the addition of 5 ml. of trifluoroacetic acid to the reaction mixture.

4,4-Dinitroheptanedinitrile.—In a 500-ml. three-necked flask was placed 50 g. (0.3 mole) of 2,2-dinitro-1,3-propanediol, 320 ml. of water and 5 g. (0.09 mole) of potassium hydroxide. Over a period of 30 minutes, 90 ml. (1.35 moles) of acrylonitrile was added dropwise, while the temperature was kept at 30°. After the addition of acrylonitrile was complete, the solution was stirred for 6 hours, during which time it turned red. Enough 30% potassium hydroxide was added to bring the *p*H to 8, and then the solution was stirred for another 3 hours. The reaction mixture became heterogeneous, consisting of a red aqueous phase and a deep red, dense oil. Extraction of the aqueous phase with three 75-ml. portions of ether gave a solid when the ether had evaporated. Recrystallization of the solid from methanol yielded two crops of crystals, weighing 7.75 and 1.65 g., m.p. 78°. The heavy oil was triturated with 25 ml. of ether, and this treatment caused solidification. The solid was collected on a suction filter and freed of adhering oil. Recrystallization from methanol yielded two crops of crystals weighing 8.61 and 2.75 g., m.p. 77–78°.[16] The total weight of 20.76 g. represented a yield of 37%, based on 2,2-dinitro-1,3-propanediol.

N-Bis-(2-cyanoethyl)-trifluoroacetamide.—A round-bottomed flask was fitted with a reflux condenser, the top of which was connected to a trap surrounded by a Dry Ice–acetone-bath. Any vapors which passed through the condenser would thus liquefy in the cold trap. A solution of 50 g. of trifluoroacetic acid and 92 g. of benzoyl chloride was heated in the flask, and when the temperature reached 65°, gas was evolved. Over a period of 2 hours, the temperature was raised to 180°, and all substances boiling below 15° condensed in the cold trap. The product was mainly trifluoroacetyl chloride, mixed with some hydrogen chloride.

A solution of 100 g. of β,β′-iminodipropionitrile in 50 ml. of chloroform was rapidly stirred while the crude trifluoroacetyl chloride was distilled into it. A white solid immediately formed and the reaction was carried on for 5 hours. The solid was filtered off, and it was identified as the hydrochloride of β,β′-iminodipropionitrile[11]; 66 g. was obtained. After the chloroform had been removed from the filtrate, the residue was distilled through a 12″ Vigreux column, yielding a water-white liquid boiling at 158° at 0–1 mm., $n^{20}D$ 1.4398.

Anal. Calcd. for $C_8H_8OF_3N_3$: C, 43.83; H, 3.68; N, 19.14. Found: C, 43.97; H, 3.39; N, 19.40.

N-Bis-(2-cyanoethyl)-3,5-dinitrobenzamide.—A solution of 4.92 g. (0.04 mole) of β,β′-iminodipropionitrile in 20 ml. of chloroform was cooled and rapidly stirred. Upon the addition of 4.55 g. (0.02 mole) of 3,5-dinitrobenzoyl chloride dissolved in 30 ml. of chloroform, a white solid formed. Stirring was carried on for 2 hours, and then the solid was removed by filtration. The total weight (dry) was 8.8 g.; the solid was a mixture of the desired product and the hydrochloride of β,β′-iminodipropionitrile. The product was extracted with water to remove the soluble hydrochloride, leaving behind 5.4 g. of a tan solid melting at 123–125°. Recrystallization from ethanol yielded short needles melting at 144–145°. When this solid was mixed with pure β,β′-iminodipropionitrile hydrochloride (m.p. 147–148°) melting occurred at 134–136° with the development of a green color. Thus, the desired N-bis-(2-cyanoethyl)-3,5-dinitrobenzamide melts close to β,β′-iminodipropionitrile hydrochloride.

Anal. Calcd. for $C_{13}H_{11}O_5N_5$: C, 49.22; H, 3.49; N, 22.08. Found: C, 49.90; H, 3.70; N, 21.64.

