TABLE I

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

	Compound	M. p., °C.[c,d]	Formula	Chlorine, % Calcd.	Chlorine, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Mol. wt. Calcd.	Mol. wt. 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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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 ± .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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(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).