amount of crystals melting 277–281°; a mixed melting point with an authentic sample of tetraphenylphthalic anhydride (m. p. 284–286°) gave 279–283°. Because of the melting point ranges observed here additional proof of the identity of the product of oxidation was obtained by ultimate analysis.

Anal. Calcd. for $C_{32}H_{20}O_3$: C, 84.94; H, 4.46. Found: C, 85.05; H, 4.51.

Tetraphenylcyclopentadienone with Furan, Pyrrole, N-Methylpyrrole and Thiophene.—Six and eight-tenths grams of furan[19] (0.1 mole) and 1.15 g. (0.003 mole) tetraphenylcyclopentadienone were heated in a closed tube at 100° for nine hours. In a second experiment the same quantities were heated at 200° for seventeen hours. In both cases the tetraphenylcyclopentadienone was recovered quantitatively and identified by a mixed melting point.

Of several experiments with pyrrole[20] the most vigorous conditions employed were as follows: 3.3 g. (0.05 mole) of pyrrole and 1.15 g. (0.003 mole) of tetraphenylcyclopentadienone were heated in a closed tube at 150–160° for twelve hours. The reaction mixture was warmed under reduced pressure to remove unreacted pyrrole. The residue melted 208–210° and a qualitative test for nitrogen was negative, showing that no addition compound had formed. Crystallization of this material from benzene and a mixed melting point showed that the residue was tetraphenylcyclopentadienone. Other experiments likewise showed no reaction.

Several experiments with N-methylpyrrole[21] and tetraphenylcyclopentadienone similar to that described above were tried but no evidence of reaction could be found even after heating at 185° for fourteen hours.

Likewise experiments with thiophene (Eastman Kodak Co.) and tetraphenylcyclopentadienone even at 150–160° for twelve hours gave negative results. The presence of 5% trichloroacetic acid[22] in one experiment had no effect.

Summary

A study of the condensation of tetraphenylcyclopentadienone with certain cyclic 1,3-diene systems has shown that tetraphenylcyclopentadienone reacts with cyclopentadiene to form an addition compound which, by hydrogenation, decarbonylation, and dehydrogenation, can be converted to 4,5,6,7-tetraphenylhydrindene. Tetraphenylcyclopentadienone does not react with furan, pyrrole, N-methylpyrrole, or thiophene even under very vigorous conditions.

CLEVELAND, OHIO
MIDLAND, MICHIGAN
RECEIVED DECEMBER 16, 1941

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[19] Prepared from furoic acid: "Organic Syntheses," Coll. Vol. I, p. 269.

[20] Prepared from ammonium mucate: "Organic Syntheses," Coll. Vol. I, p. 461.

[21] Prepared from N-methylammonium mucate; Pictet, *Ber.*, **37**, 2792 (1904).

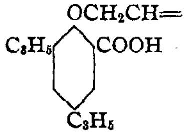
[22] Proposed as a catalyst for Diels–Alder reactions: Wasserman, French Patent 838,454 (1939); *C. A.*, **33**, 7819 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

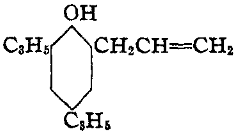
The Rearrangement of O-Crotyl-3,5-dichlorosalicylic Acid and Related Compounds

BY D. S. TARBELL AND J. W. WILSON[1]

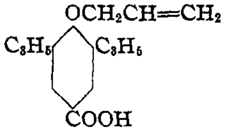
In studying the behavior of allyl ethers of various substituted phenols, Claisen found[2] that allyl ethers of substituted salicylic acids, such as O-allyl-3,5-diallylsalicylic acid (I), undergo a smooth rearrangement during which the carboxyl group is displaced by the allyl group, giving II. Carbon dioxide is evolved in the theoretical amount, and the reaction commences at about 100°—a lower temperature than is necessary for the ordinary Claisen rearrangement. Claisen also observed that carbon dioxide can be displaced smoothly from the para position, illustrated by 4-allyloxy-3,5-diallylbenzoic acid (III), which forms 2,4,6-triallylphenol quantitatively.



