[CONTRIBUTION FROM THE CHARLES EDWARD COATES CHEMISTRY LABORATORY, LOUISIANA STATE UNIVERSITY]

1,*n*-Alkyl-cyclopentanols and their Derivatives[1,2]

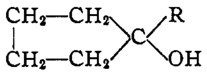
BY C. R. MCLELLAN[3] AND W. R. EDWARDS, JR.

As a series, the 1,*n*-alkyl-cyclopentanols have not previously received comprehensive study. Different authors[4] have reported the preparations of the first seven members of the series; but most of these have been characterized incompletely. Existing data concerning their physical properties were not obtained under uniform conditions; some contradictions appear in them; and few derivatives have been made from these alcohols, either for identification purposes or with a view toward their possible practical value. The peculiar structures of these compounds, in which the cyclopentyl ring fills the dual role taken by two distinct radicals in most tertiary alcohols, make prediction of their properties by analogy unreliable. The purposes of the present work were to prepare a number of these alcohols; to characterize them more completely and uniformly; to compare some of their properties with the corresponding properties of other relevant series; and to prepare and study some of their derivatives.

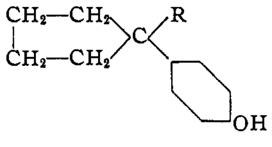
To accomplish these purposes, ten compounds of Type (I) were prepared; those in which R contained 1, 2, 3, 4, 6, 7, 8, 10, 12 and 14 carbon atoms, respectively. Compounds of Type (II) were prepared from the first seven of these.

Other derivatives prepared from Type (I) included the *p*-nitrobenzoates of five of them and the 3,5-dinitrobenzoates of all ten. Dibromo derivatives were prepared from three compounds of Type (II). With the exception of the first six alcohols of Type (I), these were new compounds.

Type (I)
1,*n*-alkyl-cyclopentanols



Type (II)
p-(1,*n*-alkyl-cyclopentyl)-phenols



Apparently no condensations of phenols with such alicyclic tertiary alcohols have been reported previously, regardless of the size of the alicyclic ring.

The 1,*n*-alkyl-cyclopentanols were prepared by the Grignard reaction from cyclopentanone and the appropriate alkyl bromides. Their purifications presented some difficulty, due chiefly to the formation of alkanes during the syntheses, and to ready dehydration of the products themselves at distillation temperatures. Data serving to characterize the members of this series appear in Tables I and III; properties of crystalline esters are included in Table II. Table IV contains data pertaining to compounds of Type II.

TABLE I

PROPERTIES OF 1,*n*-ALKYL-CYCLOPENTANOLS

Alkyl	B. p., °C., at various *p* in mm. 760[a]	300	100	20	below 10	d^0_4	d^{25}_4	n^{25}_D	M. p., °C.	Analyses,[h] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
CH_3[b]	134	110	81	..	...	..	..	..	36	..	..	..	..
C_2H_5[c]	152.5	125	96.5	74.5	...	0.9354	0.9149	1.4494	−10	73.61	73.25	12.37	12.53
C_3H_7[d]	173.5	143.5	115	83	71(8.5)	.9222	.9040	1.4502	−37.5	74.92	74.49	12.59	12.83
C_4H_9[e]	193	163	133	99	86(9)	.9144	.8957	1.4535	..	75.98	75.82	12.76	12.76
C_6H_{13}[f]	235.5	200.5	166.5[i]	124	114(9)	.9082	.8903	1.4562	..	77.57	77.63	13.03	13.14
C_7H_{15}[g]	250.5[j]	221	179.5[i]	136.5	122(9)	.9075	.8890	1.4568	..	78.18	78.09	13.13	13.16
C_8H_{17}	267.5[j]	233	198	151.5[i]	135.5(9)	.8989	.8810	1.4581	−17.5	78.70	78.49	13.23	13.20
$C_{10}H_{21}$	...	..	...	...	133(7)[i]	.8906	.8728	1.4590	−18	79.56	78.84	13.37	13.34
$C_{12}H_{25}$	...	..	...	...	142.5(3)[j]	...	.8626	1.4574	2	80.23	79.91	13.48	13.52
$C_{14}H_{29}$	...	..	...	...	164.5(2)[j]	...	.8556	1.4570	16.2	80.76	80.80	13.57	13.59