N-Bis-(2-cyanoethyl)-benzylamine.—A solution of 24.6 g. (0.2 mole) of β,β′-iminodipropionitrile and 12.7 g. (0.1 mole) benzyl chloride in 30 ml. of chloroform was stirred and heated to reflux for 12 hours. A solid slowly formed, and this was removed by suction filtration. As the chloroform solvent was removed, more solid formed, which was identified as the salt of β,β′-iminodipropionitrile, and this too was removed by filtration. The dense yellow residue was cooled to −75°, but no crystals appeared. Distillation through a short Vigreux column gave a very pale liquid boiling at 176° and 0.5 mm., $n^{20}D$ 1.5275. This was identified as N-bis-(2-cyanoethyl)-benzylamine.

Anal. Calcd. for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.45; H, 7.14; N, 19.81.

Attempted Polymerization of N-Bis-(2-cyanoethyl)-benzylamine with Formaldehyde.—A solution of 0.195 g. of *s*-trioxane (6.5 mmoles of HCHO) and 1 ml. of concd. sulfuric acid in 5 ml. of 90% formic acid was warmed to 30–35°. During the addition of 1.36 g. (6.4 mmoles) of N-bis-(2-cyanoethyl)-benzylamine, the temperature rose and an ice-water bath was used to keep it at 30–35°. After stirring for 75 minutes, the clear solution was poured into 50 ml. of water at 5°, but no solid material formed. No solid was obtained when a sample of the solution was treated with sodium chloride. However, when the solution was basified with excess 20% aqueous sodium hydroxide, a milky emulsion formed. This mixture was extracted with ethylene chloride, which cleared up the emulsion. Removal of the ethylene chloride left behind 1.09 g. of a dense liquid which was identified as N-bis-(2-cyanoethyl)-benzylamine by its refractive index.

Acknowledgments.—We are indebted to the Office of Naval Research for the financial support of this work and we wish to thank Mrs. M. Wyman for technical assistance.

LAFAYETTE, INDIANA

[CONTRIBUTION NO. 195 FROM THE GOODYEAR RESEARCH LABORATORIES]

The Synthesis and Polymerization of Some Allyl Esters of Carbamic Acid

BY C. E. GLEIM

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A number of allyl esters of carbamic acid have been synthesized. Their properties, as well as those of some of their polymers, are reported.

A convenient method of synthesizing allyl carbamates is the reaction of allyl chloroformate with amino compounds. The reactions are generally carried out at a temperature of 0 ± 10° in the presence of pyridine as an acid acceptor. A general procedure for their preparation is the dropwise addition of the chloroformate with stirring to a cold solution of the amino compound in pyridine. The resulting mixture is then poured into cold dilute hydrochloric acid from which the carbamate is separated, washed with dilute sodium bicarbonate solution, and purified.

The aldehyde condensation derivatives of the carbamates are prepared by treating an aldehyde with a carbamate in the presence of an acid catalyst. The general procedure for their preparation is the addition of an acid catalyst with cooling to a stirred solution of the aldehyde and carbamate followed by the addition of water, neutralization and purification.

Table I lists the allyl carbamates which have been prepared and indicates the source of each ester as well as the percentage yield. Certain physical properties of the esters are reported in Table II.