I



II



III

O-Allylsalicylic acid and similar compounds with a free ortho position were reported by Claisen to rearrange exclusively to the free ortho position without loss of carbon dioxide. O-Allyl-*o*-cresotic acid, which has a free para position, gave the displacement product, 2-allyl-6-methylphenol, and the para product, 3-methyl-5-allylsalicylic acid, in a ratio of three to one. This latter result would indicate that when the normal rearrangement is possible, it and the displacement reaction go at similar rates. Claisen's observa-

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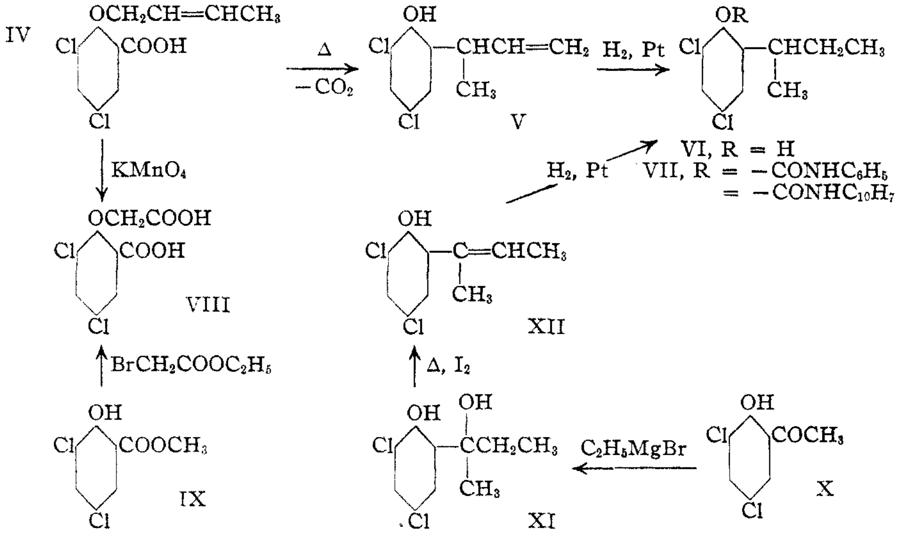
[1] Sherman Clarke Fellow, 1941–1942.

[2] Claisen and Eisleb, *Ann.*, **401**, 21 (1913); Claisen, *ibid.*, **418**, 69 (1918). For summary of the Claisen rearrangement, *cf.* Tarbell, *Chem. Rev.*, **27**, 495 (1940).

tion on O-allylsalicylic acid infers that this is not true for compounds with a free ortho position, a result not in agreement with the present work.



Our purpose in studying these displacement reactions more closely was to determine first whether the rearrangement of a substituted allyl group to the ortho position with displacement is accompanied by inversion (attachment of the allyl group by the γ-carbon). We also wished to determine whether the rearrangement with displacement does go at a lower temperature than the ordinary rearrangement. After some unpromising preliminary experiments with O-cinnamyl-*o*-cresotic acid, we found that O-crotyl-3,5-dichlorosalicylic acid (IV) was a suitable compound for study of the first question, and we examined crotyl 2,4-dichlorophenyl ether and O-allylsalicylic acid for information on the second. O-Allyl-3,5-dichlorosalicylic acid and allyl 2,4-dichlorophenyl ether were examined to find the effect on ease of rearrangement of the change from crotyl to allyl.

O-Crotyl-3,5-dichlorosalicylic acid (IV) was prepared by the usual methods from crotyl bromide and methyl 3,5-dichlorosalicylate (IX), and its structure proved by oxidation with permanganate to the aryloxyacetic acid VIII. The product actually isolated from the oxidation was a compound melting at 255°, which formed VIII when recrystallized from 3 *N* hydrochloric acid; the structure of VIII was proved by its synthesis from methyl 3,5-dichlorosalicylate (IX) and ethyl bromoacetate, followed by hydrolysis. The first product of the oxidation was probably some kind of anhydride, since it was hydrolyzed to VIII.

O-Crotyl-3,5-dichlorosalicylic acid rearranges at its melting point (122°). A sample heated to 130° for four minutes yielded 20% of 3,5-dichlorosalicylic acid and 58% of twice distilled 2,4-dichloro-6-(α-methylallyl)-phenol (V). The homogeneity of V was shown by constancy of refractive index and preparation of derivatives in good yield from its reduction product; its structure was proved by synthetic, rather than degradative, procedures, since initial attempts at degradation were not promising. It was reduced catalytically to 2-(*s*-butyl)4,6-dichlorophenol (VI, R = H) and this compound was characterized as the phenyl- and α-naphthyl-urethan (VII, R = $-CONHC_6H_5$ and $-CONHC_{10}H_7$).