[a] Interpolated values. [b] B. p. 135° (759 mm.), m. p. 35–37° (ref. 4). [c] B. p. 154.5–155.2°, d^{15}_4 0.9225, $n^{11.5}_D$ 1.4578 (ref. 4). [d] B. p. 175.2–175.7°, d^{20}_4 0.9044, d^{15}_4 0.9083, n^{20}_D 1.4540 (ref. 4). [e] B. p. 195.4–195.9°, $d^{19.6}_4$ 0.8989, $n^{19.15}_D$ 1.4562 (ref. 4). [f] B. p. 85–86° (4 mm.) (ref. 4); d^{20}_4 0.8921 by Plate and 0.9019 by Zelinsky and co-workers; n^{20}_D 1.4600 by Plate and 1.4629 by Zelinsky and co-workers. [g] B. p. 91–92° (3 mm.), d^{20}_4 0.8817, n^{20}_D 1.4604 (ref. 4). [h] Analyses are the averages of duplicate determinations. [i] First slight visible evidence of decomposition. [j] Pronounced decomposition.

TABLE II

ESTERS OF 1,*n*-ALKYL-CYCLOPENTANOLS

Alkyl	*p*-Nitrobenzoates M. p., °C.[a]	% N Calcd.	% N Found	3,5-Dinitrobenzoates M. p., °C.[a]	% N Calcd.	% N Found
CH_3	83	5.62	5.54	115.5	9.52	9.02
C_2H_5	52.5	5.32	5.58	108.3	9.09	8.90
C_3H_7	59.5	5.05	5.21	82	8.69	8.66
C_4H_9	31	4.81	5.49	75.3	8.33	7.80
C_6H_{13}	...	...	...	86.5	7.69	7.92
C_7H_{15}	26	4.20	4.69	76.8	7.40	8.05
C_8H_{17}	...	...	...	77	7.14	7.35
$C_{10}H_{21}$	...	...	...	78	6.66	6.78
$C_{12}H_{25}$	...	...	...	81.3	6.25	6.48
$C_{14}H_{29}$	...	...	...	81.5	5.88	6.18

[a] Melting points listed are mean values of melting ranges of 1° or less.

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(1) Taken from Ph.D. dissertation of C. R. McLellan, Louisiana State University, May, 1941.

(2) Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1941.

(3) Ethyl Gasoline Corporation Fellow.

(4) Zelinsky and co-workers, *Ber.*, **35**, 2683 (1902); **66B**, 1422 (1933); Chavanne and Becker, *Bull. soc. chim. belg.*, **36**, 591 (1927); Plate, *Compt. rend. Acad. Sci. U. R. S. S.*, **24**, 257 (1939)

Table III

Parachors of 1,n-Alkyl-cyclopentanols

Alkyl	d^{25}_4	d^{50}_4	Surface tension at 25°	Surface tension at 50°	Parachor at 25°	Parachor at 50°
CH_3	...	0.8935	...	26.45	...	254.2
C_2H_5	0.9148	.8930	30.05	27.40	292.2	292.5
C_3H_7	.9041	.8805	29.17	26.76	330.5	331.1

Data in this table were obtained by Katherine Owen and O. R. Quayle, of Emory University, in friendly coöperation.

Table IV

Properties of p-(1,n-Alkyl-cyclopentyl)-phenols

Alkyl	B. p., °C. (mm.)[a]	M. p., °C.[b]	M. p., °C.,[b] 2,6-dibromo deriv.	Analyses,[c] equiv. Br abs. per mole phenol	Bacteriostatic power,[d] zone of inhib., mm. *Staph. aureus*
CH_3		95.5	...	3.99, 3.93	5.0
C_2H_5	137(2.5)	96.3	97	4.07, 4.05	6.0
C_3H_7	135(1.0)	67.5	104.5	3.90, 3.95[e]	5.0
C_4H_9	151(2.0)	57.5	69	3.92, 3.96	5.0
C_6H_{13}	163(2.1)	61.8	...	4.04, 4.00	0
C_7H_{15}	174.5(2.5)	53.3	...	4.06, 4.03	0
C_8H_{17}		42.8	...	.. ..[f]	0

[a] Boiling points given are mean values of 2° boiling ranges or less. [b] Melting points given are mean values of melting ranges of 1° or less. [c] Analysis by reaction with bromine to give the 2,6-dibromo derivative. Theoretical value, 4.00. [d] Bacteriostatic powers determined by Agar Cup-plate test, by W. C. Harden and associates, Hynson, Westcott and Dunning, Inc., Baltimore, Md., in friendly coöperation. Control: no. 390 (3,5-dibromo-hydroxy-benzyl-phenol): 3.0 mm. All compounds, including control, gave negative results with *E. coli*. [e] *Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.29; H, 9.87. Found: C, 82.73; H, 9.82. [f] *Anal.* Calcd. for $C_{18}H_{30}O$: C, 83.14; H, 11.03. Found: C, 82.51; H, 11.16.

