tion presented here could be a useful supplement to the standard methods for determining absolute configuration.

In all tables, unless otherwise specified, the rotations were measured in water. A solvent other than water is indicated by the following symbols appearing after the specific rotation value: A—acetone, C—chloroform, E—ethanol, M—methanol, P—pyridine. The epimeric pairs that do not conform to our predictions are underlined.

Acknowledgments. Thanks are due to Dr. S. R. Sen-Gupta and Dr. S. K. Bhattacharyya for their interest and to Dr. F. Kagan for valuable suggestions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Physiologically Active Compounds. II. Hydrochlorides of Aminoesters of Substituted Benzilic and Glycolic Acids[1]

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Thirty-nine aminoester hydrochlorides of substituted benzilic and glycolic acids were synthesized. Two of these compounds appear to be more active in experimental animals than atropine in preventing mortality from an anticholinesterase compound and four of them exhibit the highest anticholinergic activity. One compound previously reported offers some advantage over three of these as an anticholinergic.

In a previous paper[3] it was shown that many aminoesters of benzilic acids show some physiological activity. This article reports further studies of the preparation and physiological activity of such compounds.

The benzilic acids, with the exception of certain phenyl-substituted ones, utilized in the preparation of the hydrochlorides listed in Table I, were prepared by or were available from the methods of Smith and Shacklett.[4] The syntheses of the exceptions are listed below. Ethyl-3-phenylbenzilate (II) was prepared from 3-bromodiphenyl (I) which

(1) A portion of this paper was presented at the Southeastern Regional Meeting of the American Chemical Society, Durham, N. C., November, 1957.

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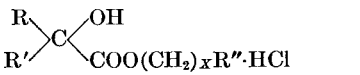
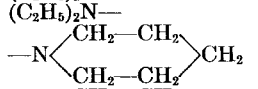
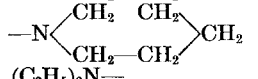
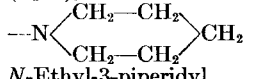
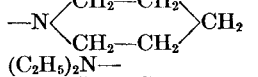
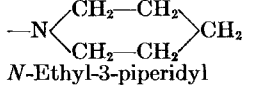
(3) H. A. Smith, C. A. Buehler, and K. V. Nayak, *J. Org. Chem.*, **21**, 1423 (1956).

(4) H. A. Smith and C. D. Shacklett, *J. Am. Chem. Soc.*, **75**, 2654 (1953).