The reduced phenol VI was synthesized readily from 2,4-dichlorophenyl acetate. The latter yielded 3,5-dichloro-2-hydroxyacetophenone by the Fries reaction, and treatment of this product with excess ethylmagnesium bromide gave 2-(3,5-dichloro-2-hydroxyphenyl)-butanol-2 (XI). This carbinol was dehydrated by heating with a trace of iodine to 2,4-dichloro-6-(α-methylpropenyl)-phenol (XII) (or double bond isomer) which yielded VI on catalytic reduction. The urethans of the synthetic phenol VI melted at the same point as those from the sample prepared from the rearrangement product V, and mixed melting points showed no depression.

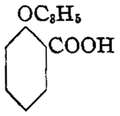
This proves the structure of V, and shows that the rearrangement to the ortho position with displacement of carbon dioxide goes with inversion, just as does the ordinary rearrangement.[3] This point was further substantiated in the present work by showing that crotyl 2,4-dichlorophenyl ether gives the same product V which is produced by the acid IV.

The rates of rearrangement of the allyl and crotyl ethers of 3,5-dichlorosalicylic acid were compared by heating in a closed system attached to a gas buret and measuring the rate of evolution of carbon dioxide. It was found that the crotyl

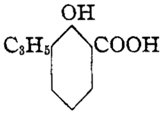
[3] Claisen and Tietze, *Ber.*, **58**, 275 (1925); *ibid.*, **59**, 2344 (1926).

ether evolves carbon dioxide more rapidly at 120° than the allyl ether does at 140°. This same effect was observed in comparing the crotyl and allyl ethers of 2,4-dichlorophenol; the former rearranged 21% in one hour at 160–163°, and the latter gave little if any rearrangement at this temperature, and only 33% reaction at 184–186° for one hour. The crotyl ethers thus rearrange more rapidly in both cases, and the displacement reaction in these examples goes more rapidly than does the rearrangement of the corresponding ethers without the carboxyl group.

The allyl ether of salicylic acid was investigated, since Claisen[2] gave few experimental details of his work. Several runs showed that about 28% of the theoretical amount of carbon dioxide was evolved rapidly at 160–170°, and that therefore the rearrangement to the free ortho position giving XIV, and the rearrangement with displacement, giving 2-allylphenol, are simultaneous processes. This result was confirmed by a larger run in which 23% of 2-allylphenol and 64% of 3-allylsalicylic acid (XIV) were isolated and identified. The possibility that XIV might be the sole primary product of the reaction and that the 2-allylphenol isolated was produced by subsequent decarboxylation of XIV was excluded by showing that XIV does not lose carbon dioxide at an appreciable rate at 160–170°. The cinnamyl ether of salicylic acid yielded about 10% of the theoretical amount of carbon dioxide at 120° in twenty minutes. Claisen's statement that acids like O-allylsalicylic acid rearrange only to the free ortho position is therefore incorrect.



XIII



XIV

To determine whether the ion corresponding to IV could rearrange as readily as the free acid, IV was heated in dimethylaniline at 150° for one hour. Little carbon dioxide was evolved, but cleavage of the ether linkage seemed to be complete. The reaction product was a complex mixture, from which 13% of 3,5-dichlorosalicylic acid and 23% of impure methyl 3,5-dichlorosalicylate were isolated. The remainder of the product was an oil yielding impure 3,5-dichlorosalicylic acid on alkaline hydrolysis. Apparently the reaction takes a different course from the reactions between carboxylic acids and tertiary amines studied by v. Braun and Weissbach[4]; they isolated a small yield of the amide of the secondary amine and occasionally a trace of ester. They accounted for these products thus

$$R_3N + R'COOH \longrightarrow (R_3NCOR')OH \longrightarrow R_2NCOR' + ROH$$

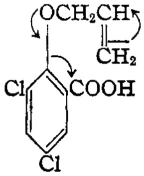
with the ester formed by subsequent esterification.

Because esterification of an alcohol in a tertiary amine as solvent seems unlikely, and because of the relatively good yield of ester in our experiments, it seems more likely that the ester in our work is formed by decomposition of the amine salt

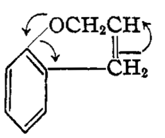
$$RCOONH(CH_3)_2C_6H_5 \longrightarrow RCOOCH_3 + CH_3NHC_6H_5$$

The decomposition of quaternary ammonium salts of carboxylic acids is a well-known method of esterification.[5]

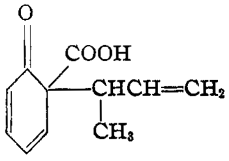
The experiment with dimethylaniline indicates that the O-allyl-3,5-dichlorosalicylate ion does not rearrange.