In Fig. 1, the boiling points of the 1,n-alkyl-cyclopentanols are plotted against their molecular weights, along with the boiling points of compounds of several other series. Between the curve for the 1,n-alkyl-cyclopentanols and the one given by a series of non-cyclic tertiary alcohols, there is a relationship approximately similar to the relationship between the curves for n-alkylcyclopentanes, and for n-alkanes, respectively. The quantitative difference produced by the ring is slightly greater in the case of the alcohols. The difference in boiling point which may be ascribed to the presence of a cyclopentyl ring is seen (by reference to curves A, B and E) to be small compared to the difference between primary and tertiary alcohols of non-cyclic type.

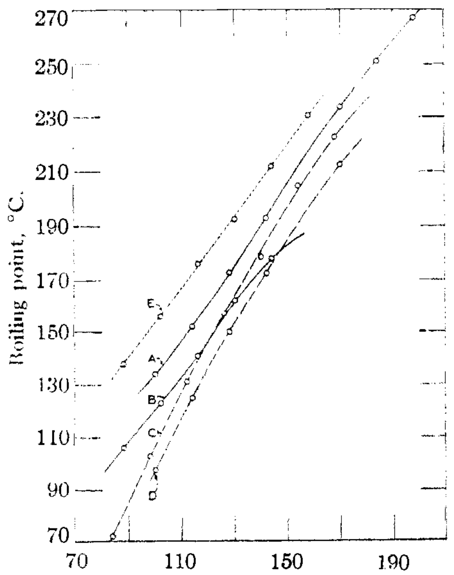

Fig. 1.—A, 1,N-Alkyl-cyclopentanols; B, N-alkyl-dimethylcarbinols; C, N-alkyl-cyclopentanes; D, N-alkanes; E, normal primary alcohols.

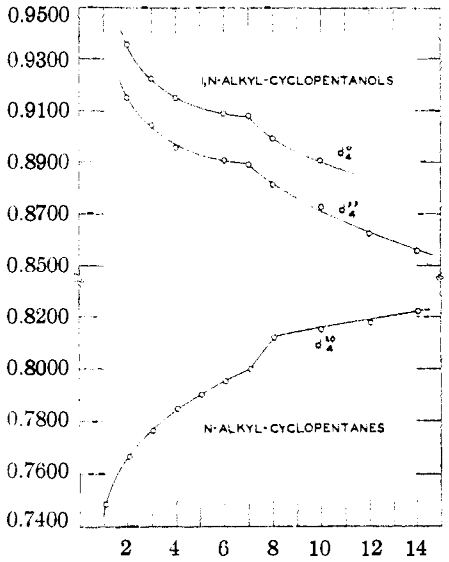

Fig. 2.

Figure 2 shows a remarkable break at the heptyl in the curve given by the densities. The densities of the n-alkylcyclopentanes taken from the literature[4,5] show a similar break in the same region. This appears to be due to the relationship between the sizes of the alkyl groups and of the cyclopentyl ring, and to the distinct difference in their configurations, a difference which includes the relative elasticity of the alkyl groups as compared to the rigidity of a five-membered ring. When the alkyl group is small, the cyclopentyl group is dominant, in the sense that it presents the chief obstacle to closer packing of the molecules; therefore it is chiefly responsible for the molecular volume. The curve from the methyl to the heptyl compound reflects this condition. At the point where the alkyl group has so increased in size as to become the dominant group, the situation changes sharply. Above this point, the alkyl-cyclopentanols constitute what is actually a different series as far as densities are concerned. An abrupt change in the slope of the density curve

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(5) Schmidt and Gemassmer, *Ber.*, **73**, 359 (1940). The value for the density of n-hexylcyclopentane was taken from Plate (ref. 4). Use of the much lower value reported at an earlier date by Zelinski (ref. 4) would have caused the break to appear at this point rather than at the heptyl.

results, at the point at which dominance shifts from one group to the other.