TABLE 1

ESTER HYDROCHLORIDES OF SUBSTITUTED BENZILIC ACIDS

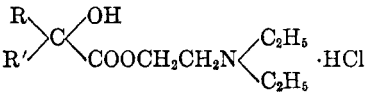


No.	R	R′	R″	X	Yield, %	Melting Point, °C.	Analyses			
							Calculated		Found	
							C	H	C	H
26	2-$CH_3C_6H_4$	2-$CH_3C_6H_4$	*N*-Ethyl-3-piperidyl	0	69	186–187	68.38	7.49	68.20	7.70
27	3-$CH_3C_6H_4$	3-$CH_3C_6H_4$	*N*-Ethyl-3-piperidyl	0	81	150–151	68.38	7.49	68.02	7.33
28	4-$(CH_3)_2CHC_6H_4$	4-$(CH_3)_2CHC_6H_4$	$(C_2H_5)_2N$—	2	64	181–182	69.70	8.55	69.47	8.82
29	2-$CH_3OC_6H_4$	2-$CH_3OC_6H_4$	$(C_2H_5)_2N$—	2	65	171–172	62.33	7.13	61.78	7.25
30	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	$(C_2H_5)_2N$—	2	77	167–168.5	62.33	7.13	62.42	7.20
31	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$		2	92[a]	181–182	63.37	6.94	63.08	7.11
32	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$		2	53[a,b]	147–148	58.30	6.52	58.10	6.62
33	2,3-$(CH_3O)_2C_6H_3$	2,3-$(CH_3O)_2C_6H_3$	$(C_2H_5)_2N$—	2	83	184–185	59.56	7.08	59.33	7.29
34	3,4-$(CH_3O)_2C_6H_3$	3,4-$(CH_3O)_2C_6H_3$	$(C_2H_5)_2N$—	2	79	167.5–168.5	59.56	7.08	59.30	7.27
35	3,4-Methylenedioxyphenyl	C_6H_5	$(C_2H_5)_2N$—	2	73	164–165.5	61.83	6.43	61.71	6.46
36	3-$C_6H_5C_6H_4$	C_6H_5	$(C_2H_5)_2N$—	2	73	136–137	70.97	6.87	70.79	6.86
37	4-$C_6H_5C_6H_4$	C_6H_5	$(C_2H_5)_2N$—	2	60	178–179	70.97	6.87	71.50	7.00
38	4-$C_6H_5C_6H_4$	C_6H_5		2	70	189–190	71.77	6.69	71.56	6.62
39	4-$C_6H_5C_6H_4$	C_6H_5	*N*-Ethyl-3-piperidyl	0	65	149–150	71.74	6.69	71.27	6.72
40	3-$C_6H_5C_6H_4$	3-$C_6H_5C_6H_4$	$(C_2H_5)_2N$—	2	59	158–159	74.47	6.64	74.74	6.75
41	3-$C_6H_5C_6H_4$	3-$C_6H_5C_6H_4$		2	68	197–198	75.05	6.49	75.14	6.53
42	4-$C_6H_5C_6H_4$	4-$C_6H_5C_6H_4$	$(C_2H_5)_2N$—	2	72	183–185	74.47	6.64	74.11	6.82
43	4-$C_6H_5C_6H_4$	4-$C_6H_5C_6H_4$		2	47	192–193	75.05	6.49	74.83	6.47
44	4-$C_6H_5C_6H_4$	4-$C_6H_5C_6H_4$	*N*-Ethyl-3-piperidyl	0	74	190–191	75.05	6.49	74.50	6.28

[a] Prepared by T. A. Magee of this laboratory. [b] Methyl bromide.

TABLE II

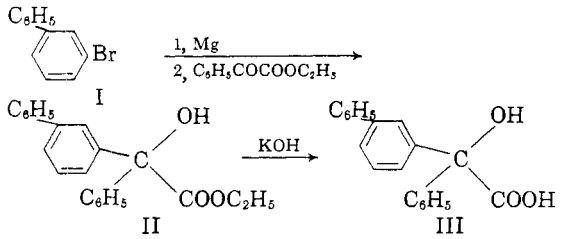
ESTER HYDROCHLORIDES OF DICYCLOHEXYLGLYCOLIC ACIDS

