

allowed to stand overnight and distilled giving a near quantitative recovery of benzyl mercaptan-S-*t*, b.p. 197.1–198.8° (271,000 d.p.m./mmole).

**Decarboxylation of 3-Phenylpropionaldehyde in the Presence of Benzyl Mercaptan-S-*t* and *n*-Propylbenzene.**—In a flask were placed freshly distilled Eastman 3-phenylpropionaldehyde (35.0 g., 0.261 mole, b.p. 101.5–102.4° at 13 mm.), *o*-dichlorobenzene (224 ml., b.p. 180–181°) *n*-propylbenzene (16.0 g., 0.133 mole, b.p. 158.8–159.3°), di-*t*-butyl peroxide (4.1 g., 0.028 mole) and benzyl mercaptan-S-*t* (3.0 g., 0.024 mole) making a one molar solution of the aldehyde. The aldehyde was decomposed (140–155°) until 26.4% of the theoretical amount of carbon monoxide had been liberated, after which 18.0 g. of active ethylbenzene was added to ensure that there would be enough for purification and subsequent degradation. Using the procedure above, ethylbenzene-*t* (16.2 g., 64.6%), b.p. 136.4–136.8°, and the *n*-propylbenzene (9.8 g., 61.3% recovery), b.p. 159.3–159.5°, were obtained after distilling twice. Gas chromatography analysis showed the ethylbenzene-*t* was 99.8% pure and that the *n*-propylbenzene was 99.9% pure. The tritium activities of these samples were measured and are given in Table II.

**Bromination of Ethylbenzene-*t*.**—The light (ultraviolet)-catalyzed bromination of ethylbenzene-*t* (11.5025 g., 0.1084 mole; resulting from the decarbonylation above) in the  $\alpha$ -position was carried out at reflux temperature in carbon tetrachloride (130 ml.) with a stoichiometric amount of *N*-bromosuccinimide (19.5750 g., 0.1084 gram atom of active bromine as determined by iodometric analysis; freshly re-

crystallized from boiling water and dried over phosphorus pentoxide). The succinimide produced was collected by filtration, repeatedly washed with cold carbon tetrachloride and recrystallized twice from hot toluene. Before the tritium activity was measured, the succinimide was shown to contain no bromine.

**Radioactivity Measurements.**<sup>23</sup>—The C<sup>14</sup> and H<sup>3</sup> activities of the compounds were determined by the liquid scintillation method<sup>24,25</sup> employing toluene as the organic solvent for all the compounds except succinimide which was dissolved in a solvent consisting of equal amounts of 1,4-dioxane and toluene. In general, counting efficiencies were about 75% for C<sup>14</sup> and 25% for H<sup>3</sup>. All net counting rates were converted to disintegrations per minute (d.p.m.) by measurement of the exact counting efficiencies with calibrated H<sup>3</sup> and C<sup>14</sup> solutions.

**Acknowledgment.**—The author wishes to thank Drs. V. P. Guinn, J. H. Raley and M. M. Wald for valuable discussions during the course of this work. Dr. V. P. Guinn also furnished the radioactivity measurements.

(23) All of the radioactivity measurements were carried out by Dr. V. P. Guinn of the Shell Development Co.

(24) V. P. Guinn, paper presented at Northwestern University Conference on Liquid Scintillation Counting, August, 1957, in press, Pergamon Press.

(25) C. D. Wagner and V. P. Guinn, *Nucleonics*, **13** (10), 56 (1955). EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

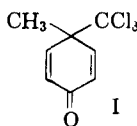
## A New Synthesis of 3,4-Dichlorocoumarins<sup>1</sup>

BY MELVIN S. NEWMAN AND SIDNEY SCHIFF

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A new synthesis of 3,4-dichlorocoumarins, which involves the aluminum chloride-catalyzed reaction of perchloropropylene with phenols, is described. The 4-chloro group in these coumarins is reactive and easily displaced by several nucleophilic reagents.

The reaction of *p*-cresol with carbon tetrachloride under the influence of aluminum chloride affords 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (I).<sup>2,3</sup>



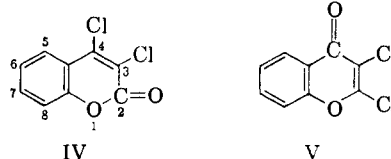
In seeking to extend the generality of this reaction, the condensations of cresol with benzotrichloride<sup>4</sup> and substituted benzotrichlorides<sup>5</sup> were studied. Although these reactions led to the formation of several new substances, no compounds analogous to I were isolated.

We now show that the condensation of *p*-cresol and of other phenols with hexachloropropene in the presence of aluminum chloride yields 3,4-dichlorocoumarins. The scope and limitations of this new reaction as well as the reactions of the 3,4-dichlorocoumarins form the subject matter of this paper.

