Phenylisocyanate with α-Benzylidene-β,β-diphenylhydrazone and with α-Ethylidene-β,β-diphenylhydrazone.—Sealed tubes containing one molecular proportion of benzylidene-diphenylhydrazone with one of phenylisocyanate and with two of phenylisocyanate were heated for various periods of time at 180–200°. A light brown, viscous liquid was obtained which solidified to a transparent resin on cooling; benzylidene-phenylhydrazone was the only crystalline material that could be obtained from a solution of this resin in alcohol. The mother liquors on evaporation left a resin from which no crystalline substances could be isolated either before or after steam-distillation. Ethylidene-diphenylhydrazone, when heated with one and with two molecular proportions of phenylisocyanate, similarly gave resinous products from which phenylcyanurate was the only crystalline product isolated.

Summary

Phenylisocyanate resembles the ketenes in the addition compounds that it forms with some alkyl Schiff bases, two molecular proportions adding to yield a 6-membered ring; aryl Schiff bases, on the other hand, do not give similar compounds, probably adding but one molecular proportion of the isocyanate to form unstable 4-membered rings which could not be isolated; attempts to add phenylisocyanate to the CH:N linking in hydrazones were not successful.

CLEVELAND, OHIO

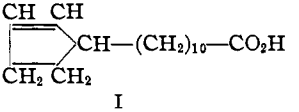
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SYNTHESIS OF A HOMOLOG OF CHAULMOOGRIC ACID. Δ^2-CYCLOPENTENYLACETIC ACID. VII

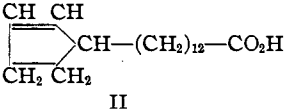
BY C. R. NOLLER[1] WITH ROGER ADAMS

RECEIVED JUNE 24, 1926 PUBLISHED SEPTEMBER 4, 1926

The successful syntheses of dihydrohydnocarpic and dihydrochaulmoogric acids[2c] and many of their homologs[2g] has led us to determine whether a similar procedure might not be employed to obtain hydnocarpic acid (I) and chaulmoogric acid (II) and their homologs.



I



II

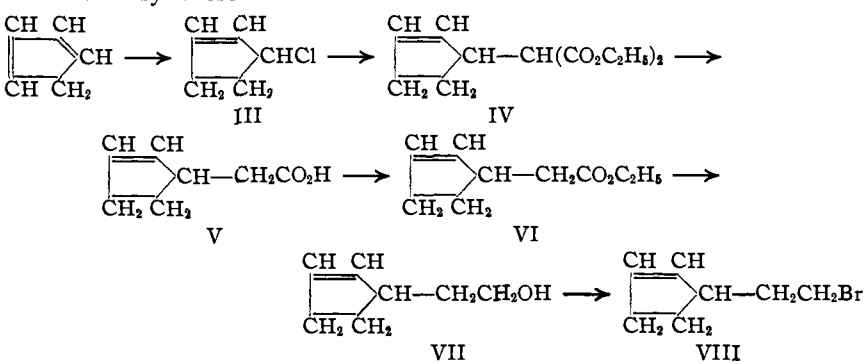
Although the preparation of hydnocarpic acid itself,[2a] the immediate goal, has not yet been reached, nevertheless a very important step forward has been made by finding a most satisfactory method for preparing certain Δ^2-cyclopentenyl compounds which may be used as intermediates in syn-

[1] This communication is an abstract of a portion of a thesis submitted by C. R. Noller in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

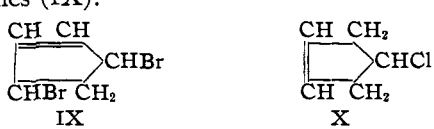
[2] (a) Shriner with Adams, THIS JOURNAL, **47**, 2727 (1925). (b) Noller with Adams, *ibid.*, **48**, 1074; (c) 1080 (1926). (d) Hiers with Adams, *ibid.*, **48**, 1089 (1926). (e) VanDyke and Adams, *ibid.*, **48**, 2393 (1926). (f) Sacks with Adams, *ibid.*, **48**, 2395 (1926). (g) Hiers with Adams, *ibid.*, **48**, 2385 (1926).

theses in this field. This communication describes the preparation of *dl*-Δ^2-cyclopentenylacetic acid (V) and *dl*-β-(Δ^2-cyclopentenyl) ethanol (VII). The former is a *dl* homolog of the natural acids and the latter, after conversion to the corresponding bromide, may be made into the Grignard reagent and condensed according to the methods used by Noller and Adams[2b] and by Hiers and Adams[2d,2g] to obtain various acids containing the Δ^2-cyclopentenyl group. In fact, *dl*-methyl hydroxyhydnocarpate has already been prepared.

