catalytic reduction of aromatic compounds to aromatic amines by means of hydrogen and platinum or palladium colloid or black has been frequently used, no systematic study has been made to deter-

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[1] (a) Voorhees with Adams, THIS JOURNAL, **44**, 1397 (1922). (b) Carothers with Adams, *ibid.*, **45**, 1071 (1923); (c) **46**, 1675 (1924); (d) **47**, 1047 (1925). (e) Adams and Shriner, *ibid.*, **45**, 2171 (1923); (f) **46**, 1683 (1924). (g) Kaufmann with Adams, *ibid.*, **45**, 3029 (1923). (h) Pierce with Adams, *ibid.*, **47**, 1098 (1925). (i) Kern and Shriner with Adams, *ibid.*, **47**, 1147 (1925). (j) Heckel with Adams, *ibid.*, **47**, 1712 (1925). (k) Tuley with Adams, *ibid.*, **47**, 3061 (1925). (l) Adams and Garvey, *ibid.*, **48**, 477 (1926). (m) Hiers and Adams, *Ber.*, **59**, 162 (1926).

[2] This communication is an abstract of a portion of theses submitted by F. L. Cohen and O. W. Rees, in partial fulfilment of the requirements for the degree of Master of Science in Chemistry, at the University of Illinois.