sulfonate and sodium dodecyl sulfate as the paraffin-chain salts.

We have no explanation to offer at the present time for the effect of concentration of paraffin-chain salt, although the phenomenon is not surprising in view of the profound effect of paraffin-chain salts upon the absorption spectrum of the dye.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
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RECEIVED JUNE 28, 1949

NEW COMPOUNDS

p,*p*'-Dichlorobenzhydryl-β-cyanoethyl Ether

Ten grams (0.04 mole) of *p*,*p*'-dichlorobenzhydrol[1] (m. p. 88–89°) and 1.0 ml. of phenyltrimethylammonium hydroxide (Monsanto, 20% aqueous solution) were dissolved in 40 ml. of purified dioxane. A solution of 2.3 g. (0.04 mole) of redistilled acrylonitrile in 10 ml. of dioxane was added dropwise with stirring. After pouring into 200 ml. of water, the oil layer was separated. On standing overnight 11 g. (91%) of solid melting 52–66° formed. Crystallization from 50 ml. of 95% ethanol gave 7.6 g. (67%) melting 74–76°.[2] For analysis a sample was recrystallized; m. p. 75–76.5°.

Anal. Calcd. for $C_{16}H_{13}OCl_2N$: Cl, 23.2; N, 4.58. Found: Cl, 22.45; N, 4.43.

Attempts to hydrolyze this cyanide in alkaline solution to β-(*p*,*p*'-dichlorobenzhydroxy)-propionic acid unexpectedly cleaved the ether linkage with the formation of *p*,*p*'-dichlorobenzhydrol. Five grams (0.016 mole) of the ether and 50 ml. of 15% aqueous sodium hydroxide were refluxed for twenty-four hours. At the end of this time the evolution of ammonia had practically ceased. After cooling and filtering 2.5 g. of solid, m. p. 83–85°, was collected. A mixed melting point with authentic *p*,*p*'-dichlorobenzhydrol was 84–88°. Acidification of the filtrate gave no precipitate. With 50 ml. of 25% sodium hydroxide solution and four hours of refluxing, the yield of alcohol was 97% of the theoretical.

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(1) Montagne, *Rec. trav. chim.*, **24**, 120 (1905).

(2) This is essentially the procedure used by Bruson, THIS JOURNAL, **64**, 2457 (1942), and subsequent papers, to prepare many cyanoethyl ethers.

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RECEIVED AUGUST 15, 1949

Derivatives of Di-(*p*-chlorophenyl)-acetic Acid

Di-(*p*-chlorophenyl)-acetic acid, m. p. 164–166°, was made by the alkaline hydrolysis of DDT.[1]

Methyl Di-(*p*-chlorophenyl)-acetate.—From 16.9 g. (0.06 mole) of di-(*p*-chlorophenyl)-acetic acid, 20 ml. (14.2 g., 0.44 mole) of methanol and 1 ml. of concentrated sulfuric acid reacted at reflux for four hours there was obtained 9 g. (54%) of ester boiling at 208–212° (5–6 mm.). On standing overnight the product crystallized; m. p. 37–39° (see Table I for analysis).

Phenacyl Di-(*p*-chlorophenyl)-acetate.—From 8 g. (0.03 mole) of acid as the salt and 6.23 g. (0.032 mole) of phenacyl bromide reacted in the usual way at reflux for two hours 8.0 g. (71%), m. p. 129–130°, of ester formed.[2] A sample purified by crystallization from benzene melted 132–133°.

Di-(*p*-chlorophenyl)-acetic Anhydride.—A mixture of 20 g. (0.07 mole) of acid and 15.7 g. (0.15 mole) of reagent grade acetic anhydride was refluxed gently for two hours. Distillation at 0.5 mm. gave 2.1 g. at 135–165°, 14.7 g. at 165–195°, 0.2 g. at 195–260° and 2 g. of black residue. Redistillation of the 165–195° fraction gave 11.6 g. at 180–190° (0.5 mm.). Addition of ether precipitated 8.9 g. of yellow solid melting 82–123°. Crystallization from 12 ml. of dry chloroform gave 2.6 g., m. p. 158–163°; a mixed melting point with di-(*p*-chlorophenyl)-acetic acid gave 159–164°. Repeated crystallizations of the chloroform-soluble portion from benzene-petroleum ether (b. p. 60–70°) (1/2 by volume) finally gave 2.6 g. of faintly yellow needles melting 104–105.5°.

Hydrolysis of 0.5 g. of the anhydride by refluxing with 10 ml. of 10% sodium hydroxide solution gave 0.4 g. of di-(*p*-chlorophenyl)-acetic acid, m. p. 163–165°; mixed m. p. 163–165°.