Cyclopentadiene adds dry hydrogen chloride 1–4, thus producing Δ^2-cyclopentenyl chloride[3] (III). This in turn may be condensed with malonic ester to give an excellent yield of Δ^2-cyclopentenyl-malonic ester (IV) which by saponification and decomposition gives Δ^2-cyclopentenyl acetic acid (VI). This Δ^2-cyclopentenylacetic acid is readily converted to the corresponding ester (VI) and reduced with sodium and alcohol to Δ^2-cyclopentenyl ethanol VII. The corresponding bromide (VIII) is being used for further syntheses.



Although no direct proof has been given in this investigation that the double bond in the cyclopentenyl chloride or the compounds derived from it is in the Δ^2 position, several facts leave little doubt that this conclusion is correct. In the first place Thiele[4] showed that bromine adds 1–4 to cyclopentadiene. He obtained two *cis-trans* isomeric dibromocyclo pentenes which on oxidation yielded, respectively, inactive and racemic α-γ-dibromoglutaric acid. Hence the original bromides must be Δ'-2,5-dibromocyclopentenes (IX).



It seems logical to assume, therefore, that hydrogen chloride also adds 1–4.

Other evidence in favor of 1–4 addition is that if 1–2 addition had taken

[3] Kraemer and Spilker, *Ber.*, **29**, 552 (1896). Noeldechen, *Ber.*, **33**, 3348 (1900).

[4] Thiele, *Ann.*, **314**, 301 (1901).

place, a mixture of two isomeric cyclopentenyl chlorides might be expected having Structures III and X, whereas 1–4 addition would yield only Compound III. In the preparation of the chloride and in subsequent reactions, excellent yields were obtained and there were no indications of more than a single product at any step.

Finally Δ^2-cyclopentenyl chloride should contain a very reactive halogen atom whereas in Δ^3-cyclopentenyl chloride (X) the halogen should be no more reactive than that in an ordinary secondary alkyl chloride. Actually it was found that the compound formed is very reactive. For example, it reacts practically quantitatively and rapidly with sodio-malonic ester in the cold, whereas ordinary alkyl chlorides usually require refluxing to bring about condensation. More rigorous proof of the structure of these compounds is now being attempted.

Mr. G. H. Coleman has kindly tested the sodium *dl*-Δ^2-cyclopentenyl acetate bacteriologically. He finds no bactericidal action toward *B. leprae*. Whether this ineffectiveness is due to the short side chain or to the lack of optical activity must be decided only after more compounds are available.

Experimental Part

Δ^2-Cyclopentenyl Chloride, III.—Dry hydrogen chloride was passed into 86 g. of freshly redistilled cyclopentadiene at a temperature of $-20°$ to $-15°$ until it was saturated. This operation required from one and one-half to two hours. The mixture was allowed to stand for two hours at a temperature of $-15°$ to $-5°$. The crude product was then distilled under diminished pressure into a flask cooled to $-20°$ to $-15°$. The total distillate amounted to 112–119 g. (84–89%); b. p., 25–31° at 30 mm. This compound is a colorless liquid and fairly stable when kept at $-15°$. At room temperature it rapidly decomposes. It was condensed with sodio-malonic ester immediately after distillation.

A sticky residue remained in the flask after distillation of the chloride, which in some respects resembled rubber. It was quite elastic and was soluble in benzene but insoluble in alcohol and in ether.

