allowed to stand for four days with occasional warming. Ice was next introduced to decompose excess hydride reagent and the reaction complex then hydrolyzed with dilute sulfuric acid. The ether layer was removed and the aqueous layer extracted with fresh ether. The combined ether extracts were then washed with water and extracted with dilute sodium carbonate solution to remove unreacted podocarpic acid. After drying over anhydrous potassium carbonate the ether solution was concentrated and hexane added. On cooling transparent cubes of podocarpinol crystallized out of solution; m. p. 177–178.5°. Recrystallization from ether gave 3.7 g. (56%) of pure material; m. p. 178–179°.

Anal.[8] Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.09; H, 9.08.

In an earlier run in which the total reaction time was two hours a yield of 4.6% of podocarpinol was obtained.

Methylation of podocarpinol with dimethyl sulfate in the usual manner gave O-methylpodocarpinol (m. p. 90–91°), first prepared by Campbell and Todd.[4] A mixed m. p. with the O-methylpodocarpinol prepared as described below showed no depression.

O-Methylpodocarpinol (V). (*a*) **From O-Methylpodocarpoyl Chloride (IV).**—Reaction between 33 g. of O-methylpodocarpoyl chloride (m. p. 61°) in 1 liter of ether and 10 g. of lithium aluminum hydride in 800 ml. of ether was carried out over a period of four days. The mixture was worked up in the same manner as described above (m. p. 91°) from which 28 g. (92%) of pure O-methylpodocarpinol was obtained after one crystallization from ether–hexane.

(*b*) **From Methyl O-Methylpodocarpate (III).**—Lithium aluminum hydride (8 g.) in 400 ml. of ether was treated with 15 g. of methyl O-methylpodocarpate m. p. 158–159° in 300 ml. of ether as above. From this experiment there was obtained 12.7 g. (93%) of O-methylpodocarpinol; m. p. 91°.

(8) Analysis by Dr. Carl Tiedcke Microlaboratories, New York.

RIDBO LABORATORIES, INC.
PATERSON 3, NEW JERSEY RECEIVED JANUARY 12, 1948

NEW COMPOUNDS

α-Nitrostilbene Analogs

The *alpha*-nitrostilbenes are physiologically active. Also compounds of the *alpha*, *beta*-diphenylethylamine type obtained by further reduction have been reported to have a selective effect in damaging sarcoma cells.[3]

Accordingly we have prepared nitro compounds of this type and submitted them to the National Cancer Institute for testing.

1-α-Thienyl-2-phenyl-2-nitroethylene was prepared by mixing 9.0 g. phenylnitromethane, 8.1 g. 2-thiophenealdehyde[4] and 3 ml. of a 10% solution of methylamine in methanol, warming gently, then shaking for three hours at room temperature. The bright yellow crystals which separated weighed 4.9 g. After triple recrystallization from absolute ethanol the product melted at 123° cor.

Anal. Calcd. for $C_{12}H_9O_2SN$: C, 62.34; H, 3.90; N, 6.06. Found: C, 62.45; H, 3.76; N, 6.06.

(1) Present address: Medical School, University of Tennessee, Memphis, Tennessee.

(2) Present address: Plough, Inc., Memphis, Tennessee.

(3) Shear, *et al.*, *Approaches to Tumor Chemotherapy*, American Association for the Advancement of Science, Washington, D. C. (1947), page 236 ff.; also Hartwell and Kornberg, THIS JOURNAL, **67**, 1607 (1946).

(4) Purchased from Arapahoe Chemicals, Inc., Boulder, Colo.

1-α-Furyl-2-*o*-chlorophenyl-2-nitroethylene was prepared by mixing 7.82 g. of *o*-chlorophenylnitromethane, 4.36 g. of freshly distilled furfural, and 5.16 cc. of a 16% solution of methylamine in methanol. The crystals which separated on standing three days weighed 3.96 g. The product was dissolved in absolute ethanol and the solution decolorized with activated carbon. After recrystallization from absolute ethanol the melting point was 101.1° cor.

Anal. Calcd. for $C_{12}H_8NO_3Cl$: C, 57.72; H, 3.21; N, 5.61. Found: C, 57.92; H, 3.12; N, 5.53.