In our first experiments, hexachloropropylene was allowed to react with the salt formed by

treating *p*-cresol with aluminum chloride in carbon disulfide. After hydrolysis a solid was isolated from which a colorless compound, C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>Cl<sub>2</sub>, II, was obtained on vacuum sublimation.<sup>6</sup> On oxidation of II with chromic acid an acid, C<sub>10</sub>H<sub>4</sub>O<sub>4</sub>Cl<sub>2</sub>, III, was obtained. This suggested that a methyl group had been oxidized to a carboxyl.<sup>6</sup> After it was found that hexachloropropene reacted with phenol to give a compound, C<sub>9</sub>H<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>, which appeared analogous to II, all further work was carried out with the compound obtained from phenol.

Two structures were believed likely: 3,4-dichlorocoumarin (IV) and 2,3-dichlorochromone (V).



A decision in favor of structure IV was reached when 3-chloro-4-hydroxycoumarin<sup>7</sup> was converted into a compound identical with ours by treatment with phosphorus oxychloride in pyridine. This conversion was not conclusive by itself as the

(6) This compound was first obtained by A. G. Pinkus who carried out preliminary experiments but did not prove the structure.

(7) F. Arndt, L. Loewe, R. Ün and E. Ayça, *Ber.*, **84**, 319 (1951).

(1) Taken from the Ph.D. Thesis of S. Schiff, O.S.U., 1958.

(2) T. Zincke and R. Suhl, *Ber.*, **39**, 4148 (1906).

(3) M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954).

(4) M. S. Newman and A. G. Pinkus, *ibid.*, **19**, 985 (1954).

(5) M. S. Newman and A. G. Pinkus, *ibid.*, **19**, 996 (1954).

coumarin and chromone ring systems are interconvertible under some conditions.<sup>7</sup> However, the infrared absorption spectrum of our compound had a strong band at 5.76  $\mu$ . Coumarins absorb in the 5.70–5.90  $\mu$  region, whereas chromones absorb at 6.00–6.10  $\mu$ .<sup>8</sup> Coumarin absorbs at 5.78  $\mu$  and a sample of 6-methylchromone<sup>9</sup> at 6.02  $\mu$ .

The new synthesis of 3,4-dichlorocoumarin (IV) constitutes the only known method for the direct synthesis of this type of halogenated coumarin.<sup>10</sup> The only other coumarin syntheses which yield coumarins halogenated in the heterocyclic ring involve the condensation of phenol with a diethyl haloöxaloacetate<sup>11</sup> and cyclization of a halogenated acrylic acid.<sup>12</sup> Other halogenated coumarins have been made by the halogenation of a preformed coumarin.<sup>13</sup> In review of the novelty of this method we have explored its generality. The results are summarized in Table I, although it

TABLE I  
YIELDS OF 3,4-DICHLOROCOUMARINS FROM VARIOUS PHENOLS

Substituent on phenol	Substituted coumarin <sup>a</sup>	Yield, %	Trichloro-acrylate, % <sup>b</sup>
None	None	28	
<i>p</i> -Methyl	6-Methyl	72	
<i>p</i> -Methoxy	6-Methoxy <sup>c</sup>	4	
<i>p</i> -Chloro	6-Chloro	90 <sup>d</sup>	2.4
<i>m</i> -Chloro	7-Chloro <sup>e</sup>	18	
<i>o</i> -Chloro	8-Chloro	1.6	
2,4-Dichloro	6,8-Dichloro	46	18
3,4-Dichloro	6,7-Dichloro <sup>e</sup>	69	
2,4,5-Trichloro			26
3-Methyl-4-chloro	6-Chloro-7-methyl <sup>e</sup>	85	
<i>p</i> -Bromo	6-Bromo	44	

<sup>a</sup> All coumarins had chlorines in the 3- and 4-positions. <sup>b</sup> Substituted phenyl trichloroacrylates. <sup>c</sup> Mainly tar formation in this case. <sup>d</sup> A study of reaction conditions was made in this case; see Experimental. <sup>e</sup> The structure of these compounds is assumed; see text for discussion.

should be realized that the yields reported in most cases do not represent the maximum obtainable. The most extensive study of reaction variables was made with *p*-chlorophenol. A yield of 90% of 3,4,6-trichlorocoumarin was obtainable in this case. In general the yields of 3,4-dichlorocoumarins are good when a methyl or a chlorine is in the *p*-position to the phenolic group. However,

(8) E. Knoblock and F. Prochazka, *Chem. Listy*, **9**, 1285 (1953).

(9) Prepared from 2-hydroxy-5-methylacetophenone and ethyl formate by the method of R. Mozingo, *Org. Syntheses*, **21**, 42 (1941).

(10) Previous syntheses of coumarins are reviewed by S. M. Sethna and N. M. Shah, *Chem. Revs.*, **36**, 1 (1945), and by R. C. Elderfield, "Heterocyclic Compounds," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 173–216.