TABLE I

ALLYL ESTERS OF CARBAMIC ACID

	Ester	Yield, %	Source
I	Allyl carbamate[a]	85	Allyl chloroformate and ammonia in benzene
II	Allyl (N-carballyloxy)-carbamate)[b]	18	Allyl chloroformate and allyl (N-sodium) carbamate, or (N-carballyloxy)-carbamyl chloride and allyl alcohol
III	Ethylene bis-(N-carballyloxycarbamate)[c]	55	(N-Carballyloxy)-carbamyl chloride and ethylene glycol, or ethylene bischloroformate and allyl (N-sodium)-carbamate
IV	Bis-(N,N'-carballyloxy)-urea[d]	55	Allyl carbamate and phosgene
V	Allyl (N-allyl)-carbamate	70	Allyl chloroformate and monoallylamine
VI	Bis-(N,N'-carballyloxy) hydrazine[e]	93	Allyl chloroformate and hydrazine hydrate
VII	Allyl (N-carballyldioxy)-carbamate[f]	70	Allyl chloroformate and (N-hydroxyl allyl carbamate, prepared from hydroxylamine and allyl chloroformate in aqueous sodium carbonate
VIII	Allyl (N-allyloxy)-carbamate	31	Allyl chloride and the sodium derivative of allyl (N-hydroxyl) carbamate
IX	(N-Carballyldioxy) (N'-carballyloxy)-urea[g]	45	Allyl chloroformate and hydroxylurea
X	(N-Carballyloxy)-ethylenediamine[h,i]	19	Diallyl carbonate and ethylenediamine
XI	Bis-(N,N'-carballyloxy)-ethylenediamine[h,i]	74	Diallyl carbonate and ethylenediamine
XII	Allyl (N-methylol)-carbamate	80	Allyl carbamate and formaldehyde in aqueous K_2CO_3
XIII	Allyl (N-carballyldioxymethyl)-carbamate	50	Allyl chloroformate and allyl (N-methylol)-carbamate
XIV	Allyl (N-carballyldioxyethyl)-carbamate[j]	65	Allyl chloroformate and monoethanolamine
XV	Allyl bis-(N-carballyldioxyethyl)-carbamate	60	Allyl chloroformate and diethanolamine
XVI	Allyl (N-carballyldioxymethyl, methyl)-carbamate	68	Allyl chloroformate and aldehyde ammonia
XVII	Allyl (N-carballyldioxyphenyl)-carbamate[j]	77	Allyl chloroformate and *p*-aminophenol
XVIII	Allyl (N-carballyloxymethyl)-carbamate[k]	39	Allyl alcohol and (N-carballyloxy)-aminoacetate, prepared in 23% yield from allyl chloroformate and methyl aminoacetate
XIX	Bis-(N,N'-carballyloxy)-methylenediamine[l]	80	Allyl carbamate, formalin and a trace of hydrogen chloride
XX	Bis-(N,N'-carballyloxy)-methyl, -methylenediamine	80	Allyl carbamate, acetaldehyde and a trace of dilute hydrochloric acid
XXI	Bis-(N,N'-carballyloxy) furyl, methylenediamine	90	Allyl carbamate and furfural in glacial acetic acid
XXII	Allyl anhydroformaldehyde-carbamate	88	Allyl carbamate, formalin and concd. hydrochloric acid
XXIII	Allyl anhydroacetaldehyde-carbamate	90	Allyl carbamate, acetaldehyde and concentrated hydrochloric acid
XXIV	Allyl anhydrocitral-carbamate	65	Allyl carbamate, citral and glacial acetic acid
XXV	Allyl anhydroglyoxal-carbamate	50	Allyl carbamate, glyoxal and concd. hydrochloric acid
XXVI	Allyl (N-isopropenyl)-carbamate	82	Methacrylamide, allyl alcohol and potassium hypobromite solution
XXVII	Allyl bis-(N-acrylyl)-carbamate	23	Allyl (N-sodium)-carbamate and acrylyl chloride in benzene
XXVIII	Allyl (N-cyano)-carbamate	30	Allyl chloroformate and cyanamide
XXIX	(N-Carballyloxy)-urea	59	Allyl chloroformate and urea or (N-carballyloxy)-carbamyl chloride and ammonia in ether

[a] C. E. Gleim, U. S. Patent 2,483,194. [b] C. E. Gleim, U. S. Patent 2,541,646. [c] A. G. Chenicek, U. S. Patent 2,401,549. [d] A. G. Chenicek, U. S. Patent 2,394,592. [e] L. N. Whitehill, U. S. Patent 2,583,980. [f] C. E. Gleim, U. S. Patent 2,579,426. [g] C. E. Gleim, U. S. Patent 2,579,427. [h] K. W. Rosenmund, German Patent 676,049. [i] J. G. Lichty and N. V. Seeger, U. S. Patent 2,464,519. [j] I. E. Muskat and F. Strain, U. S. Patent 2,390,551. [k] C. E. Gleim, U. S. Patent 2,508,249. [l] A. G. Chenicek, U. S. Patent 2,385,911.