XV



XVI



XVII

This may be because a hydrogen bond is necessary between the carboxyl hydrogen and the ether oxygen. In view of the ease of para rearrangement, however, where a similar hydrogen bond is not possible, it is more probable that the negative charge on the carboxyl prevents rearrangement by preventing the electron shifts indicated in XV. The usual Claisen rearrangement is explained[6] plausibly as involving the shifts indicated in XVI, with the γ-carbon and ortho carbon forming a bond simultaneous with the breaking of the carbon–oxygen bond, to give an ortho-quinonoid structure. Such a structure derived from O-crotyl-3,5-dichlorosalicylic acid (IV) would be XVII, which is a β-keto acid and would give the observed rearrangement product on decarboxylation and enolization. The possibility of an intermediate of the type of XVII was suggested by Claisen.[2]

This picture is in agreement with the observation that crotyl ethers rearrange more readily than allyl ethers, since the methyl group, being electron-repelling, will favor the electron drift indi-

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[4] v. Braun and Weissbach, *Ber.*, **63**, 489 (1930).

[5] Fuson, Corse and Horning, THIS JOURNAL, **61**, 1290 (1939).

[6] Cope and Hardy, *ibid.*, **62**, 441 (1940), for example.

cated in XV. The ethers of 3,5-dichlorosalicylic acid should rearrange more easily than the ethers of 2,4-dichlorophenol, as is observed, because the carboxyl group is electron-attracting and would be expected to weaken the carbon–oxygen bond in the ether by drawing the electrons of the oxygen toward the ring. This would also make the carbon carrying the carboxyl more negative and promote bond formation with the γ-carbon of the allyl group. This assumes that the rate-determining step is the formation of an intermediate of type XVII, which probably decarboxylates and enolizes extremely rapidly.

The difference in ease of rearrangement of O-allyl-3,5-dichlorosalicylic acid and O-allylsalicylic acid itself is striking; the former reacts at 130–140° and the latter at a comparable rate only at 175°. This difference may be due to the polar effect of the chlorine atoms, but two allyl groups in the nucleus have the same effect in III.

Experimental[7]

O-Crotyl-3,5-dichlorosalicylic Acid (IV).—A mixture of 44.2 g. of methyl 3,5-dichlorosalicylate,[2] 27.8 g. of crotyl bromide,[8] 28 g. of powdered anhydrous potassium carbonate and 139 g. of methyl ethyl ketone was refluxed for six hours. After addition of 300 cc. of water, the mixture was extracted three times with petroleum ether (b. p. 60–70°); the extract was washed several times with 10% sodium hydroxide solution, with water and dried over calcium chloride. The dried solution was evaporated to 63 g. on the steam-bath and saponified without purification by stirring for fifteen minutes with 200 g. of 30% potassium hydroxide in methanol. After the addition of 400 cc. of water and one extraction with petroleum ether, the alkaline solution was acidified with dilute hydrochloric acid. The nearly white precipitate was recrystallized twice from petroleum ether, and 30.1 g. (58%) obtained, m. p. 121.5–122.5°. The mother liquors yielded 3.8 g. of less pure material, m. p. 118–121°.

Anal. Calcd. for $C_{11}H_{10}O_3Cl_2$: C, 50.6; H, 3.9; neutral equivalent, 261. Found: C, 50.4; H, 3.9; neutral equivalent, 261.

2,4-Dichloro-6-carboxyphenoxyacetic Acid (VIII)

A. By Oxidation of O-Crotyl-3,5-dichlorosalicylic Acid (IV).—A suspension of 2.0 g. of the acid IV was stirred vigorously, while a solution of 4.0 g. of potassium permanganate in 175 cc. of water was added dropwise. After standing overnight, the manganese dioxide was removed by filtration, the solution acidified, diluted to 500 cc. and heated to dissolve the solid product. On cooling, 1.7 g. of material separated, which decomposed at 257–259° after recrystallization from water. The same material was obtained on crystallization from glacial acetic acid, acetone–water and dioxane–water; from 3 *N* hydrochloric acid long thin needles of VIII were obtained, m. p. 210–211°. The yield in the oxidation was 53%.