2-(*p*,*p*'-Dichlorobenzhydryl)-benzimidazole.—From 8 g. (0.028 mole) of acid and 3.2 g. (0.03 mole) of freshly crystallized *o*-phenylenediamine reacted in the usual way there was obtained 5.0 g., 50%, melting 246–248°, after crystallization from 1/1 alcohol-benzene.[3]

Di-(*p*-chlorophenyl)-acetyl Chloride.—A mixture of 8 g. (0.029 mole) of acid and 11 g. (0.09 mole) of purified thionyl chloride was refluxed for four hours. Removal of the excess chloride gave 8.5 g. (95%) of a brown oil which decomposed on vacuum distillation at 3–4 mm. Attempted crystallization from petroleum ether (b. p. 60–70°) gave an oil which did not crystallize at 0°. Hydrolysis of 2.0 g. of the acid chloride with ice yielded 1.7 g. of di-(*p*-chlorophenyl)-acetic acid, m. p. 158–162°, mixed melting point, 159–163°.

Di-(*p*-chlorophenyl)-acetamide.—Seven grams (0.023 mole) of the acid chloride and 12 ml. (0.092 mole) of ice cold concentrated ammonium hydroxide gave 5.5 g., (85%) of crude amide melting 136–138° dec. Several crystallizations from 95% ethanol gave a product melting 152–154°.

Di-(*p*-chlorophenyl)-acetanilide.—A mixture of 8 g. (0.03 mole) of the acid chloride, 5.5 g. (0.06 mole) of redistilled aniline and 100 ml. of benzene was refluxed for one-half hour. The benzene layer was decanted from the aniline hydrochloride, washed with water, 5% sodium carbonate solution, 10% hydrochloric acid, and water, and evaporated to give 1.2 g. melting 205–206°. Extraction of the aniline hydrochloride with benzene in a Soxhlet extractor gave 5.8 g., m. p. 203–206°, for a total yield of 7.0 g., 75%. Crystallization from 1/1 benzene-pyridine gave a product melting 205–206°.

Di-(*p*-chlorophenyl)-aceto-4-chloranilide.—Prepared as the acetanilide from 9.5 g. (0.034 mole) of acid chloride, 8.9 g. (0.07 mole) of *p*-chloroaniline and 50 ml. of benzene with two and one-half hours' reflux. The crude product, 9.5 g., 72% melting 220–240° dec. was crystallized from benzene: m. p. 258–260°.

***p*,*p*'-Dichlorobenzhydryl Phenyl Ketone.**—A Friedel-Crafts reaction of 9.4 g. (0.088 mole) of aluminum chloride in 50 ml. of reagent grade benzene with 18.2 g. (0.06 mole) of di-(*p*-chlorophenyl)-acetyl chloride in 100 ml. of benzene at 0–10° for one hour gave 19.5 g. (94%) of crude ketone melting 81–86°. Crystallization from 80 ml. of 95% ethanol gave 14.0 g. (67%), m. p. 90–91°.

Di-(*p*-chlorophenyl)-acetonitrile.—A mixture of 5.0 g. (0.018 mole) of di-(*p*-chlorophenyl)-acetamide and 9.5 g. (0.08 mole) of freshly purified thionyl chloride was refluxed for four hours, cooled, and poured onto 200 g. of ice. After extraction with ether the crude nitrile was vacuum distilled at 2 mm. but decomposition was apparent. Another portion of the ether extract on standing

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(1) Grummitt, Buck and Egan, *Org. Syn.*, **26**, 21 (1946).

(2) Shriner and Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley & Sons, New York, N. Y., 1948, p. 157.

(3) Pool, Harwood and Ralston, THIS JOURNAL, **59**, 178 (1937).