The polymer of anhydroformaldehyde allyl carbamate was studied most extensively since it is easily prepared from relatively cheap raw materials. The colorless, transparent, insoluble and infusible polymer has a Rockwell "M" hardness of 98 and was prepared by heating the monomer (which may exist as a dimer or trimer) in an oven maintained at 55° for 20 hours in the presence of 2.5% of benzoyl peroxide. A slightly modified A.S.T.M. method of testing showed the polymer to be insoluble in acetone, 95% ethanol, gasoline, carbon tetrachloride, toluene and ethyl acetate. It is also insoluble in 30% sulfuric acid and 10% solutions of sodium hydroxide, hydrochloric acid and nitric acid. It is attacked strongly, however, by concentrated nitric and sulfuric acids.

Tables III, IV and V offer a comparison of certain properties of anhydroformaldehyde allyl carbamate with those of other polymeric materials.

The conditions used for the polymerization of some other allyl esters of carbanic acid are listed in Table VI. The monoallyl esters formed thermoplastic polymers whereas the diallyl esters formed transparent polymers of the insoluble and infusible type. The Rockwell "M" hardness of the polymers varied from 80 to 105 with the exception of a

TABLE II

PHYSICAL PROPERTIES OF ALLYL ESTERS OF CARBAMIC ACID

Ester	Formula	B.p., °C.	Mm.	M.p.,[c] °C.	n_D	°C.	d_4	°C.	N Analyses, % Calcd.	Found
I	$C_4H_7O_2N$	73.5	2		1.4520	28	1.080	28	13.87	13.82
II	$C_8H_{11}O_4N$	145–147[d]	3		1.4728	23	1.159	25	7.57	7.59
III	$C_{12}H_{16}O_8N_2$	[a]							8.85	9.62
IV	$C_9H_{12}O_5N_2$			70					12.30	11.80
V	$C_7H_{11}O_2N$	84.5–85	3		1.4566	28	0.997	28	9.93	9.63
VI	$C_8H_{12}O_4N_2$			88–89					14.00	14.95
VII	$C_8H_{11}O_5N$	143–145	3		1.4558	28	1.163	26	6.96	6.48
VIII	$C_7H_{11}O_3N$	90–92	2		1.4569	30	1.066	30	8.92	9.15
IX	$C_9H_{12}O_6N_2$			62–63					11.45	11.00
X	$C_6H_{12}O_2N_2$	160	2		1.4775	26	1.674	26	19.45	19.95
XI	$C_{10}H_{16}O_4N_2$			89–90					12.28	11.44
XII	$C_5H_9O_3N$	[a]			1.4818	28	1.120	28	10.69	10.30
XIII	$C_9H_{13}O_5N$	[a]							6.50	7.20
XIV	$C_{10}H_{15}O_5N$	151–152	3		1.4630	28	1.142	28	6.11	5.83
XV	$C_{16}H_{23}O_8N$	[a]			1.4667	20	1.159	30	3.56	4.30
XVI	$C_{10}H_{15}O_5N$	165–170[b]	3		1.5600	25			6.11	6.18
XVII	$C_{14}H_{15}O_5N$			89–90.5					5.08	4.55
XVIII	$C_9H_{13}O_4N$	126–128	1		1.4653	24	1.114	26	7.05	7.44
XIX	$C_9H_{14}O_4N_2$			108–109					13.08	12.85
XX	$C_{10}H_{16}O_4N_2$			105–106					12.28	11.52
XXI	$C_{13}H_{16}O_5N_2$			140.5					10.00	9.78
XXII	$C_6H_7O_2N$	185[b]	2		1.4870	30	1.174	30	12.40	12.84
XXIII	$C_6H_9O_2N$	[a]							11.01	11.95
XXIV	$C_{14}H_{21}O_2N$	163–173[b]	2		1.5170	25	1.018	25	5.95	5.58
XXV	$C_{10}H_{12}O_4N_2$	[a]							12.50	10.92
XXVI	$C_7H_{11}O_2N$	60	2		1.5398	28	2.017	30	9.93	9.63
XXVII	$C_{10}H_{11}O_4N$	150–160[b]	2		1.4653	24	1.120	30	6.70	6.54
XXVIII	$C_5H_6O_2N$			162–163					22.22	19.00
XXIX	$C_5H_8O_3N_2$			161–162					19.50	18.95