B. From Methyl 3,5-Dichlorosalicylate.—The method of Koelsch[9] was not successfully applied to dichlorosalicylic acid or its methyl ester. The diester (presumably the dimethyl ester) of VIII was obtained in 30% yield by refluxing ethyl bromoacetate, sodium methylate and methyl 3,5-dichlorosalicylate in methanol for three hours. Recrystallized from petroleum ether (b. p. 20–40°), it gave no ferric chloride test and melted at 57–59°. Hydrolysis of the diester with 30% methanolic potassium hydroxide gave 91% yield of VIII; m. p. after recrystallization from 3 *N* hydrochloric acid, 208–210°. The identity of samples prepared in A and B was shown by mixed melting points.

Anal. Calcd. for $C_9H_6O_5Cl_2$: C, 40.8; H, 2.3; neutral equivalent, 132.5. Found: C, 40.4; H, 1.8; neutral equivalent, 133.

Rearrangement of O-Crotyl-3,5-dichlorosalicylic Acid (IV) to 2,4-Dichloro-6-(α-methylallyl)-phenol (V).—After some preliminary experiments, 13.49 g. of IV was heated for four minutes at 130–131° in a carbon dioxide atmosphere. The product was dissolved in petroleum ether and extracted with aqueous sodium bicarbonate; acidification of the extract yielded 1.73 g. of solid, m. p. 214–221°, which when recrystallized from water–alcohol gave 1.37 g. of white needles, m. p. 223–225°. A mixed melting point showed that it was 3,5-dichlorosalicylic acid, the amount isolated crude corresponding to 20% of the starting ether. The petroleum ether solution was next extracted several times with Claisen alkali, and from this was obtained 2,4-dichloro-6-(α-methylallyl)-phenol (V) with b. p. 95–110° (5 mm.). Redistillation into three fractions, having $n^{25}D$ 1.5554, 1.5559 and 1.5558 gave a total yield of 6.5 g., b. p. 95–98° (5 mm.). The redistilled product represents a 58% yield. Distillation of the fraction unextracted by Claisen alkali yielded 0.54 g. (5%), b. p. about 150° (5 mm.), $n^{25}D$ 1.5328.

The **phenylurethan** of V, prepared with pyridine as catalyst, melts at 103–104°. *Anal.* Calcd. for $C_{17}H_{15}O_2NCl_2$: C, 60.7; H, 4.5. Found: C, 60.8; H, 4.6.

2,4-Dichloro-6-(*s*-butyl)-phenol (VI, R = H).—The rearrangement product V (1.82 g.) from O-crotyl-3,5-dichlorosalicylic acid (IV) was reduced with Adams catalyst in alcohol for about three hours. The product boiled at 142° (22 mm.) and was collected in two fractions, $n^{25}D$ 1.5392 and 1.5390; yield, 90%. The synthetic product obtained from reduction of 2,4-dichloro-6-(α-methylpropenyl)-phenol (XII) had $n^{25}D$ 1.5392.

The phenylurethan of 2,4-dichloro-6-(*s*-butyl)-phenol (VI, R = $-CONHC_6H_5$) was recrystallized three times from ligroin, m. p. 114–115°.

Anal. Calcd. for $C_{17}H_{17}O_2NCl_2$: C, 60.4; H, 5.1. Found: C, 60.4; H, 5.2.

The α-naphthylurethan (VI, R = $-CONHC_{10}H_7$) recrystallized from ligroin had m. p. 151–153°.

Anal. Calcd. for $C_{21}H_{19}O_2NCl_2$: C, 64.9; H, 4.9. Found: C, 64.8; H, 4.8.

Both urethans were prepared from VI (R = H) which had come from the rearrangement product V and from the

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[7] All melting points corrected; analyses by J. W. Wilson and R. W. King.

[8] Young and Lane, THIS JOURNAL, **59**, 2051 (1937).

[9] Koelsch, *ibid.*, **53**, 304 (1931).

synthetic material; the properties were identical and there was no depression in the respective mixed melting points.

2,4-Dichlorophenyl Acetate.[10]—2,4-Dichlorophenol (43.9 g.), 31.5 g. of acetic anhydride and 21 g. of pyridine gave 51.8 g. (94%) of 2,4-dichlorophenyl acetate, $n^{25}\mathrm{D}$ 1.5304, b. p. 133–134° (22 mm.).