Δ^2-Cyclopentenylmalonic Ester, IV.—To 700 cc. of absolute alcohol placed in a three-neck flask fitted with a mechanical stirrer and efficient reflux condenser was added 29.9 g. (1.3 moles) of clean metallic sodium. After solution of the sodium in alcohol and cooling to 40–50°, 208 g. (1.3 moles) of redistilled malonic ester was slowly added. The solution was cooled as low as possible in an ice- and water-bath without causing the precipitation of the sodium salt (about 5°) and then 112 g. (1.1 moles) of cyclopentenyl chloride was added over a period of one hour. The mixture was allowed to stand overnight at room temperature and then refluxed for one and one-half hours during stirring. The product was worked up in the usual way and distilled under diminished pressure. A small low-boiling fraction of about 25 g. distilled first, followed by the main fraction of cyclopentenyl-malonic ester boiling over a range of 5°. The yield was 208–218 g. (84–88%). On redistillation, it boiled at 120° (corr.) at 6 mm.; n_D^{20}, 1.4536; d_4^{20}, 1.0507.

Anal. Subs., 0.2094: CO_2, 0.4860; H_2O, 0.1514. Calcd. for $C_{12}H_{18}O_4$: C, 63.69; H, 8.01. Found: C, 63.30; H, 8.03.

Δ^2-Cyclopentenylmalonic Acid.—A mixture of 113 g. (0.5 mole) of cyclopentenyl-

malonic ester and a solution of 60 g. of sodium hydroxide in 500 cc. of water was boiled until the ester was completely in solution, and then for two hours longer. The solution was evaporated over a free flame until the salt began to crystallize, cooled and acidified with concd. hydrochloric acid to the Congo red end-point, and extracted with ether until no more malonic acid was obtained on evaporation of the solvent from a portion of the last extraction. As much of the ether as possible was distilled from a steam-bath and the residue taken up in hot benzene. All of the product dissolved at first but, on boiling, the remaining ether was removed and the cyclopentenylmalonic acid separated. After cooling, the malonic acid was filtered with suction; yield, 83 g. (97.6%). Recrystallization from benzene gave colorless crystals; m. p., 149–149.5° (corr.), with loss of carbon dioxide.

Anal. Subs., 0.1326: CO_2, 0.2733; H_2O, 0.0717. Calcd. for $C_8H_{10}O_4$: C, 56.44; H, 5.94. Found: C, 56.21; H, 6.01.

Δ^2-Cyclopentenylacetic Acid, V.—In a 500cc. round-bottomed flask fitted with a reflux condenser was placed 127.5 g. (0.75 mole) of Δ^2-cyclopentenylmalonic acid. This was carefully heated in a metal bath to a temperature of 150–160°, when carbon dioxide began to be liberated. If the heating above the melting point is too rapid, the evolution of carbon dioxide is so great that some of the cyclopentenylacetic acid is carried out of the condenser. After complete liquefaction had taken place it was heated for one hour to a temperature of 190°. On vacuum distillation there was obtained 91–93 g. of Δ^2-cyclopentenylacetic acid; b. p., 95–100° at 4 mm. (96–99%). On redistillation, it boiled at 94–95° (corr.) at 3 mm.; n_D^{20}, 1.4682, d_4^{20}, 1.0519.

Anal. Subs., 0.1986: CO_2, 0.4823; H_2O, 0.1425. Calcd. for $C_7H_{10}O_2$: C, 66.61; H, 8.01. Found: C, 66.23; H, 7.97.

Ethyl Δ^2-cyclopentenylacetate, VI.—A solution of 87.5 g. (0.7 mole) of Δ^2-cyclopentenylacetic acid in 300 cc. of absolute ethyl alcohol containing nine drops of concd. sulfuric acid was refluxed for six hours. It was then treated with sufficient 40% potassium hydroxide solution to neutralize all of the sulfuric acid (alkaline to Congo red). The yield of a practically pure product boiling over a range of 3° was 87.5–89.5 g. (81–83%). On redistillation, the product boiled at 85–86° (corr.) at 15 mm.; n_D^{20}, 1.4480; d_4^{20}, 0.9659.

Anal. Subs., 0.2002: CO_2, 0.5110; H_2O, 0.1622. Calcd. for $C_9H_{14}O_2$: C, 70.08; H, 9.17. Found: C, 69.77; H, 9.00.