(11) E. H. Huntress and R. T. Olsen, *THIS JOURNAL*, **70**, 2831 (1948). About 15% yields of ethyl 3-chloro- and 3-bromocoumarin-4-carboxylates were obtained.

(12) R. Adams and R. S. Ludington, *ibid.*, **67**, 794 (1945). A 4-iodocoumarin derivative was obtained in unstated yield.

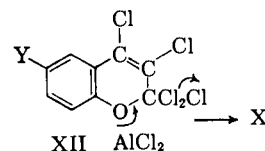
(13) For example see W. H. Perkin, *Ann.*, **187**, 115 (1871); D. Molho and C. Mentzer, *Compt. rend.*, **223**, 1141 (1946); W. C. Stoesser and E. H. Sommerfeld, U. S. Patent, 2,562,873 (1951); J. C. Heath, S. Z. Cardon and H. S. Halbedel, U. S. Patent, 2,466,657 (1949); H. S. Halbedel and J. C. Heath, U. S. Patent, 2,478,824 (1949); H. R. Eisenhauer and K. P. Link, *THIS JOURNAL*, **76**, 1647 (1954); C. Mentzer and P. Meunier, *Compt. rend.*, **225**, 1329 (1947), also *Bull. soc. chim.*, **10**, 356 (1943); R. Anschütz, *Ann.*, **367**, 169, 253 (1909); D. P. Spalding, H. S. Mosher and F. C. Whitmore, *THIS JOURNAL*, **72**, 5338 (1950).

with 2,4-dichlorophenol the yield is decreased because of the formation of an intermediate which gives 2,4-dichlorophenyl trichloroacrylate on hydrolysis. In the case of 2,4,5-trichlorophenol, the only crystalline product isolated was 2,4,5-trichlorophenyl trichloroacrylate (26% yield). Single unsuccessful attempts to effect condensation with hexachloropropene were carried out with these various phenols: *p*-nitrophenol, 4-chloro-2-nitrophenol, resorcinol,  $\beta$ -naphthol; *p*-phenylphenol (in these five cases the phenols were recovered in good yield);  $\alpha$ -naphthol, *o*-phenylphenol, *m*-methoxyphenol, 1,4-dichloro-2-naphthol, 1-chloro-2-naphthol and *p-t*-butylphenol (44% yield of IV obtained, the *t*-butyl group being lost).

The structures of 3,4,7-trichloro-, 3,4,6,7-tetrachloro- and 3,4,6-trichloro-7-methylcoumarins were not proved. Rather it was assumed that ring closure occurred to give these structures since *m*-chlorophenol yields 4-chloro-2-hydroxybenzenesulfonic acid,<sup>14</sup> 3,4-dichlorophenol yields 4,5-dichloro-2-hydroxybenzenesulfonic acid,<sup>15</sup> and 4-chloro-3-methylphenol yields 5-chloro-2-hydroxy-4-methylbenzenesulfonic acid<sup>16</sup> on sulfonation.

Possible mechanisms for the aluminum chloride-catalyzed reactions of phenolic compounds with polyhalogenated substances have been presented.<sup>3,4</sup> The formation of 3,4-dichlorocoumarins can be accommodated within the framework of these mechanisms, as shown below.

In the general case, the phenol VI reacts with one equivalent of aluminum chloride to yield the salt VII which can react at the oxygen or at the *o*- or *p*-positions in the nucleus. We believe the reactions leading to 3,4-dichlorocoumarin formation occur by a nucleophilic displacement of a chlorine of the trichloromethyl group on perchloropropylene by the anion of the salt VII (reacting at an *o*-carbon) to yield the cyclohexadienone intermediate VIII.<sup>17</sup> The latter reacts with aluminum chloride to form a new salt, IX, and hydrogen chloride. This salt IX then cyclizes to the complex X by an intramolecular SN2' reaction.<sup>18</sup>



On hydrolysis with water, X yields the final product XI.

It is possible, but deemed less likely, that the condensation can be effected by nucleophilic displacement of a chlorine of the trichloromethyl group of hexachloropropene by the anion of VII (reacting at the oxygen) to give the pentachloroallyl ether of VI. This ether could then undergo a Claisen rearrangement to form VIII, after which

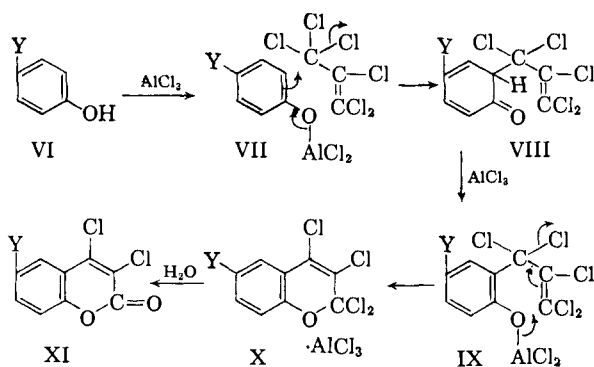
(14) H. H. Hodgson and A. Kershaw, *J. Chem. Soc.*, 1419 (1930).