3,5-Dichloro-2-hydroxyacetophenone (X).[11]—A mixture of 67.6 g. of 2,4-dichlorophenyl acetate and 48.1 g. of anhydrous aluminum chloride heated at 135–145° for forty minutes and decomposed in the usual way yielded 24 g. of pure X, m. p. 94–96°, 4.9 g., m. p. 90–98° and 31.1 g. of starting material, b. p. 125–140° (24 mm.). Presumably longer heating during the Fries reaction would give a higher yield.

2-(3,5-Dichloro-2-hydroxyphenyl)-butanol-2 (XI).—To a solution of ethylmagnesium bromide prepared from 27.5 g. of ethyl bromide and 6.13 g. of magnesium in 115 cc. of ether was added over a period of one hour a solution of 24.6 g. of 3,5-dichloro-2-hydroxyacetophenone (X) in 250 cc. of ether. After stirring for two and one-half hours, the reaction mixture was decomposed with ice and dilute sulfuric acid, and the aqueous layer was extracted with ether. Evaporation of the dried combined ether solution and extracts to 60 cc. and addition of 100 cc. of ligroin yielded, after concentration to 50 cc., 15.5 g. (53%) of white crystals of XI, m. p. 108–109°, unchanged by recrystallization from ligroin. Concentration of the mother liquor gave 4.8 g. of less pure material, m. p. 101–107°, which, when recrystallized, gave 3.8 g., m. p. 107–109°, bringing the total yield to 68%.

Anal. Calcd. for $C_{10}H_{12}O_2Cl_2$: C, 51.1; H, 5.2. Found: C, 50.9; H, 5.4.

2,4-Dichloro-6-(α-methylpropenyl)-phenol (XII).—2-(3,5-Dichloro-2-hydroxyphenyl)-butanol-2 (XI) (3.4 g.) was heated in an oil-bath with a crystal of iodine for a few minutes until ebullition of vapor ceased. The product was distilled, b. p. 140–142° (25 mm.), and weight 2.7 g. (86%); $n^{25}\mathrm{D}$ 1.5653. Structure XI is the most probable, but some of it may be the isomeric compound with the double bond going into the methyl group.

Rearrangement of O-Allylsalicylic Acid.—Preliminary runs on small amounts showed that about 28% of the theoretical amount of carbon dioxide was evolved in a few minutes at 170°, and no more gas was given off until the temperature was raised to 200°. Blank runs on 3-allylsalicylic acid showed that it does not decarboxylate below 200° at an appreciable rate, and at 200° the rate accounts for the carbon dioxide evolved from the rearrangement mixture above. O-Allylsalicylic acid (12.3 g.) was rearranged in a nitrogen atmosphere in a test-tube fitted with a thermometer by immersing in a bath at 175°. Bubbling began when the temperature of the product reached 155°, and the reaction became so vigorous that the temperature rose rapidly to 235° before the tube could be cooled, the temperature being over 175° for one minute. The mixture was then held between 175–180° for twenty-five minutes. It was worked up by dissolving in ether and extracting with sodium carbonate solution; the extract yielded on acidification and recrystallization from petroleum ether-benzene 7.8 g. (64%) of material with m. p. 94–95°, which was shown to be 3-allylsalicylic acid by a mixed melting point with an authentic sample. Evaporation of the ether and distillation yielded 2.1 g. (23%) of 2-allylphenol, b. p. 98–100° (13 mm.), $n^{24}\mathrm{D}$ 1.5443.[12]

Comparison of Rearrangement of Crotyl and Allyl Ethers of 3,5-Dichlorosalicylic Acid.—The allyl ether[2] was heated up to 140° and the amount of gas evolved was measured. Half of the theoretical amount of carbon dioxide was evolved in eleven minutes at 120–140° (six minutes above 130°) and 85% in thirty-three minutes.

The crotyl ether evolved 55% of the theoretical amount and gave no more gas on heating to 140°. Half of this amount was given off in five minutes at 120–121° and the reaction was virtually complete in twenty-five minutes. The rate of evolution of gas when corresponding amounts (about one-quarter) had reacted shows that this reaction is faster at 120° than the rearrangement of the allyl ether (above) at 140°.