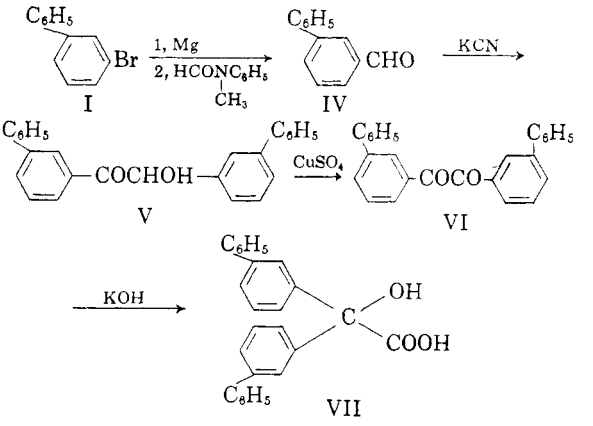


No.	R	R′	Yield, %	Melting Point, °C.	Analyses Calculated C	Calculated H	Found C	Found H
45[a]	C_6H_{11}	C_6H_{11}	72[b]	258–259	62.14	9.85	62.58	9.58
46[c]	C_6H_{11}	C_6H_{11}	35	212–213	65.01	9.87	65.03	9.78
47	2-$CH_3C_6H_{10}$	C_6H_{11}	76	165–166.5	64.67	10.34	64.46	10.60
48	3-$CH_3C_6H_{10}$	C_6H_{11}	86	181–182	64.67	10.34	64.42	10.14
49	4-$CH_3C_6H_{10}$	C_6H_{11}	87	190.5–192	64.67	10.34	64.89	10.42
50	2-$CH_3C_6H_{10}$	2-$CH_3C_6H_{10}$	80	163.5–164.5	65.40	10.48	65.35	10.63
51	2,3-$(CH_3)_2C_6H_9$	C_6H_{11}	79	174–175	65.40	10.48	65.65	10.21
52	2,4-$(CH_3)_2C_6H_9$	C_6H_{11}	79	155–156	65.40	10.48	65.02	10.31
53	2,6-$(CH_3)_2C_6H_9$	C_6H_{11}	81	181–182	65.40	10.48	65.52	10.71
54	3,4-$(CH_3)_2C_6H_9$	C_6H_{11}	80	177.5–178.5	65.40	10.48	65.59	10.36
55	3,5-$(CH_3)_2C_6H_9$	C_6H_{11}	73	171.5–173	65.40	10.48	65.23	10.53
56	3-$CH_3C_6H_{10}$	3-$CH_3C_6H_{10}$	84	178.5–179.5	65.40	10.48	65.48	10.42
57	4-$CH_3C_6H_{10}$	4-$CH_3C_6H_{10}$	82	187–188	65.40	10.48	65.75	10.41
58	2,3,5-$(CH_3)_3C_6H_8$	C_6H_{11}	76	193–194	66.07	10.61	66.29	10.32
59	3,4,5-$(CH_3)_3C_6H_8$	C_6H_{11}	90	216.5–218	66.07	10.61	66.32	10.38
60	3,5-$(CH_3)_2C_6H_9$	3,5-$(CH_3)_2C_6H_9$	84	183–184	66.71	10.73	66.49	10.47
61	4-$(CH_3)_2CHC_6H_{10}$	4-$(CH_3)_2CHC_6H_{10}$	84	185–187	67.86	10.95	67.63	11.16
62	3-$C_6H_{11}C_6H_{10}$	C_6H_{11}	43	133–134	68.16	10.56	68.01	10.26
63	4-$C_6H_{11}C_6H_{10}$	C_6H_{11}	76	174.5–175.5	68.16	10.56	68.21	10.77
64	2,3,6-$(CH_3)_3C_6H_8$	C_6H_{11}	76	199–200	66.07	10.61	65.91	10.35

[a] Dimethylaminoester prepared by T. A. Magee of this laboratory. [b] Based on free acid. [c] Piperidinoester prepared by T. A. Magee of this laboratory.

in turn was prepared from 2-aminodiphenyl by the method of Huber and co-workers.[5] The bromo compound upon treatment with magnesium and ethyl phenylglyoxylate[6] gave the ethyl ester which on saponification produced 3-phenylbenzilic acid (III).





2-Phenylbenzilic acid could be prepared neither by an analogous procedure from 2-bromodiphenyl, through the action of 2-diphenylmagnesium iodide on isonitrosoacetophenone, nor through a mixed benzoin condensation of benzaldehyde and 2-phenylbenzaldehyde. The Grignard reagent of 3-bromodiphenyl (I) reacted with *N*-methylformanilide to produce 3-phenylbenzaldehyde (IV) which was subjected to the benzoin condensation to produce 3,3′-diphenylbenzoin (V). The latter was oxidized with copper sulfate in pyridine to the corresponding benzil (VI) which on rearrangement with potassium hydroxide gave 3,3′-diphenylbenzilic acid (VII). It is interesting to note that the 2,2′-diphenylbenzilic acid could not be produced because of the failure of 2-phenylbenzaldehyde to undergo the benzoin condensation.

The hydrochlorides of the aminoesters in Table I were prepared by the method of Blicke and Grier[7] in which the proper benzilic acid was refluxed with the aminoethyl chloride in dry isopropyl alcohol.