(15) W. F. Beech, *ibid.*, 212 (1948).

(16) R. F. von Walther and K. Demmelmeier, *J. prakt. Chem.*, **92**, 107 (1915).

(17) Alternately, the intermediate VIII could be formed by an SN2' reaction of the anion of VII (reacting at an *o*-carbon) on the terminal carbon of the double bond of perchloropropylene.

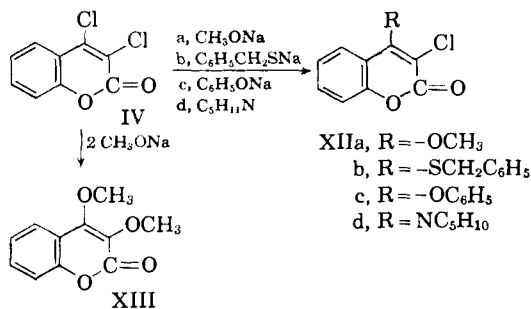
(18) Alternately, the salt IX may undergo an allylic rearrangement to XII which then may cyclize by an intramolecular nucleophilic displacement of a chlorine of the trichloromethyl group.



the reaction would follow the same course described above. In alkylations of phenoxides with allyl chloride, both O- and C-alkylation occurs<sup>19</sup> and the rearrangement of O-alkylated ether to phenol requires heating. However, no pentachloroallyl ethers have been studied and the temperature required to cause these to rearrange to compounds of type VIII is not known. Similarly, the effect of aluminum chloride catalysis on such a rearrangement is unknown.

The isolation of trichloroacrylates of *p*-chlorophenol, 2,4-dichlorophenol and 2,4,5-trichlorophenol (see Table I) indicates that reaction on the oxygen can occur. Furthermore, 2,4-dichlorophenyl trichloroacrylate could be cyclized to 3,4,6,8-tetrachlorocoumarin (5% yield). However, we prefer the mechanism first proposed above for the coumarin synthesis.

When a solution of 3,4-dichlorocoumarin (IV) in methanol containing one equivalent of sodium methoxide was refluxed for 30 minutes, a 90% yield of 3-chloro-4-methoxycoumarin<sup>7</sup> was obtained. The structure was established by comparison with an authentic sample furnished by Professor F. Arndt.<sup>7</sup> When absolute alcoholic solutions of sodium benzylmercaptide and of piperidine were refluxed with 3,4-dichlorocoumarin, excellent yields of 3-chloro-4-benzylmercaptocoumarin and of 3-chloro-4-piperidinocoumarin were obtained. These structures were not proved but assumed because of the structure of 3-chloro-4-methoxycoumarin established as described above. On reaction with sodium phenoxide in phenol, a low yield of 3-chloro-4-phenoxy coumarin was obtained.



When 3,4-dichlorocoumarin was treated with two equivalents of sodium methoxide in methanol a good yield of 3,4-dimethoxycoumarin was ob-

(19) D. S. Tarbell, in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 2.

tained. However, attempts to prepare bis-piperidino and bis-benzylmercapto analogs failed.

4-Methoxy and 4-benzylmercapto-3-chloro-6-methylcoumarins and 3,4-dimethoxy-6-methylcoumarin were prepared in similar ways from 3,4-dichloro-6-methylcoumarin, but no attempts were made to study the reactions of the other 3,4-dichlorocoumarins described in this paper.

### Experimental<sup>20</sup>

**3,4-Dichlorocoumarin Synthesis.**—The general process consisted of adding a solution of 0.03 mole of the phenol in 25 ml. of carbon disulfide dropwise to a slurry of 0.06 mole of aluminum chloride<sup>21</sup> in 25 ml. of carbon disulfide. The mixture was stirred at room temperature until evolution of hydrogen chloride was essentially complete and then 0.03 mole of hexachloropropene,<sup>22</sup> b.p. 75–78° at 7–8 mm., *n*<sub>D</sub><sup>20</sup> 1.5473, was added dropwise during 10 minutes. The color always became dark and the reaction was allowed to continue at room temperature until evolution of hydrogen chloride slowed down or stopped.<sup>23</sup> The solvent then was removed under reduced pressure and the residue hydrolyzed with ice and sulfuric acid. The solids were well washed with dilute acid and water and then were dried under vacuum. Frequently the best procedure for obtaining pure coumarins was to sublime this solid in small portions (about 1 g.) under reduced pressure. The sublimate then was crystallized from alcohol (in the case of 6-methoxy-3,4-dichlorocoumarin, aqueous alcohol was used, and, for 3,4,6,7-tetrachlorocoumarin, Skellysolve C, petroleum ether, b.p. 90–97°). The melting points and analyses of the dichlorocoumarins prepared in this way are listed in Table II.