Reaction of the Allyl Ether in Dimethylaniline.—O-Allyl-3,5-dichlorosalicylic acid (2.38 g.) was heated in 11.9 g. of purified dimethylaniline at 150° for one hour. The mixture was dissolved in hydrochloric acid and extracted with petroleum ether, leaving a white solid, which was taken up in ether. From the ether solution was obtained 0.23 g. of 3,5-dichlorosalicylic acid (13%) m. p. 220–225° and 0.50 g. of impure methyl 3,5-dichlorosalicylate, m. p. 130–139° (23%). Two recrystallizations from glacial acetic acid yielded 0.21 g. of the pure ester, m. p. 146–148°, identified by mixed melting point. Evaporation of the petroleum ether solution yielded 1.25 g. of yellow oil, which on saponification with Claisen alkali yielded 0.42 g. of the dichlorosalicylic acid, and 0.43 g. of impure material.

Crotyl 2,4-Dichlorophenyl Ether.—A mixture of 12.1 g. of dichlorophenol, 11.2 g. of crotyl bromide and 11.0 g. of powdered anhydrous potassium carbonate, when refluxed in 50 cc. of methyl ethyl ketone for seven hours and worked up by the usual procedure, yielded 15.0 g. of crotyl 2,4-dichlorophenyl ether, b. p. 90–103° (3 mm.). This was redistilled and 12.0 g. (74%) was obtained, $n^{25}\mathrm{D}$ 1.5498. The ether was rearranged to V, $n^{25}\mathrm{D}$ 1.5553, in 83% yield by heating in boiling diethylaniline for two hours. To get a comparison with the allyl ether, 2.23 g. was heated without solvent in a nitrogen atmosphere for one hour at 160–163°; 21% of the product was soluble in Claisen alkali, and 79% was insoluble.

Allyl 2,4-Dichlorophenyl Ether.[13]—This compound was prepared by the above method in 85% yield; b. p. 98–99° (2 mm.); $n^{25}\mathrm{D}$ 1.5522; d^{25}_{25} 1.258. Four grams, after heating for one hour at 184–186°, yielded 2.55 g. (64%) insoluble in Claisen alkali, and 1.30 g. (33%) was soluble, representing 33% rearrangement.

Summary

1. O-Crotyl-3,5-dichlorosalicylic acid rearranges smoothly with inversion to yield 2,4-di-

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[10] Fischer, *Ann. Suppl.*, **7**, 180 (1870), gives the b. p. as 244–245° at atmospheric pressure.

[11] Chien and Yin, *J. Chinese Chem. Soc.*, **7**, 40 (1939) [*C. A.*, **34**, 1979 (1940)].

[12] Claisen, ref. 2, gives b. p. 99° (12 mm.) and Lauer and Leekley, This Journal, **61**, 3042 (1939), give $n^{20}\mathrm{D}$ 1.5453 for 2-allylphenol.

[13] Claisen and Tietze, *Ann.*, **449**, 81 (1926); Raiford and Howland, This Journal, **53**, 1051 (1931).

chloro-6-(α-methylallyl)-phenol, whose structure was proved by reduction to 2,4-dichloro-6-(*s*-butyl)-phenol and synthesis of this compound. Heating the acid in dimethylaniline gives cleavage and very little rearrangement; methyl 3,5-dichlorosalicylate and the corresponding acid are present in the reaction product.

2. O-Allylsalicylic acid rearranges to give 64% of 3-allylsalicylic acid and 23% of 2-allylphenol.

3. O-Allyl-3,5-dichlorosalicylic acid rearranges more slowly than the crotyl compound, and allyl 2,4-dichlorophenyl ether also rearranges more slowly than crotyl 2,4-dichlorophenyl ether.

4. The relation of these observations to the mechanism of the Claisen rearrangement is discussed.

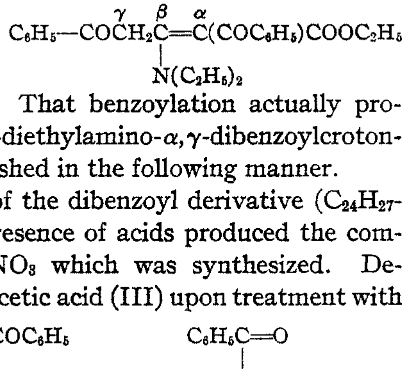
ROCHESTER, NEW YORK RECEIVED DECEMBER 4, 1941

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

The Action of Benzoyl Chloride on Ethyl β-Diethylaminocrotonate

BY WALTER M. LAUER AND NORMAN H. CROMWELL[1,2]