[a] Decomposes on heating. [b] With decomposition. [c] Uncorrected. [d] C. E. Slimowicz and E. F. Degering, THIS JOURNAL, 71, 1044 (1949), m.p. 43–45°.

TABLE III

PHYSICAL PROPERTIES OF SOME POLYMERS

	Plate glass	Anhydroformaldehyde allyl carbamate	Diethylene glycol bisallyl carbonate (CR39)	Methyl methacrylate (Plexiglass)
Monomer, sp. gr.		1.175	1.133	0.945
Polymer, sp. gr.	2.50	1.31	1.32	1.19
Sp. gr. change during cure, %		15.20	16.50	25.90
Benzoyl peroxide concn., %		2.5	3.0	0.2–0.5
Rockwell "M" hardness		95	91	88
Tensile, p.s.i.	6500	5000	6000	7500
Modulus of elasticity, p.s.i.	1,000,000	240,000	270,000	400,000
Modulus of rupture	6500	10,000	9,000	14,000
Abrasion resistance[a]	1	6.5	1.1	12.1

[a] Abrasion resistance was relative to plate glass. The higher values indicate lower abrasion resistance.

TABLE IV

ELECTRICAL PROPERTIES OF SOME GLASSES

Sample[a]	Rockwell "M" hardness	Dielectric constant	Specific resistivity, ohm cm.[b]	Dissipation factor, %
Pyrex glass		2.762	7.37×10^{13}	1.111
Diethylene glycol bisallyl carbonate	95	4.236	Above 10^{16}	0.824
Diethylene glycol bisallyl carbonate	100	4.624	8.17×10^{15}	0.810
Anhydroformaldehyde allyl carbamate	90	2.663	2.61×10^{15}	1.410
Anhydroformaldehyde allyl carbamate	95	2.317	2.25×10^{15}	2.229

[a] Samples ranged in thickness from 0.195 to 0.412 cm. [b] Samples were conditioned for one hour at 35° before being tested in a capacitance bridge with both a.c. and d.c. at this same temperature. All a.c. measurements were made at 1000 cycles per second.

few that are listed in Table VII. All of the monomers in Table VI were polymerized at or above their melting points. The transparent resins having Rockwell "M" hardness values of 75 or more were glasslike in nature. Polymer hardness was found to increase until a maximum degree of polymerization was reached. Polymerization time varied inversely as the temperature and as the catalyst concentration. Too high a temperature or too high a catalyst concentration tends to cause polymer discoloration and cracking. The conversion to polymeric materials was practically quantitative since monomer volatility decreases rapidly as polymerization takes place.

Allyl monomers which failed to polymerize when heated for several hours with peroxide catalysts are listed in Table VII. Some of these monomers were not isolated in pure form which may account for their resistance to peroxide catalyzed polymerization. However, two of these allyl monomers, RNHCOOR and RONHCOOR, were carefully purified.

Most of the allyl esters of carbamic acid will undergo copolymerization with other monomers to give a modification of polymer properties. Some of

TABLE V

OPTICAL PROPERTIES OF SOME POLYMERS

Polymer	Light transmission, %[a] Before aging White[b] light	Before aging 500 mμ	100 hr. aging[c] White[b] light	100 hr. aging[c] 500 mμ	200 hr. aging[c] White[b] light	200 hr. aging[c] 500 mμ	Haze, % Before aging	Haze, % After[b] aging
Anhydroformaldehyde allyl carbamate	92.0	92.0	88.5	88.0	87.0	83.5	2.23	2.81
Diethylene glycol bis-allyl carbamate (CR-39)	92.0	91.5	90.2	87.0	89.3	85.0	2.04	2.39
Methyl methacrylate (Plexiglass)	92.0	92.0	92.0	92.0	92.0	92.0	1.5–2.0	1.5–2.0

[a] The aging characteristics of a polymer are not necessarily inherent in the monomer as the technique of polymerization and the history of the polymer are factors which can determine the aging properties. [b] Light from a tungsten filament. [c] Aged in a Fadeometer.