1-*m*-Nitrophenyl-2-phenyl-2-nitroethylene was prepared by mixing 3 ml. of phenylnitromethane, 3.0 g. of *m*-nitrobenzaldehyde,[5] 0.5 ml. of 10% methylamine and 6 ml. of methanol. After standing four days the solution was diluted with 25 ml. of petroleum ether and chilled in Dry Ice. The yield of crystals was only 0.4 g. (7.5%). After recrystallization from absolute ethanol the melting point was 112.0° cor.

Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 62.22; H, 3.70; N, 10.37. Found: C, 62.60; H, 3.75; N, 10.12.

1-*p*-Nitrophenyl-2-phenyl-2-nitroethylene, reported by Baker and Wilson[6] as melting at 155°, was prepared by us and found to melt at 157.5° cor., after repeated recrystallization.

Acknowledgment.—We wish to acknowledge our indebtedness to Dr. M. J. Shear and Dr. Jonathan L. Hartwell of the National Cancer Institute for suggestions and encouragement, to Mr. Charles A. Kinser and Mrs. Margaret M. Ledyard of the National Institute of Health for carrying out the microanalyses recorded above, and to the National Cancer Institute for financial assistance.

(5) Purchased from Eastman Kodak Company, Rochester, N. Y.

(6) Baker and Wilson, *J. Chem. Soc.*, 842–848 (1927).

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3-Chloro-6-methoxy-8-nitroquinoline

To a stirred mixture of 300 ml. of concentrated hydrochloric acid, 50.4 g. of 3-nitro-4-aminoanisole and 85.2 g. of arsenic acid, at 100°, there was added 30.0 g. of α-chloroacrolein during one hour. After an additional hour at 100°, the mixture was poured on ice. A solid which separated was filtered off and recrystallized from acetone; yield 16 g., m. p. 151–153°. Recrystallization from methanol raised the m. p. to 159.5–160°.

Anal. Calcd. for $C_{10}H_7ClN_2O_3$: C, 50.31; H, 2.94; Cl, 14.88; N, 11.74. Found: C, 50.68; H, 2.84; Cl, 15.06; N, 11.75.

The original aqueous filtrate gave no product on neutralization.

THE DIVISION OF MEDICINAL CHEMISTRY
THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH
NEW BRUNSWICK, N. J.
HARRY L. YALE

RECEIVED JANUARY 23, 1948

New Compounds as Insect Repellents

The compounds listed in Table I were prepared as part of a project to discover new insect repellents.[1]

2,2-Diethyl-1,3-Propanediol.—A solution of 43 g. of potassium hydroxide in 400 ml. of 95% ethanol was added to an ice-cooled, well-stirred mixture of 167 g. of 38% formaldehyde solution and 100 g. of 2-ethylbutyraldehyde (Eastman Kodak Co.) at such a rate that the tem-

(1) This work was performed under Contract NDCrc 136 between Harvard University and the Office of Scientific Research and Development, with Paul D. Bartlett as official investigator.

TABLE I

Compound	Boiling point[a] °C.	Mm.	M. p., °C.	$n^{25}D$	Yield, %	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
2,2-Diethyl-1,3-propanediol	130–133	16	53–55	1.4574[b]	76	$C_7H_{16}O_2$	63.6	12.2	63.9	12.5
2,2-Diethyl-1,3-propanediol diacetate	73– 76	0.5	...	1.4332	65	$C_{11}H_{20}O_4$	61.1	9.3	61.0	9.4
2-(*p*-Methoxyphenyl)-5,5-diethyl-*m*-dioxane	167	2.5	30–32	1.5122[b]	49	$C_{15}H_{22}O_3$	72.0	8.9	72.1	9.0
1-Phenyl-1,3-propanediol dipropionate	114–117	0.3	...	1.4880	83	$C_{15}H_{20}O_4$	68.2	7.6	68.7	7.8
n-Propyl piperonylate	101–103	0.3	...	1.5295	72[c]	$C_{11}H_{12}O_4$	63.5	5.8	63.0	5.9
n-Butyl piperonylate	101–104	0.1	...	1.5238	60[c]	$C_{12}H_{14}O_4$	64.9	6.4	64.5	6.3
n-Amyl piperonylate	117–120	0.1	52–53	....	50[c]	$C_{13}H_{16}O_4$	66.1	6.8	66.6	7.1
n-Propyl *p*-methoxycinnamate	110–120	0.1	13–14	1.5706	73	$C_{13}H_{16}O_3$	70.9	7.3	70.9	7.4
Isoamyl *p*-methoxycinnamate	156–158	0.7	...	1.5549	72	$C_{15}H_{20}O_3$	72.6	8.1	72.7	7.8
Diisopropyl hexahydrophthalate	136–138	10	...	1.4421	48	$C_{14}H_{24}O_4$	65.6	9.4	65.7	9.5
Di-*n*-butyl hexahydrophthalate	135–136	0.7	...	1.4511	77	$C_{16}H_{28}O_4$	67.6	9.9	67.1	10.1
Benzaldehyde di-*n*-butyrate	128–130	1	...	1.4791	77	$C_{15}H_{20}O_4$	68.2	7.6	68.7	7.9
p-*n*-Propylphenethyl alcohol	97– 98	1	...	1.5155	36	$C_{11}H_{16}O$	80.4	9.8	79.9	10.0
N-Cyclohexyl-N-phenylpropionamide	122	0.2	86–87	....	81	$C_{15}H_{21}NO$	77.9	9.2	78.3	8.9