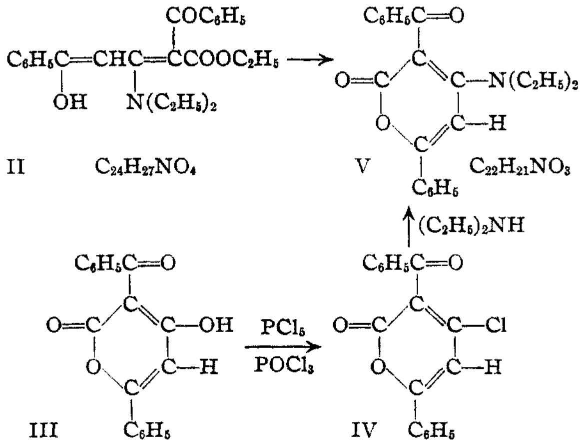
The acylation of β-aminocrotonic esters has not been extensively investigated, but examples of both C- and N-acylation have been reported.[3,4] The present study is concerned with the action of benzoyl chloride on ethyl β-diethylaminocrotonate (I). Instead of the expected monobenzoyl derivative, ethyl β-diethylamino-α,γ-dibenzoylcrotonate (II)



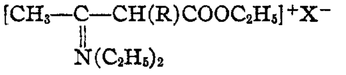
$C_6H_5-CO\overset{\gamma}{C}H_2\underset{N(C_2H_5)_2}{\overset{\beta}{C}}=\overset{\alpha}{C}(COC_6H_5)COOC_2H_5$

was obtained. That benzoylation actually produced ethyl β-diethylamino-α,γ-dibenzoylcrotonate was established in the following manner.

Hydrolysis of the dibenzoyl derivative ($C_{24}H_{27}NO_4$) in the presence of acids produced the compound $C_{22}H_{21}NO_3$ which was synthesized. Dehydrobenzoylacetic acid (III) upon treatment with phosphorus pentachloride yielded the monochloro derivative (IV) which in turn was transformed to 3-benzoyl-4-diethylamino-6-phenylpyrone (V).

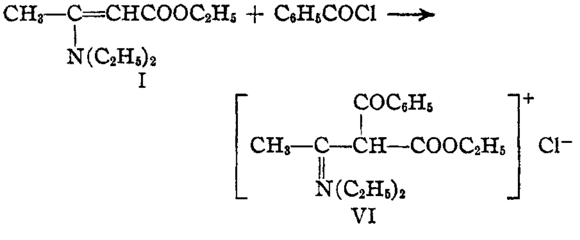


Earlier work,[5] dealing with the alkylation of ethyl β-diethylaminocrotonate, has shown that alkyl halides react in a manner requiring direct attachment of the alkyl group to the α-carbon atom to form a salt of the type



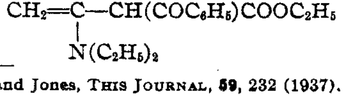
$$[CH_3-\underset{\overset{\|}{N(C_2H_5)_2}}{C}-CH(R)COOC_2H_5]^+X^-$$

If benzoylation with benzoyl chloride in dry ether follows this same course, then the initial step in the process can be formulated as



$$\underset{\underset{I}{N(C_2H_5)_2}}{CH_3-C}=CHCOOC_2H_5 + C_6H_5COCl \longrightarrow \underset{VI}{\left[CH_3-\underset{\overset{\|}{N(C_2H_5)_2}}{C}-\overset{COC_6H_5}{CH}-COOC_2H_5\right]^+Cl^-}$$

The introduction of the benzoyl group should decrease the basicity of the aminocrotonate and, therefore, a proton transfer from VI to I is to be expected. Presumably, the free base, derived from VI by the loss of a proton, upon benzoylation yields the hydrochloride of the dibenzoyl derivative, ethyl β-diethylamino-α,γ-dibenzoylcrotonate, which was actually isolated. Since the second benzoyl group attaches itself to the γ-carbon, it seems likely that the immediate precursor of the dibenzoyl derivative possesses the structure



$$\overset{\gamma}{C}H_2=\underset{N(C_2H_5)_2}{\overset{\beta}{C}}-\overset{\alpha}{C}H(COC_6H_5)COOC_2H_5$$

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(1) An abstract of a thesis submitted for the Ph.D. degree, June, 1939.

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(3) Collie, *Ann.*, **226**, 309 (1884).

(4) Benary, *et al.*, *Ber.*, **42**, 3912 (1909); **50**, 65 (1917); **59**, 2548 (1926).

(5) Lauer and Jones, THIS JOURNAL, **59**, 232 (1937).