TABLE VI

POLYMERIZATION CONDITIONS FOR CARBAMIC ACID ESTERS

	Compound[a]	Catalyst Type	Concn.,[k] %	Polymerization Temp., °C.	Time, hr.
I	NH_2COOR[b,c]	Benzoyl peroxide	5.0	60	60
XII	$HOCH_2NHCOOR$[d,e]	Benzoyl peroxide	2.5	65	48
XXVII	$(CH_2{=}CH{-}CO)_2NCOOR$	Benzoyl peroxide	2.5	55	36
XXVI	$CH_2{=}C(CH_3)NHCOOR$	Benzoyl peroxide	2.5	55	48
II	$ROCONHCOOR$	Benzoyl peroxide	3.0	65	5
VII	$ROCOONHCOOR$	Benzoyl peroxide	5.0	55	20
XIII	$ROCOOCH_2NHCOOR$	Benzoyl peroxide	2.5	50	36
XVI	$ROCOOCH(CH_3)NHCOOR$[e]	Benzoyl peroxide	5.0	55	48
XIV	$ROCOOCH_2CH_2NHCOOR$[f]	Benzoyl peroxide	2.5	55	20
XV	$(ROCOOCH_2CH_2)_2NCOOR$	Benzoyl peroxide	5.0	55	68
VI	$ROCONHNHCOOR$[g]	Benzoyl peroxide	5.0	90 (50)	4 (20)
XVIII	$ROCONHCH_2COOR$[h]	Benzoyl peroxide	5.0	65	39
XXII	$(CH_2{=}NCOOR)_x$[i]	Benzoyl peroxide	2.5	55	20
XXIII	$(CH_3CH{=}NCOOR)_x$[i]	Benzoyl peroxide	5.0	65	120
III	$ROCONHCOOC_2H_4OCONHCOOR$[j]	Benzoyl peroxide	5.0	50	40
IX	$ROCOONHCONHCOOR$	*t*-Butyl hydroperoxide	3.0	65	36
IV	$ROCONHCONHCOOR$	*t*-Butyl hydroperoxide	0.1	75	15
XIX	$ROCONHCH_2NHCOOR$	*t*-Butyl hydroperoxide	1.0	115	10
XX	$ROCONHCH(CH_3)NHCOOR$	*t*-Butyl hydroperoxide	1.0	115	36
XI	$ROCONHCH_2CH_2NHCOOR$	*t*-Butyl hydroperoxide	0.1	95	24
XXV	$ROCON{=}CH{-}CH{=}NCOOR$[e]	*t*-Butyl hydroperoxide	2.5	100	15

[a] R represents the allyl radical. [b] Polymer Rockwell "M" hardness = 65. [c] Polymer opaque. [d] Polymer Rockwell "M" hardness = 58. [e] Polymer Rockwell "M" hardness = 60. [f] Polymer specific gravity = 1.275. [g] Heated at 90° for 4 hours and at 50° for 20 hours. [h] Polymer specific gravity = 1.277. [i] Monomer may also exist as a dimer or trimer. [j] Polymer Rockwell "M" hardness = 55. [k] Per cent. by weight.

TABLE VII

	Compound[a]	Catalyst Type	Concn.,[c] %	Temp., °C.	Time, hr.
V	$RNHCOOR$	Benzoyl peroxide	5.0	55	120
VIII	$RONHCOOR$	Benzoyl peroxide	5.0	55	120
XXIV	$C_9H_{15}CH{=}NCOOR$[b]	Benzoyl peroxide	5.0	65	36
XXVIII	$NCNHCOOR$	*t*-Butyl hydroperoxide	5.0	165	8
XVII	$ROCOOC_6H_4NHCOOR$	*t*-Butyl hydroperoxide	2.0	100	28
X	$NH_2CH_2CH_2NHCOOR$	*t*-Butyl hydroperoxide	2.0	55	36
XXIX	$NH_2CONHCOOR$	*t*-Butyl hydroperoxide	1.0	165	24

[a] R represents the allyl radical. [b] Anhydrocitral allyl carbamate. [c] Per cent. by weight.

the monomers have been particularly useful as cross-linking agents and a number of copolymers have been prepared.