In some preparations of 3,4-dichlorocoumarins trichloroacrylate esters of the starting phenols were obtained, as described below.

***p*-Chlorophenyl Trichloroacrylate.**—After the carbon disulfide had been removed from the reaction product from *p*-chlorophenol and hexachloropropene as described above and the residue treated with dilute sulfuric acid, the organic solids were extracted with carbon tetrachloride in some runs. After removal of this solvent and recrystallization of the residue from alcohol there was obtained a 2.4% yield (in the most favorable case) of *p*-chlorophenyl trichloroacrylate as colorless needles, m.p. 66.9–67.3°, infrared absorption at 5.73(s)  $\mu$ .

*Anal.* Calcd. for C<sub>9</sub>H<sub>6</sub>Cl<sub>3</sub>O<sub>2</sub>: C, 37.8; H, 1.4; Cl, 49.6. Found: C, 37.8, 37.8; H, 1.4, 1.4; Cl, 49.5, 49.7.

**2,4-Dichlorophenyl Trichloroacrylate.**—After removal of carbon disulfide from the reaction product from 2,4-dichlorophenol and hexachloropropene and hydrolysis of the residue with acid, the solids were recrystallized from alcohol. On dilution of the mother liquor from the first crystallization with an equal volume of water a solid separated. This was dried and extracted with Skellysolve F (petroleum ether, b.p. 35–40°). The filtrate was evaporated to dryness and the residue recrystallized from alcohol to yield 2,4-dichlorophenyl trichloroacrylate as colorless needles, m.p. 94.8–95.3°, infrared absorption at 5.64(s)  $\mu$ , in 18% yield.

*Anal.* Calcd. for C<sub>9</sub>H<sub>4</sub>Cl<sub>4</sub>O<sub>2</sub>: C, 33.7; H, 0.9; Cl, 55.3. Found: C, 33.4; H, 1.3; Cl, 55.6.

This compound was also prepared in 41% yield by the reaction of trichloroacrylyl chloride (prepared by refluxing a mixture of trichloroacrylic acid,<sup>24</sup> thionyl chloride and benzene for 22 hours) with 2,4-dichlorophenol in benzene containing excess dry pyridine for one hour at 0–10°. The compound thus prepared proved identical to that isolated as described above. On alkaline hydrolysis trichloroacrylic acid and 2,4-dichlorophenol were isolated in good yields.

When a solution of 1.60 g. of 2,4-dichlorophenyl trichloroacrylate in 20 ml. of carbon disulfide was added to a

(20) All melting points are corrected unless otherwise noted. All micro-analyses by Galbraith Laboratories, Knoxville, Tenn.

(21) Powdered aluminum chloride, obtained from the Ohio-Apex Division of the Food Machinery and Chemical Corporation, Nitro, W. Va., was used for all Friedel-Crafts reactions.

(22) Obtained from Halogen Chemicals, Inc., Columbia, S. C.

(23) In the cases where chlorinated phenols were used reaction times of 1.5 to 2 hours were generally needed. Non-chlorinated phenols usually reacted more rapidly.

(24) A. Roedig and E. Degener, *Ber.*, **86**, 469 (1953).

TABLE II  
PROPERTIES OF SUBSTITUTED 3,4-DICHLOROCOUMARINS

Substituent on 3,4-dichloro- coumarin	M.p., <sup>a</sup> °C.	Yield, <sup>b</sup> %	Analyses, <sup>c</sup> %		
			C	H	Cl
None	106.7–107.5	28	50.3 50.5	1.9 1.9	33.0 32.8
6-Methyl	161.0–162.2	72	52.4 52.6	2.6 2.9	
6-Carboxy	301–305 <sup>d</sup>	51 <sup>e</sup>	46.4 46.7	1.6 1.6	27.4 27.1
6-Chloro	133.1–134.6	90	43.3 43.1	1.2 1.4	42.6 42.6
7-Chloro	129.1–129.7	18	43.3 43.3	1.2 1.5	42.6 42.5
8-Chloro	179.0–180.0	1.6	43.3 43.3	1.2 1.2	42.6 42.4
6-Bromo <sup>f</sup>	147.5–148.3	44	36.8 36.6	1.0 1.2	24.1 24.0
6-Methoxy	157.1–158.3	4	49.0 49.0	2.5 2.6	28.9 28.9
6,7-Dichloro	152.0–152.9	69	38.1 38.0	0.7 0.8	49.9 49.2
6,8-Dichloro	161.6–163.3	46	38.1 38.0	0.7 1.1	49.9 50.1
6-Chloro-7-methyl	178.2–178.8	85	45.6 45.7	1.9 1.9	40.4 40.3