[a] Fractionations were through a five-inch indented Claisen distillation head. [b] For super-cooled liquid. [c] Based on piperonylic acid.

perature did not exceed 16°. The resultant solution stood at room temperature for three days, was neutralized with carbon dioxide, and the alcohol was removed by distillation. The oily layer was taken up in ether and the extract was washed once with a small amount of water, dried with magnesium sulfate and distilled.

2,2-Diethyl-1,3-Propanediol Diacetate.—A solution of 23.5 g. of 2,2-diethyl-1,3-propanediol and 75 ml. of acetic anhydride was heated on a steam-bath for twelve hours with 10 g. of sodium acetate.

2-(*p*-Methoxyphenyl)-5,5-diethyl-*m*-dioxane.—A solution of 21 g. of 2,2-diethyl-1,3-propanediol, 23.8 g. of anisaldehyde, 0.2 g. of *p*-toluenesulfonic acid and 50 ml. of benzene was refluxed overnight in an apparatus which trapped water as formed.

1-Phenyl-1,3-propanediol Dipropionate.—A solution of 30 g. of 1-phenyl-1,3-propanediol,[2] 76 ml. of propionic anhydride and 63 ml. of pyridine was heated at 100° for two hours and distilled.

Piperonylates.—The acid chloride[3] of piperonylic acid[4] was heated at 100° with pyridine and a several-fold excess of suitable alcohol.

***p*-Methoxycinnamates.**—These esters were obtained by transesterification. A solution of ethyl *p*-methoxycinnamate[5] in 3 parts by weight of the appropriate alcohol containing 0.2% of dissolved sodium was slowly distilled through a short Vigreux column.

Hexahydrophthalates.—Dimethyl hexahydrophthalate, b. p. 91–93° (1.3 mm.), $n^{25}D$ 1.4567, was obtained in 92% yield by hydrogenation of dimethyl phthalate over Raney nickel at 175°. It was converted to higher esters by transesterification as described for the *p*-methoxycinnamates.

Benzaldehyde Di-*n*-butyrate.—A drop of 95% sulfuric acid was added to a solution of 25 g. of benzaldehyde in 41 g. of butyric anhydride. Heat was evolved. After the solution had cooled back to room temperature, it was taken up in ether and the ether solution was washed with water, dried, and distilled.

***p*-*n*-Propylphenethyl Alcohol.**—To an ether solution of the Grignard reagent prepared from 50 g. of *p*-bromo-*n*-propylbenzene (Eastman Kodak Co.) there was added with stirring 12 g. (10% excess) of ethylene oxide. A gum precipitated. While stirring continued, the ether was removed by distillation, toluene being gradually added to take its place. The mixture was stirred for an hour at 95° and poured while still hot into aqueous ammonium chloride solution. The oil which separated was taken up in ether and the ether extract was dried over magnesium sulfate and distilled.

N-Cyclohexyl-N-phenylpropionamide.—A solution of 28 g. of cyclohexylaniline (Monsanto Co.) and 47 g. of propionic anhydride was refluxed for eight hours and distilled. The product was recrystallized from hexane.

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(2) Prins, *Chem. Weekblad*, **16**, 1510 (1919); Fourneau, Benoit and Firmenich, *Bull. soc. chim.*, **47**, 858, 894 (1930).

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(4) Blatt, "Organic Syntheses," Coll. Vol. 2, John Wiley, New York, N. Y., 1943, p. 538.

(5) Reychler, *Bull. soc. chim.*, [3] **17**, 510 (1897).

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