For the most part the aminoester hydrochlorides listed in Table II were prepared by the complete hydrogenation of the benzilic ester analogs (obtained as indicated above) in glacial acetic acid using Adams' platinum oxide as a catalyst. The single variation in this total procedure occurred with compound 46 in which the unreduced ester was prepared by the method of Hill and

(5) W. F. Huber, M. Renoll, A. G. Rossou, and D. T. Mowry, *J. Am. Chem. Soc.*, **68**, 1111 (1946).

(6) C. D. Shacklett, *The Catalytic Hydrogenation of Benzilic Acid*, M.S. thesis, University of Tennessee, 1947.

(7) F. F. Blicke and N. Grier, *J. Am. Chem. Soc.*, **65**, 1727 (1943).

Holmes[8] wherein the methyl ester was refluxed with the appropriate amino alcohol.

The tests which are described in the previous paper[3] were made in the Physiology Division of the Directorate of Medical Research in the U. S. Army Chemical Warfare Laboratories at Army Chemical Center, Md., by Drs. Gerald Groblewski, J. H. Wills, and John F. O'Leary, to whom we are greatly indebted. The results of the tests are found in Tables III, IV, and V. An examination of these tables shows that:

1. Two compounds, the diethylaminoethylester hydrochloride, 37, and the 3-*N*-ethylpiperidinoester hydrochloride, 39, of 4-phenylbenzilic acid, appear to be more active than atropine in preventing mortality from an anticholinesterase compound.

2. The most actively anticholinergic compounds of the thirty-nine reported here are 2, 35, 49, and 59. Compounds 35 and 59 are surpassed in activity by compound 11, the synthesis of which was described in the previous paper and for which anticholinergic tests are now available. This compound has much more marked effects on blood pressure and respiration than any of the four new compounds.

3. Compounds effective in dilating the pupil of the eye without significant irritant action are 26, 33, 35, 39, 43, and 44. Compounds 36 and 40, which resemble 33 and 35 in being diethylaminoethanol derivatives, are as active as the latter two compounds in dilating the pupil, but are definitely irritating.

EXPERIMENTAL[9]

β-Aminoethyl chlorides. These chlorides were prepared by the procedures given for β-diethylaminoethyl chloride and β-*N*-piperidinoethyl chloride in the previous paper.[3]

N-Ethyl-3-chloropiperidine. The action of thionyl chloride on tetrahydrofurfuryl alcohol gave a 73% yield of tetrahydrofurfuryl chloride.[10] The method of Biel[11] was employed in which tetrahydrofurfuryl chloride, diethylamine, and sodium iodide produced *N,N*-diethyltetrahydrofurfuryl amine in a 53% yield. This amine was converted to *N*-ethyl-3-hydroxypiperidine by means of hydrogen bromide in an 80% yield. Thionyl chloride was used to convert the hydroxy compound to *N*-ethyl-3-chloropiperidine hydrochloride and aqueous sodium hydroxide was employed to give *N*-ethyl-3-chloropiperidine.

β-Aminoester hydrochlorides of substituted benzilic acids. These were prepared as described in the previous paper.[3]

Ethyl 3-phenylbenzilate (II). 3-Bromodiphenyl (I) and ethyl phenylglyoxylate were prepared by the methods of Huber and coworkers[5] and Shacklett,[6] respectively. In a 1-l., three-necked flask equipped with a reflux condenser, mechanical stirrer, and a dropping funnel was placed 2.51 g. (0.11 mole) of magnesium in an atmosphere of nitrogen. Enough dry ether was added to cover the magnesium and 23.4 g. (0.10 mole) of 3-bromodiphenyl in 300 ml. of dry ether was added dropwise as the mixture was stirred vigorously. After the addition was complete, the solution was refluxed for 2 hr. In another 1-l., three-necked flask equipped as before was placed 17.8 g. (0.10 mole) of ethyl phenylglyoxylate in 200 ml. of dry ether, and the prepared Grignard reagent was added dropwise. This solution was refluxed for 2 hr. and 250 ml. of a dilute hydrochloric acid solution was added dropwise. The ethereal layer was separated and the aqueous phase was extracted with two 150-ml. portions of ether. The combined ether extracts were dried with anhydrous magnesium sulfate and the ether was removed by heating. The residue was distilled *in vacuo*, b.p. 213–218° (1 mm.), to give 18 g. (55%) of pure product.