<sup>a</sup> All melting points are corrected and represent analytical samples. <sup>b</sup> The yields are based on starting phenol and represent recrystallized material which melted very close to the m.p. reported in *a*. <sup>c</sup> The first lines of values represent calculated values and the second line the analytical result; in most cases the results were in duplicate and one has been omitted. <sup>d</sup> M.p. w. decompn. and uncor. <sup>e</sup> This compound was prepared by oxidation of 6-methyl-3,4-dichlorocoumarin; yield based thereon. <sup>f</sup> This bromo compound formed pale yellow needles; in all other cases the dichlorocoumarins were colorless solids.

suspension of 1.46 g. of aluminum chloride in 10 ml. of carbon disulfide the mixture darkened. After stirring at room temperature for 30 minutes dilute hydrochloric acid was added. On fractional crystallization, using Skellysolve F and alcohol as described above, there was obtained 81% of starting 2,4-dichlorophenyl trichloroacrylate, m.p. and mixed m.p. 94–96° uncor., and 5% of 3,4,6,8-tetrachlorocoumarin, m.p. and mixed m.p. 161–165° uncor. The identity also was confirmed by the infrared absorption spectrum.

**2,4,5-Trichlorophenyl Trichloroacrylate.**—A solution of 19.7 g. of 2,4,5-trichlorophenol,<sup>25</sup> m.p. 62.0–63.5°, in 35 ml. of carbon disulfide was added to a suspension of 29.4 g. of aluminum chloride in 50 ml. of carbon disulfide and the mixture stirred at room temperature for 10 minutes. After addition of 24.9 g. of hexachloropropene the reaction mixture was stirred for 18 hours and then freed of solvent under reduced pressure. After treating the oily residue with ice and dilute acid, the organic fraction was crystallized thrice from alcohol to yield 9.2 g. (26%) of colorless needles of the ester, m.p. 105.7–106.4° uncor., infrared absorption at 5.73(s)  $\mu$ .

*Anal.* Calcd. for C<sub>9</sub>H<sub>2</sub>O<sub>2</sub>Cl<sub>6</sub>: C, 30.4; H, 0.6; Cl, 59.9. Found: C, 30.3; H, 0.6; Cl, 59.2.

**3,4-Dichlorocoumarin (IV).**—In addition to the preparation of IV from phenol and hexachloropropene, IV also was made by refluxing a mixture of 1.00 g. of 3-chloro-4-hydroxycoumarin,<sup>26</sup> 8 ml. of phosphorus oxychloride and 2 ml. of dry pyridine for one hour. After pouring into dilute acid

(25) Obtained from the Eastman Kodak Co.

(26) Prepared as described by Arndt *et al.*, ref. 7, from 3-bromo-4-hydroxycoumarin. H. R. Eisenhauer and K. P. Link, *THIS JOURNAL*, **76**, 1647 (1954), who prepared the latter from 4-hydroxycoumarin; see J. Boyd and A. Robertson, *J. Chem. Soc.*, 174 (1948).

the organic material was extracted with ether. The ether layer was chromatographed over 2:1 silicic acid–Celite (a filter aid) using ether–benzene–Skellysolve B in the ratio 1:2:200 to yield 0.66 g. (60%) of IV, m.p. 105–107° uncor. Identity was established by mixed m.p. and by infrared absorption spectra.

**3-Chloro-4-methoxycoumarin (XIIa).**—A solution containing the sodium methoxide from 0.19 g. of sodium in 20 ml. of methanol and 1.90 g. of IV was refluxed for 30 minutes. After dilution with water and crystallization of the precipitate from Skellysolve B (petroleum ether, b.p. 65–70°) there was obtained 1.55 g. (90%) of XIIa, m.p. 87.9–88.6°, infrared absorption at 5.84(s)  $\mu$ .

*Anal.* Calcd. for C<sub>10</sub>H<sub>7</sub>O<sub>3</sub>Cl: C, 57.0; H, 3.4; Cl, 16.8. Found: C, 57.0; H, 3.4; Cl, 16.8.

**3,4-Dimethoxycoumarin (XIII).**—In a reaction similar to the above except that twice the amount of sodium was used and the reaction mixture was held at reflux for 3 hours there was obtained (70% yield) colorless needles, m.p. 75.4–76.8°, infrared absorption at 5.85(s)  $\mu$ , after recrystallization from Skellysolve B.

*Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>O<sub>4</sub>: C, 64.1; H, 4.9. Found: C, 64.2, 63.9; H, 4.8, 4.9.

**3-Chloro-4-benzylmercaptocoumarin (XIIb).**—To the sodium ethoxide solution made by adding 0.15 g. of sodium in 25 ml. of absolute alcohol was added 0.80 g. of benzylmercaptan and 1.40 g. of IV. After refluxing for 1 hour the solvent was removed under reduced pressure. Crystallization of the residue from alcohol yielded 1.72 g. (87%) of colorless prisms of XIIb, m.p. 96.9–97.6°, infrared absorption at 5.78(s)  $\mu$ .