TABLE I

DI-(*p*-CHLOROPHENYL)-ACETIC ACID DERIVATIVES

	Compound	M. p., °C.[c,d]	Formula	Chlorine, %		Nitrogen, %		Mol. wt.	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
1	Methyl di-(*p*-chlorophenyl)-acetate	37–39	$C_{15}H_{12}Cl_2O$	24.6	24.2			295	295[f]
2	Phenacyl di-(*p*-chlorophenyl)-acetate	132–133	$C_{22}H_{16}Cl_2O_3$	17.8	17.9			399	378[e]
3	Di-(*p*-chlorophenyl)-acetic anhydride	104–105.5	$C_{28}H_{18}Cl_4O_3$	26.1	26.3			544	548[g]
4	2-(*p*,*p*′-Dichlorobenzhydryl)-benzimidazole	246–248	$C_{20}H_{13}Cl_2N_2$	20.1	19.4	7.95	7.81		
5	Di-(*p*-chlorophenyl)-acetyl chloride	Oil	$C_{14}H_9Cl_3O$	35.4	34.9				
6	Di-(*p*-chlorophenyl)-acetamide	152–154	$C_{14}H_{11}Cl_2NO$	25.3	25.0	5.00	4.60		
7	Di-(*p*-chlorophenyl)-acetanilide[a]	205–206	$C_{20}H_{15}Cl_2NO$	19.9	19.9	3.93	4.03		
8	Di-(*p*-chlorophenyl)-aceto-4-chloroanilide	258–260	$C_{20}H_{14}Cl_3NO$	27.2	27.3	3.59	3.65		
9	*p*,*p*′-Dichlorobenzhydryl phenyl ketone	90–91	$C_{20}H_{14}Cl_2O$	20.9	20.9			341	353[h]
10	Di-(*p*-chlorophenyl)-acetonitrile[b]	85–86	$C_{14}H_9Cl_2N$	27.1	25.8	5.34	5.62		

[a] Described by Gatzi and Stammbach, *Helv. Chim. Acta*, **29**, 563 (1946), as melting 202–204° in a paper published after our synthesis had been done. [b] Despite the sharp m. p., analysis shows that this compound is not pure. [c] These m. p.'s are uncorrected. [d] The m. p.'s of the corresponding diphenylacetic acid (m. p. 148–149°) derivatives were taken from the literature for comparison; they are 1, 60°; 3, 98°; 5, 56–57°; 6, 167–168°; 7, 180–181°; 9, 136–137°. In these examples the diphenylacetic acid derivatives frequently are higher melting. [e] Saponification values of this ester ran 75–100% over the calculated, probably as the result of a secondary reaction of phenacyl alcohol with alkali. Boiling point rise molecular weights in benzene gave high values, indicative of association. This value was found by the Rast camphor method. [f] By saponification equivalent. [g] By neutral equivalent. [h] By b. p. rise in benzene.

partially crystallized to give 1.5 g. of solid melting 83–85°. Crystallization from 10 ml. of 95% ethanol gave 1.0 g. (18%) melting 85–86°. Despite the sharp melting point, analysis indicated an impure compound.

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RECEIVED AUGUST 15, 1949

COMMUNICATIONS TO THE EDITOR

GEOMETRIC ISOMERS OF 1-PHENYL-1,3-BUTADIENE

Sir:

1-Phenyl-1,3-butadiene made by the hydrolysis of the cinnamaldehyde–methylmagnesium bromide addition compound in 30% sulfuric acid[1] has been shown to be the pure *trans* isomer by its quantitative Diels–Alder reaction with maleic anhydride.[2] Varying the conditions of hydrolysis does not, as previously reported,[3] give the *cis* and *trans* forms but only the *trans* is obtained.

cis-1-Phenyl-1,3-butadiene has been made by ultraviolet irradiation of the *trans* isomer. The *cis* compound does not react with maleic anhydride at room temperature. Irradiation of the *cis* compound isomerizes it partially to the *trans*. The two isomers differ markedly in physical properties:

	Dist. temp., °C.	Mm.	F. p., °C.	d^{25}_4	n^{25}_D	Molar ref.[a]
cis	71	11	-56.99 ± 0.04	0.9197	1.5822	47.25
trans	83	11	$4.52 \pm .04$	.9232	1.6089	48.82

[a] The molar refraction calculated from the Lorentz–Lorenz equation is 43.85.

The boiling point, density and refractive index are usually greater for the *cis* form of olefinic hydrocarbons. This is also true of piperylene.[2] The exceptional behavior of the phenylbutadienes is noteworthy.

In ultraviolet absorption spectra the *cis* form shows a maximum at 265–269 mμ, molar extinction 184×10^2, and the *trans* at 280 mμ, molar extinction 298×10^2. An outstanding difference in infrared absorption spectra is the 14.20-μ band for the *cis* and the 10.56-μ band for the *trans* which are unique for each isomer.

Neither geometric isomer adds sulfur dioxide to give a cyclic sulfone.

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RECEIVED OCTOBER 13, 1949

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(1) Grummitt and Becker, THIS JOURNAL, **70**, 149 (1948).

(2) Robey, Morrell and Wiese, *ibid.*, **63**, 627 (1941) and Craig, *ibid.*, **65**, 1006 (1943) differentiated *cis* and *trans* piperylenes by the greater reactivity of the *trans* isomer to maleic anhydride.

(3) Muskat and Herrman, *ibid.*, **53**, 252 (1931).