An analogous series of *n*-alkyl-cyclohexanols is now being investigated, to determine whether or not they exhibit the same phenomenon.

Condensation of 1,*n*-alkyl-cyclopentanols with phenol to form *p*-(1,*n*-alkyl-cyclopentyl)-phenols resulted in somewhat smaller yields than usual for this type of reaction. The octyl compound was never thoroughly purified; and an attempted preparation of the decyl compound was unsuccessful. Tests of the bacteriostatic strengths of these substituted phenols showed the first four to be rather effective toward the Gram-positive *Staphylococcus aureus*, but wholly ineffective toward the Gram-negative *E. coli*. The higher members of the series were ineffective toward both organisms.

Experimental

Cyclopentanone.—Cyclopentanone was prepared from adipic acid[6] by the method of Thorpe and Kon,[7] and purified by the modification of Wagner.[8]

1,*n*-Alkyl-cyclopentanols.—These compounds were prepared from cyclopentanone and the appropriate alkylmagnesium bromides, by the method of Zelinsky and Namjetkin.[4] All but the lauryl and myristyl compounds were purified by repeated fractional distillations, at pressures ranging from atmospheric to 1 mm. All were colorless liquids, except the methyl compound which was a crystalline solid, and the lauryl which possessed a faint yellow color. They had peppermint-like odors. The methyl compound was slightly soluble in water; this solubility diminished regularly with increase in size of the alkyl group. They were all soluble in the usual organic solvents; yields were 50% for the methyl, 35–40% for ethyl through decyl, and 20% for lauryl and myristyl.

The 1,*n*-heptyl-cyclopentanol presented a special problem, since the tetradecane formed during its synthesis boils very close to the alcohol at all pressures between a few millimeters and one atmosphere. Consequently, although the crude alcohol was redistilled several times until an almost constant-boiling product was obtained, it seems unlikely that this impurity was eliminated completely.[9]

Purification of 1,*n*-Lauryl-cyclopentanol-1 and 1,*n*-Myristylcyclopentanol-1.—As these compounds decomposed on distillation even at 1 mm., they were purified by recrystallization at low temperatures. At the conclusion of the preparation by the Grignard reaction, the ethereal extract containing crude 1,*n*-lauryl-cyclopentanol-1 was washed with water and dried; the ether was then removed by evaporation on a steam-bath, gradually reducing the pressure to 4 mm. The oily residue was dissolved in three times its volume of 95% ethanol and chilled in an ice–salt-bath. Solid impurities consisting chiefly of tetracosane precipitated, and were removed by filtration. The filtrate was concentrated on a steam-bath, at a pressure of 2.5 mm. The oily residue was dissolved in an equal volume of anhydrous ether, and chilled in dry-ice. Crystals of the product precipitated. These were filtered on a Buchner funnel packed with dry-ice, washed once with ether previously chilled, and quickly transferred to a suitable container. Upon reaching room temperature, these crystals melted, forming an oily liquid with a faint yellow color; this was taken to be 1,*n*-lauryl-cyclopentanol-1. Further recrystallizations yielded a smaller amount of product having the same physical characteristics. Minor differences in details were observed in purifying the myristyl compound.

1,*n*-Alkyl-cyclopentyl-*p*-nitrobenzoates and -3,5-dinitrobenzoates.—These esters were prepared from the 1,*n*-alkyl-cyclopentanols by the method of Conn, Collett and Lazzell,[10] allowing several days for each reaction. They were recrystallized from ether, or petroleum ether, or a mixture of the two.

***p*-(1,*n*-Alkyl-cyclopentyl)-phenols.**—These were prepared by condensation of the 1,*n*-alkyl-cyclopentanols with phenol, employing two different methods; that of Huston and Hedrick,[11] and that of Welsh and Drake,[12] a method which had given particularly good yields with certain tertiary alcohols containing aromatic rings. In the present work, however, there was little to choose between results of the two methods. The products were purified by fractional distillation at reduced pressures, followed by recrystallization from petroleum ether; the methyl member of the series was purified solely by successive recrystallizations; yields ranged from 27 to 39%.