*Anal.* Calcd. for C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>ClS: Cl, 11.7; S, 10.6. Found: Cl, 11.8, S, 10.7.

**3-Chloro-4-phenoxy coumarin (XIIc).**—After 0.07 g. of sodium had reacted with 4.3 g. of phenol held near 70°, 0.65 g. of IV was added and the temperature raised to 115–120° for 1 hour. Volatile organic constituents were removed by steam distillation and resulting tan residue was recrystallized from alcohol–water to yield 0.25 g. (31%) of colorless plates of XIIc, m.p. 88.8–90.4°, infrared absorption at 5.79(s)  $\mu$ .

*Anal.* Calcd. for C<sub>15</sub>H<sub>9</sub>O<sub>3</sub>Cl: C, 66.1; H, 3.3; Cl, 13.0. Found: C, 65.7, 65.8; H, 3.2, 3.4; Cl, 13.1, 12.9.

**3-Chloro-4-piperidinocoumarin (XIIId).**—A solution of 1.40 g. of piperidine and 1.76 g. of IV in 20 ml. of absolute ethanol was refluxed for 2 hours. The solvent was removed under reduced pressure and the residue was washed with water. Recrystallization of the dried residue from Skellysolve B yielded 1.78 g. (82%) of yellow needles of XIIId, m.p. 123.6–125.0°, infrared absorption at 5.87(s)  $\mu$ .

*Anal.* Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>ClN: C, 63.8; H, 5.4; Cl, 13.4; N, 5.3. Found: C, 63.7; H, 5.6; Cl, 13.6; N, 5.3.

**Derivatives of 6-Methylcoumarin.**—By procedures almost identical to those described above, 3,4-dichloro-6-methylcoumarin was converted into 3-chloro-4-methoxy-6-methylcoumarin, colorless needles, m.p. 107.8–108.5°, in 80% yield; 3,4-dimethoxy-6-methylcoumarin, cream colored needles, m.p. 63.9–64.8°, in 56% yield; and 3-chloro-4-benzylmercapto-6-methylcoumarin, yellow needles, m.p. 122.6–123.8°, in 72% yield.

*Anal.* Calcd. for C<sub>11</sub>H<sub>9</sub>O<sub>3</sub>Cl: C, 58.8; H, 4.0; Cl, 15.8. Found: C, 58.9; H, 4.3; Cl, 15.7. Calcd. for C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>: C, 65.4; H, 5.5. Found: C, 65.4; H, 5.7. Calcd. for C<sub>17</sub>H<sub>13</sub>O<sub>2</sub>ClS: C, 64.4; H, 4.1; Cl, 11.2; S, 10.1. Found: C, 64.6; H, 4.1; Cl, 11.1, S, 10.3.

**3-Chloro-4-hydroxy-6-methylcoumarin.**—In one experiment, a solution of 0.85 g. of 3-chloro-4-methoxy-6-methylcoumarin, 0.65 g. of piperidine and 25 ml. of absolute alcohol (which had not been carefully protected from moisture) was refluxed for 138 hours. After pouring on ice and acidifying, a colorless solid was obtained. Recrystallization from alcohol yielded 0.73 g. (91%) of 3-chloro-4-hydroxy-6-methylcoumarin as colorless needles, m.p. 248.5–249.5° uncor.; infrared absorption at 5.88(s), 3.17(m)  $\mu$ .

*Anal.* Calcd. for C<sub>10</sub>H<sub>7</sub>O<sub>3</sub>Cl: C, 57.0; H, 3.4; Cl, 16.8. Found: C, 57.1, 57.0; H, 3.5, 3.6; Cl, 16.9, 16.6.

**6-Carboxy-3,4-dichlorocoumarin (III).**—A solution of 0.25 g. of 3,4-dichloro-6-methylcoumarin in 8 ml. of concentrated sulfuric acid was added dropwise to a solution of 1.1 g. of sodium dichromate in 7 ml. of water. The mixture heated

up and a white precipitate formed. When addition was complete, the green mixture was poured onto ice and the product was collected and washed with water. The product was soluble in 10% sodium hydroxide and in 10% sodium bicarbonate. Recrystallization from acetone-water yielded 0.145 g. (51%) of colorless III, m.p. 301–305° dec.

(uncor.); infrared spectrum: C=O, 5.72(s), 5.92(s); C=C, 6.20(s)  $\mu$ .

*Anal.* Calcd. for  $C_{10}H_4Cl_2O_4$ : C, 46.4; H, 1.6; Cl, 27.4. Found: C, 46.7; H, 1.6; Cl, 27.1.