3-Phenylbenzilic acid. Ethyl 3-phenylbenzilate, 18 g., was dissolved in 30 ml. of ethanol and this solution was added to 100 ml. of an aqueous solution containing 20 g. of potassium hydroxide. The solution was refluxed for 3 hr. and diluted with 200 ml. of water. Upon acidification with dilute hydrochloric acid, a precipitate formed which was removed by filtration. The solid, 11 g. (65%), was recrystallized three times from benzene to give the pure acid, m.p. 127–128°.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.92; H, 5.30. Found: C, 78.53; H, 5.34.

TABLE III

ANTICHOLINESTERASE SCREENING (TEST 1)

(Tests on rabbits with standard 2.0 mg./kg. unless otherwise indicated)

Compared to Atropine			
More Active	Equally as Active		Less Active
37	26[a]	48	27[a]
39[a]	30[a]	49[a]	28[b]
	31	50	29
	33[a]	52	
	35[a]	53	32
	38	54[c]	34[a]
	41[a]	55[a]	36[a]
	43[a]	58	40[a]
	44[a]	60[a]	42[a]
	47[a]	61[a]	51
			56[a]
			57[a]
			59[a]
			62[a]
			63

[a] Test on rats. [b] Test on rats and rabbits. [c] Dose of 0.5 mg./kg.

3-Phenylbenzaldehyde (IV). To a 1-l., three-necked flask equipped with a mechanical stirrer, dropping funnel, and a reflux condenser was added 2.51 g. (0.11 mole) of magnesium, and a solution of 23.4 g. (0.10 mole) of 3-bromodiphenyl (I) in 250 ml. of dry ether was added dropwise in an atmosphere of nitrogen. Upon completion of the reaction, 13.5 g. (0.10 mole) of Eastman grade *N*-methylformanilide was added in the course of 2 hr. A vigorous reaction began and a copious white precipitate was obtained. Any ether lost by evaporation was replaced and stirring was continued for 1 hr. The magnesium compound produced was decomposed by adding large quantities of ice and small quantities of dilute hydrochloric acid. The ether layer was removed and the aqueous portion was further extracted with a 100-ml. portion of ether. The combined extracts were dried over

(8) A. J. Hill and R. B. Holmes, U. S. Patent 2,294,770 (1946).

(9) Melting points were determined on an aluminum melting point block and are uncorrected.

(10) L. A. Brooks and H. R. Snyder, *Org. Syntheses*, **25**, 84 (1945).

(11) J. H. Biel, H. L. Friedman, H. A. Leiser, and E. P. Sprengeler, *J. Am. Chem. Soc.*, **74**, 1486 (1952). A portion of the final product was supplied by Mr. Biel to whom our thanks are due.

TABLE IV

BLOOD PRESSURE, GUT, AND RESPIRATION EFFECTS (TESTS 2, 3, 4)