For analytical purposes, the *p*-(1,*n*-alkyl-cyclopentyl)-phenols were titrated with 0.13 *N* potassium bromide–potassium bromate solution, using the method of Francis and Hill.[13]

The *p*-(1,*n*-alkyl-cyclopentyl)-phenols were colorless crystalline solids, possessing faint phenolic odors. They were soluble in most of the ordinary organic solvents, the solubility in petroleum ether increasing appreciably with increase in the size of the alkyl group. The methyl member of the series was slightly soluble in water; water solubility decreased with increase in the size of the alkyl group.

2,6-Dibromo-4-(1,*n*-alkyl-cyclopentyl)-phenols.—The *p*-(1,*n*-alkyl-cyclopentyl)-phenols were dissolved in chloroform or ligroin, and the calculated amount of a dilute solution of bromine in the same solvent added. Reaction was practically instantaneous. The solvent was removed by evaporation on a steam-bath, and the products recrystallized from ethanol–water mixtures.

Determination of Boiling Points of 1,*n*-Alkyl-cyclopentanols.—These were determined with a modified Cottrell boiling point apparatus,[14] which is drawn to scale in Fig. 3. The diameter of the tube was 3 cm. Quantities as small as 3 cc. gave satisfactory results. Short-stemmed Allihn thermometers were used. Boiling points were determined at five pressures, except when prevented by (a) thermal decomposition of the three highest alcohols; or (b) difficulty in condensing the two lowest ones at very low pressures.

Determination of Melting Points.—Melting points of the 1,*n*-alkyl-cyclopentanols were determined by the method of cooling curves, readings being taken every thirty seconds. Tubes containing the samples undergoing such treatment were separated from the cooling baths by an air jacket, so that slow and uniform cooling was achieved. The methyl member of the series was an exception; its melting point was determined in the usual way, as were the melting points of the various esters and phenols.

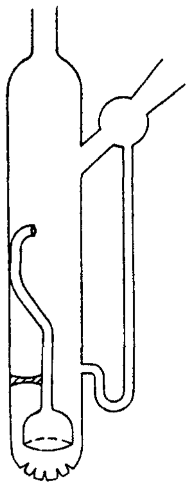

Fig. 3.—Boiling point apparatus.

Acknowledgment.—The authors thank Dr. E. Emmet Reid for his interest in the problem, and

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[6] The authors are indebted to Dr. C. D. Graves, Du Pont Experimental Station, Wilmington, Del., for a supply of adipic acid.

[7] Thorpe and Kon, "Organic Syntheses," Vol. V, John Wiley and Sons, New York, N. Y., pp. 37-39.

[8] Wagner, *J. Chem. Ed.*, **10**, 115 (1933).

[9] Plate's recent preparation of this compound (ref. 4) is subject to the same criticism, since it was purified in a similar manner. His analysis showed the carbon and hydrogen contents of his product to be high.

[10] Conn, Collett and Lazzell, THIS JOURNAL, **54**, 4370 (1932).

[11] Huston and Hedrick, *ibid.*, **59**, 2001 (1937).

[12] Welsh and Drake, *ibid.*, **60**, 59 (1938).

[13] Francis and Hill, *ibid.*, **46**, 2498 (1924).

[14] Cottrell, *ibid.*, **41**, 721 (1919). The modified tube was designed by A. R. Choppin, and constructed by E. L. Compere.

for the gift of most of the alcohols from which the bromides were prepared.

Summary

1. The 1,*n*-alkyl-cyclopentanols have been characterized as a series, through the preparation and study of four new members, together with a more complete and uniform study of six previously prepared members.

2. Some of the data thus obtained have been plotted, and compared with similar curves representing other relevant series. The unusual form of the density curves has been discussed.

3. Esters of *p*-nitrobenzoic acid have been prepared from five of these alcohols, and esters of 3,5-dinitrobenzoic acid have been prepared from all ten, and the melting points of these esters have been determined.