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## COMMUNICATIONS TO THE EDITOR

### THE FUOSS-ONSAGER CONDUCTANCE EQUATION AT HIGH CONCENTRATIONS

Sir:

Fuoss and Onsager,<sup>1,2</sup> in presenting their theory of the conductance of free ions, were careful to point out that it is applicable to dilute solutions below a concentration where the value of  $\kappa a$  is less than 0.2. They have demonstrated the validity of the theory below this concentration but, at this writing, the behavior of their conductance equation has not been investigated at higher concentrations. Mercier and Kraus<sup>3</sup> have measured the conductance of dilute solutions of tetramethylammonium picrate up to about  $3 \times 10^{-3} N$  in dioxane-water mixtures from pure water up to 70% dioxane. An analysis by Fuoss and Kraus<sup>4</sup> indicates that this electrolyte is completely dissociated over this entire range of mixtures. Accascina, prior to the advent of the Fuoss-Onsager theory, measured the conductance of  $Me_4N^+Pi^-$  in a 55% dioxane-water mixture to a concentration of 0.226  $N$ . Subsequently, Kay analyzed the data using an IBM computer<sup>5</sup> and obtained 33.39 and  $6.14 \times 10^{-8}$  for  $\Lambda_0$  and  $a$ , respectively. The results are shown graphically in Fig. 1.

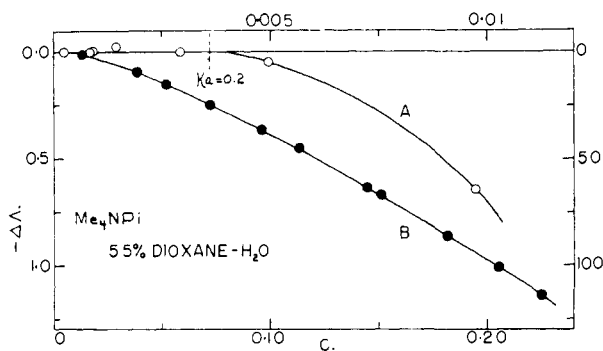


Fig. 1.—Deviation between observed and calculated equivalent conductances. A, dilute range, coordinates left and above; B, entire range, coordinates right and below.

In plot A of this figure are shown values of  $\Delta\Lambda = \Lambda_{obs} - \Lambda_{calc}$  plotted as functions of  $C$  for concentrations up to 0.01  $N$ . It will be noted that the calculated values of  $\Lambda$  closely approximate

- (1) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).
- (2) R. M. Fuoss, *This Journal*, **80**, 3163 (1958).
- (3) P. L. Mercier and C. A. Kraus, *Proc. Nat. Acad. Sci.*, **41**, 1033 (1955).
- (4) R. M. Fuoss and C. A. Kraus, *This Journal*, **79**, 3304 (1957).
- (5) Program No. 004 at the Brown Computing Center

those observed at concentrations below  $3 \times 10^{-3} N$ . The average deviation between the terms is 0.015  $\Lambda$ -unit or 0.05%. At concentrations above  $4 \times 10^{-3} N$ , calculated values begin to diverge from the experimental ones. The concentration at which  $\kappa a = 0.2$  is  $3.6 \times 10^{-3} N$ . Thus, deviations are within experimental error below this concentration but increase markedly at concentrations much beyond this limit. Plot B of Fig. 1 covers the entire concentration range up to 0.226  $N$ . It can be seen that up to about 0.01  $N$  the differences are not large enough to show on the plot. At higher concentrations, the difference increases, reaching very large values at high concentration. At the highest concentration, the calculated conductance is almost seven times the measured value.

The results of this analysis show rather convincingly that the theory reproduces the experimental values closely over the concentration range in which the approximations made in deriving the theory are justified, but, as expected, at higher concentrations the deviations become steadily greater than the experimental error. The experimental data will be presented elsewhere in due course.

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RECEIVED MARCH 9, 1959

### RELATIVE ARYL RADICAL AFFINITIES OF MONOMERS

Sir:

Evidence<sup>1,2,3</sup> has been presented that the mechanism of the Meerwein reaction involves addition of an aryl radical to a monomer followed by rapid halogen transfer from cupric chloride or from a higher chloro-complex. Thus, competitive Meerwein reactions might provide the means for measuring relative rate constants for the addition of aryl radicals to olefins. This possibility has now been realized.

Acrylonitrile (A) and methacrylonitrile (MA) were selected as reference monomers. In a typical experiment 0.4 mole of both methyl acrylate and acrylonitrile were allowed to compete for the phenyl

- (1) S. C. Dickerman, K. Weiss and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956); *This Journal*, **80**, 1904 (1958).
- (2) S. C. Dickerman and K. Weiss, *J. Org. Chem.*, **22**, 1070 (1957).
- (3) J. K. Kochi, *This Journal*, **79**, 2942 (1957).