Experimental

The following procedures may be taken as representative of those used in the preparation of the allyl esters described.

Allyl Carbamate.—Ammonia was passed into a solution of 368 g. (3 moles) of allyl chloroformate dissolved in 1000 ml. of benzene at 25 to 35° until the reaction was complete. The ammonium chloride was filtered off and the salt was washed with small quantities of benzene. Distillation of the benzene solution through a short column gave 255 g. (85% yield) of allyl carbamate (allyl urethan), b.p. 73–75° at 2 mm., d^{28}_4 1.080, $n^{28}D$ 1.4520.

Anal. Calcd. for $C_4H_7O_2N$: N, 13.87. Found: N, 13.82.

Anhydroformaldehyde Allyl Carbamate.—Concentrated hydrochloric acid (sp. gr. 1.10, 1200 g.) was added rapidly with stirring to a cooled solution (ice-water-bath) of 3712 g. (36.75 moles) of allyl carbamate and 3420 g. (41 moles) of 36% formaldehyde. The oil layer was separated, washed with cold water, cold dilute sodium bicarbonate solution, water and then dried over anhydrous sodium sulfate. The yield of neutral undistilled anhydroformaldehyde allyl carbamate was 3578 g. (88%).

Anal. Calcd. for $C_5H_7O_2N$: N, 12.40. Found: N, 12.84.

N-Carballyldioxyethyl Allyl Carbamate.—Allyl chloroformate, 964 g. (8 moles), was added at a rate of two grams per minute to a solution of 245 g. (4 moles) of monoethanolamine in 712 g. (9 moles) of pyridine at −15 to −10°. The resulting mixture was poured into cold dilute hydrochloric acid solution. The oil layer was separated, washed

with sodium bicarbonate solution and dried. Distillation of the neutral oil in small quantities through a short column gave 600 g. (65% yield) of water-white (N-carballyldioxyethyl) allyl carbamate, b.p. 151–152° at 3 mm., d^{28}_4 1.142, $n^{28}D$ 1.4630.

Anal. Calcd. for $C_{10}H_{15}O_5N$: N, 6.11. Found: N, 5.83.

Bis-(N,N'-carballyloxy)-urea.—Phosgene was passed into 202 g. (2 moles) of allyl carbamate at 50–75° during a four-hour period. The solid product was filtered off and dissolved in hot ethyl alcohol. Crystallization from alcohol gave 125 g. (55% yield) of bis-(N,N'-carballyloxy)-urea, m.p. 70°.

Anal. Calcd. for $C_9H_{12}O_5N_2$: N, 12.30. Found: N, 11.80.

AKRON, OHIO

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

Hydantoins from Alicyclic Ketones and Aldehydes

BY EDWARD S. ROTHMAN AND ALLAN R. DAY

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A series of new hydantoins of the 1-, 5- and spiro-5,5-substituted types derived from alicyclic ketones and aldehydes have been synthesized. A stereoisomer of the spirohydantoin derived from *l*-menthone has been prepared and evidence is presented to demonstrate the optical purity of the isomer obtained from *l*-menthone. 1-*l*-Menthyl-5,5-diethylbarbituric acid and 1-*d*-bornyl-5,5-diethylbarbituric acid were prepared also.