4. Seven *p*-(1,*n*-alkyl-cyclopentyl)-phenols have been prepared by condensation of these alcohols with phenol, and characterized. Their bacteriostatic strengths have been determined. Four of them were found to be effective toward *Staph. aureus.*

5. Three 2,6-dibromo-4-(1,*n*-alkyl-cyclopentyl)-phenols have been prepared, and their melting points determined.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Coupling of α,β-Unsaturated Compounds with Diazonium Salts[1]

BY C. F. KOELSCH AND VIRGIL BOEKELHEIDE

In a previous paper[2] it was shown that the reaction between acrylonitrile and diazonium chlorides in buffered solutions and in the presence of cupric chloride led to the formation of α-chlorohydrocinnamonitriles. Since Meerwein, Buchner and van Emster[3] had considered that in similar reactions the aryl group always became attached to the α-carbon of β-substituted α,β-unsaturated compounds, it was believed that an explanation of the anomalous results with acrylonitrile might involve steric hindrance. This belief is now shown to be without foundation, for the behavior of acrylonitrile is not anomalous. Also some of the structures advanced by the earlier investigators are now shown to be incorrect, and a new reaction mechanism is proposed.

The experimental results of the present investigation will first be summarized.

(a) Methyl crotonate and 2,4-dichlorobenzenediazonium chloride yielded methyl α-chloro-β-(2,4-dichlorophenyl)-butyrate.[4] Similarly ethyl crotonate and benzene- (and *p*-chlorobenzene-) diazonium chloride yielded ethyl α-chloro-β-phenyl- (and *p*-chlorophenyl-) butyrate.

(b) Crotonic acid and *p*-nitrobenzenediazonium chloride gave α-chloro-β-(*p*-nitrophenyl)-butyric acid.[5]

(c) Methyl cinnamate and *p*-chlorobenzenediazonium chloride yielded methyl β-chloro-α-(*p*-chlorophenyl)-hydrocinnamate.[6]

(d) Cinnamalacetic acid and benzenediazonium chloride gave 1,4-diphenylbutadiene.

(e) Methyl cinnamalacetate and benzene- (and *p*-chlorobenzene-) diazonium chloride gave methyl α-phenyl- (and *p*-chlorophenyl)-cinnamalacetate.

(f) Sorbic acid and benzenediazonium chloride gave 1-phenylpentadiene-1,3.

It is clearly seen that the volume occupied by the group on the β-carbon atom of the unsaturated compound is not a factor in determining the point of entry of the aryl group. A methyl group occupies at least as large a portion of the space in the immediate vicinity of the β-carbon atom as does a vinyl group, yet crotonic acid and its derivatives undergo β-coupling, whereas α-coupling takes place with the vinyl compounds listed in paragraphs d, e and f.

The following mechanism appears to account for the products obtained.

$$\begin{aligned}
&C_6H_5N_2^+ + CH_3COO^- \rightleftarrows C_6H_5N{=}NOCOCH_3 \longrightarrow \\
&\qquad C_6H_5\cdot + N_2 + CH_3COO\cdot && (1)\\
&C_6H_5\cdot + RCH{=}CHR' \longrightarrow C_6H_5CHR{-}C^{\cdot}HR' \text{ (I)} && (2)\\
&\text{(I)} + Cu^{++} \longrightarrow Cu^+ + C_6H_5CHR{-}C^+HR' \text{ (II)} && (3)\\
&Cu^+ + CH_3COO\cdot \longrightarrow Cu^{++} + CH_3COO^- && (3a)\\
&\text{(II)} + Cl^- \longrightarrow C_6H_5CHR{-}CHClR' && (4)\\
&\text{(II)} \longrightarrow H^+ + C_6H_5CR{=}CHR' && (4a)
\end{aligned}$$

Equation 1 shows the function of the buffer; the diazonium salt cannot, but the homopolar diazoacetate can decompose easily into a free phenyl radical.[7] Equation 2 represents the "electron pairing"[8] attack of the free radical on the unsaturated compound. The structure of I is determined by considerations analogous to those advanced by Mayo and Walling[9] to account for the orientations observed in Kharasch's peroxide

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[1] From the Ph. D. Thesis of Virgil Boekelheide, September, 1943.

[2] Koelsch, THIS JOURNAL, **65**, 57 (1943).

[3] Meerwein, Buchner and van Emster, *J. prakt. Chem.*, **152**, 237 (1939).

[4] Meerwein, Buchner and van Emster believed that this compound was methyl β-chloro-α-(2,4-dichlorophenyl)-butyrate.

[5] Meerwein, Buchner and van Emster reported that this compound was β-chloro-α-(*p*-nitrophenyl)-butyric acid.

[6] The structure of this product was reported correctly by Meerwein, Buchner and van Emster.

[7] Hey, *Ann. Rep. Chem. Soc.*, **37**, 280 (1940).

[8] Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 259.

[9] Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).