A portion of the cyclopentenylacetic acid was recovered from the sodium carbonate washings of the ether solution of the crude product by evaporation to a small volume and acidifying.

β-(Δ^2-Cyclopentenyl)Ethanol, VII.—To 15.4 g. (0.1 mole) of ethyl-Δ^2-cyclopentenylacetate placed in a three-neck flask fitted with a mechanical stirrer and an efficient reflux condenser was added 100 cc. of absolute ethyl alcohol. The solution was heated almost to boiling and then 10 g. of clean metallic sodium was added in small pieces during stirring, at first slowly and then more rapidly. The addition of sodium should be as rapid as possible without allowing the mixture to foam out of the flask and into the condenser. Stirring was continued until all of the sodium had reacted. About 60 cc. of water was added and the solution boiled for one-half hour. The alcohol was then distilled through a column until the temperature of the vapor reached 83°. About 200 cc. of water was added to the reaction mixture, and the upper layer was separated and washed twice with water. The aqueous layer and washings were extracted twice with ether and the ether extracts combined with the alcohol layer and dried over anhydrous magnesium sulfate. After the ether had been distilled from a steam cone, the residue was distilled under diminished pressure, when there was obtained 10 g. (89%)

of practically pure cyclopentenyl ethanol boiling over a range of 2°. On redistillation the alcohol boiled at 86–87° (corr.) at 16 mm.; n_D^{20}, 1.4721; d_4^{20}, 0.9446.

Anal. Subs., 0.1928: CO_2, 0.5259; H_2O, 0.1852. Calcd. for $C_6H_{12}O$: C, 74.93; H, 10.80. Found: C, 74.39; H, 10.70.

The yield of alcohol decreased slightly when larger quantities of ester were reduced, dropping to about 82% on a 0.5 mole run.

Summary

A process is described for preparing Δ^2-cyclopentenylacetic acid and β-(Δ^2-cyclopentenyl)ethanol. These substances are valuable intermediates for the syntheses of derivatives and homologs of hydnocarpic and chaulmoogric acids.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE COMPOUND OF ORTHO-CRESOL AND PARA-CRESOL: A CORRECTION

BY ARTHUR E. HILL AND THOMAS W. DAVIS

RECEIVED JULY 2, 1926 PUBLISHED SEPTEMBER 4, 1926

In a recent paper on the cresols from this Laboratory,[1] evidence for the existence of a 1:1 compound was presented. Our attention has been directed to two earlier investigations of this system, by Fox and Barker[2] and by Dawson and Mountford;[3] the former found no evidence of compound formation and the latter found evidence of a compound of two molecules of the *p*-cresol with one of the *ortho*. We have repeated our investigation of the system by means of freezing-point determinations, and find that the conclusion of Dawson and Mountford is correct. Working with the greatest care to avoid undercooling and with the apparatus previously described[1] to insure absence of water, we have obtained the following data, which show a maximum for the freezing point of the compound lying near the

TABLE I

FREEZING POINTS OF *o*-CRESOL-*p*-CRESOL MIXTURES

o-Cresol, % by wt.	100	86.12	72.34	63.92	57.31	54.55	53.5[a]	52.11	
F. p., °C.	30.80	24.61	14.71	8.25	3.02	1.13	0	1.81	
Solid phase	*o*-	*o*-	*o*-	*o*-	*o*-	*o*-	*o* + comp.	comp.	
o-Cresol, % by wt.	44.70	37.19	37.19[b]	35.13[b]	33.3[a]	32.36	20.10	9.66	0
F. p., °C.	6.62	7.84	5.13	7.19	8.1	10.10	21.25	29.19	34.61
Solid phase	comp.	comp.	*p*-	*p*-	comp. + *p*-	*p*-	*p*-	*p*-	*p*-

[a] By extrapolation.

[b] Metastable.

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[1] Hill and Mosbacher, THIS JOURNAL, **47**, 2544 (1925).

[2] Fox and Barker, *J. Soc. Chem. Ind.*, **18**, 268 (1918).

[3] Dawson and Mountford, *J. Chem. Soc.*, **113**, 923 (1918).