It has been found recently that both the spirohydantoin prepared from *l*-menthone and *l*-methylurea possessed promising anticonvulsant activity when administered to mice. Subsequent clinical testing, however, showed that they were not useful for controlling convulsions in man.[1] Menthylurea is a very old compound, but the spirohydantoin from *l*-menthone was first reported in 1939.[2]

Tiffeneau and Beauvallet[3] reported that spirohydantoins prepared from cyclopentanone, cyclohexanone and cycloheptanone were ineffective against strychnine-induced spasms while those derived from isophorone and dihydroisophorone were effective. The spirohydantoins prepared from 3,5-dimethyl-, 3-ethyl-5-methyl-, 3-α-furyl-5-methyl- and 3-methyl-5-phenylcyclohexanone were reported to have little activity.[4]

In view of the unlikelihood that the compounds mentioned above are unique in possessing anticonvulsant action or even that they are the best possible compounds of this type, it was considered desirable to examine the effects of structure modification on activity. Most of the work reported here deals with the preparation of spirohydantoins from alkyl substituted cyclohexanones, for they were believed to be the most promising.

Camphorspirohydantoin had not been reported in the literature prior to the present study, although unsuccessful attempts to prepare it from camphor have been reported.[5] Camphorspirohydantoin was obtained in good yields when camphorimine was used in place of camphor as the starting material.

The use of optically active alkyl-substituted cyclohexanones naturally raises the question of whether isomerization occurs during hydantoin formation. This question has been considered, in the present investigation, only in the case of the spirohydantoin derived from *l*-menthone. *l*-Menthone, in which the methyl and isopropyl groups are in the *trans* configuration, might be expected to give two diastereoisomeric hydantoins. Since attempts to separate the spirohydantoin from *l*-menthone into diastereoisomeric modifications failed, all fractions melting at 228–229° and $[\alpha]^{24}D$ +11.7° (1.5% in ethanol), it seems likely that the spirohydantoin is a single individual and not a mixture.

Partial racemization of *l*-menthone by treatment with sulfuric acid[6] produced a mixture of *cis*- and *trans*-methylisopropylcyclohexanones, that is, *l*-menthone and *d*-isomenthone. This mixture of isomeric ketones was converted to the corresponding hydantoins. The latter were readily separated into two fractions by fractional crystallization from ethyl alcohol. The larger and more soluble fraction melted at 228–229° and was identical with the spirohydantoin from *l*-menthone. The smaller and less soluble fraction melted at 235.5–238.5°, $[\alpha]^{24}D$ +5.85° (2% in ethanol). Analyses indicated the compound to be isomeric with the spirohydantoin prepared from *l*-menthone. The second product must, therefore, be the isomer derived from the *d*-isomenthone.

An optically inactive methone from the Givaudan Corporation gave a spirohydantoin melting at 256.7–258.5°. No attempt was made to separate the product into isomeric forms.[7]

Experimental

***l*-3-*p*-Menthylamine.**—*l*-Menthone was prepared from *l*-menthol by chromic acid oxidation.[8] The ketone was converted to the corresponding oxime[9] and the latter reduced to the amine by the action of sodium and ethyl alcohol.[10] The amine was removed by steam distillation and collected in dilute hydrochloric acid. Evaporation gave 70–76%

(1) Private communication from Smith, Kline and French, Philadelphia, Pa.

(2) A. R. Day and C. F. Kelly, *J. Org. Chem.*, **4**, 101 (1939).

(3) R. Tiffeneau and M. Beauvallet, *Presse Med.*, **51**, 417 (1943).

(4) H. R. Henze, R. C. Wilson and R. W. Townley, THIS JOURNAL, **65**, 963 (1943).

(5) During the course of the present work, H. Hoyer [*Ber.*, **83**, 491 (1950)] reported the preparation of the spirohydantoin from both *d*-camphor and *dl*-camphor. He used the Bucherer procedure at elevated temperatures and pressures, yields 40–50%.

(6) E. Beckmann, *Ann.*, **250**, 335 (1889).

(7) This compound may be identical with the spirohydantoin prepared by Novelli [*Annales asoc. quim. Argentina*, **29**, 83 (1941); *C. A.*, **35**, 6576 (1941)]. He reported a m.p. of 257°.

(8) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., p. 340.

(9) E. Beckmann, *Ann.*, **250**, 325 (1889).

(10) R. L. Bateman and A. R. Day, THIS JOURNAL, **67**, 2496 (1935).