No.	Dose, Mg./Kg.	Effect on B.P. Fall in % After: Acetylcholine (2.5 γ)	Effect on B.P. Fall in % After: Histamine (1.5 γ)	Gut	B.P.	Respiration
2[a]	0.5	−77	−58	Tonus and rate decrease markedly	None	None
7[a]	0.5	+90	+38		Slight fall	
8[a]	0.5	−27	−16		Slight fall	
10[a]	0.5	−29	+100		Slight fall	
11[a]	0.5	−45	−56	Tonus and rate increase	Fall 85% then rise to 211%	Temporary apnea then increase two times
14[a]	0.5	+5	None	Tonus and rate decrease temporarily	Temporary fall (27%)	− Depth then two times increase, − rate
17[a]	0.5	−6	−22	None	Temporary fall (22%)	None
18[a]	0.5	None	−8	Slight decrease then increase in tonus and rate	Temporary fall (100%)	− Depth then +, − rate
19[a]	0.5	+33	−17		Slight fall	
20[a]	0.5	−33	+25		Moderate fall	
24[a]	0.5	−8	−59		Slight fall	+ Rate
25[a]	0.5	+5	−8		Slight fall	+ Rate
28	9.5	−13	−9	Temporary depression	−24%	+ Depth, + rate
29	6.0	+10	+17	None	−11%	− Depth
30	7.0	−30	−6	Depresses spontaneous activity and response to Ach. and Hist.	Immediate depressor effect	None
33	0.5	0	−20	None	None	None
34	0.5	+20	+51	None	None	None
35	0.5	−37	−21	Tonus decrease then increase	−18%	− Depth, + rate
36	0.5	−12	−17			
37	5.5	−5	None	None	−14%	Temporary apnea
39	0.5	None	+30		Temporary fall (31%)	
40	0.5	+17	−11		Slight fall	
41	0.5	+7	−24		Temporary fall (42%)	
44	0.5	−6	+33		Temporary fall (21%)	
47	0.5	−13	+40	None	Slight depression	None
49	0.5	−75	+27	Tonus and rate increase greatly	Temporary fall (17%)	None
51	0.5	−6	None		Slight fall	
53	0.5	−19	−40			Brief hypapnea
55	0.5	−5	−20	None	None	+ Depth, + rate
56	0.5	−3	−7	Fall	None	None
59	0.5	−36	−37	None	Slight fall	+ Rate
61	0.5	None	−7	None	Temporary fall (63%)	None
62	0.5	−4	−20			

[a] Number from previous paper, Reference 3, the physiological tests of which have not been reported previously.

TABLE V

EYE EFFECTS[a] (TESTS 5, 6)

Mydriasis: Active	Mydriasis: Moderately Active	Mydriasis: Least Active	No Definite Effect	Miosis, Active	Local Irritation, Active
26	27	31	30	46	28
33	28	41		56	36
35	45	42	37		40
36		55	49		55
39			57		57
40			60		59
43			62		61
44					62

[a] No compound produced local anesthesia.

anhydrous magnesium sulfate and the ether was removed by heating. The residue was distilled *in vacuo* to give 14 g. (86%) of a clear liquid, b.p. 138–144° (2 mm.).

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.76; H, 5.58.

The *2,4-dinitrophenylhydrazone* was prepared, m.p. 234–235°.

Anal. Calcd. for $C_{19}H_{14}N_4O_4$: C, 62.98; H, 3.89. Found: C, 62.87; H, 3.98.

3,3'-Diphenylbenzil (VI). In a 250-ml., round-bottomed flask, a solution of 8 g. of 3-phenylbenzaldehyde (IV), 3 g. of potassium cyanide in 40 ml. of water, and 80 ml. of ethanol was refluxed for 10 hr. The solution was cooled, but no crystals were formed. Upon dilution with water, an oil separated which failed to crystallize. This mixture was extracted twice with ether and the combined ethereal extracts were dried over anhydrous magnesium sulfate. The ether was removed

by heating to yield 6 g. of an orange oil. A mixture of 6 g. of this oil, 14 g. of copper sulfate pentahydrate, 100 ml. of pyridine, and 30 ml. of water was refluxed for 6 hr. The reaction mixture was poured onto 500 ml. of ice water and a semisolid formed. The liquid was decanted and the semisolid which remained was washed with water. This semisolid was dissolved in absolute ethanol and the solution was filtered to remove the insoluble copper salts. Upon cooling, a yellow solid, 2.7 g. (34%) which was removed by filtration, was formed. Recrystallization twice from absolute ethanol and once more from methanol gave the pure diketone, m.p. 119–120°.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 86.17; H, 5.13.

The *quinoxaline* derivative melted at 156°.

Anal. Calcd. for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10. Found: C, 88.16; H, 5.15.

3,3'-Diphenylbenzilic acid (VII). 3,3'-Diphenylbenzil (VI), 8 g., was dissolved in 300 ml. of dry ether and a solution of sodium ethoxide (4 g. of sodium in 50 ml. of 95% ethanol) was added. Also, 25 ml. of absolute ethanol was added to prevent precipitation of sodium ethoxide. The flask was stoppered and was allowed to stand for 24 hr. with frequent shaking. This solution was extracted with four 100-ml. portions of water and the aqueous solution was extracted with two 50-ml. portions of ether. After heating this solution to 90° to expel the ether, the solution was acidified with dilute hydrochloric acid and was cooled. The solid, which formed, was removed by filtration to give 3 g. (37%) of the crude acid. This acid was purified by recrystallization three times from benzene using Norit A each time. The pure acid melted at 155–157°.

Anal. Calcd. for $C_{26}H_{20}O_3$: C, 82.08; H, 5.30. Found: C, 82.17; H, 5.17.

β-Aminoester hydrochlorides of dicyclohexylglycolic acids. The corresponding benzilate was dissolved in glacial acetic acid and hydrogenated (3 atm.) in the presence of platinum catalyst (0.1 g. per 0.01 mole of ester) until reduction was complete. The catalyst was removed by filtration and the acetic acid was removed *in vacuo*. The solid which remained was dissolved in 10 ml. of absolute ethanol and precipitated by the addition of 90 ml. of dry ether. One more recrystallization from an ethanol-ether (1:9) mixture gave the pure product.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF EMORY UNIVERSITY]

Condensation of Abietic Acid with Formaldehyde[1]

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Abietic acid has been condensed with formaldehyde in propionic acid solution to give in 51% yield 8,9-bismethylenepropionoxyabietic acid, isolated as the cyclohexylamine salt. Hydrolysis afforded 8,9-dimethylolabietic acid. The structure of this substance was established by catalytic dehydrogenation to 1,8,10-trimethyl-2-isopropylphenanthrene and comparison with the totally synthesized compound.

Although it is known[2] that abietic acid reacts with formaldehyde and certain other aldehydes to give resinous products, the nature of these products has not been established. Indeed, very few studies[3] have dealt with the behavior of conjugated dienes in the Prins reaction with aldehydes. We wish now to report a study of the acid catalyzed reaction of abietic acid (I) with formaldehyde including the determination of structure of a major product of this reaction.

All attempts to cause abietic acid to react with formaldehyde in aqueous solution or in such inert solvents as diisopropyl ether or *p*-dioxane failed; abietic acid could be recovered unchanged in each case. Similarly, attempts to condense abietic acid with formaldehyde in the presence of aqueous sulfuric acid (10%) led to recovery of unchanged abietic acid. This result is to be contrasted with the marked effect of sulfuric acid upon abietic acid in homogeneous media; *vide infra*.

Treatment of abietic acid with paraformaldehyde and a catalytic amount of sulfuric acid in *p*-dioxane solution led to exothermic reaction and formation of condensation products. From one to four moles of formaldehyde could be made to enter into the reaction with abietic acid, the number being determined only by the number of moles of formaldehyde introduced into the reaction mixture. From none of these reactions was a homogeneous product obtained. The product resulting from reaction of 1 molar equivalent of formaldehyde with abietic acid showed neutral equivalent 327, while that calculated for a methylolabietic acid is 332. Similarly, other crude reaction products showed neutral equivalent values close to those calculated for the introduction of two, three, and four form-

(1) Abstracted from a thesis presented by Joseph L. Greene, Jr., to the Graduate Faculty of Emory University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August 1957.

(2) A. L. Osterhof, U. S. Patent **2,084,218**, June 15, 1937; H. L. Morrill, U. S. Patent **2,519,780**, Aug. 22, 1950; R. R. Whetstone, W. J. Raab, and S. A. Ballard, U. S. Patent **2,568,426**, Sept. 18, 1951; W. E. St. Clair, M.S. Thesis, Tulane University, 1949.

(3) See E. Arundale and L. A. Mikeska, *Chem. Revs.*, **51**, 505 (1952).