sorption of its conjugate acid, the absorption of the aldehyde remaining in the basic solution could be calculated and subtracted from the spectrum of the aldehyde-imine mixture, leaving the spectrum of the imine. The conclusion that the imine is obtained as the product of the reaction of ammonia with a very dilute aldehyde solution appears further borne out by the comparison of these spectra with the spectra of *N*-(*p*-dimethylaminobenzylidene)-*n*-butylamine and its conjugate acid as shown in Fig. 2.

The mean values of k_2 at 0° and 25°, given in Table I, were used in calculating the energy and entropy of activation for the reaction, with the result that E_a = 10.9 kcal./mole and $\Delta S^{\ddagger}_a$ = −43.7 e.u. The close correspondence with the values for the reaction of this same aldehyde with *n*-butylamine (8.0 kcal./mole and −41.9 e.u.)[6b] and *t*-butylamine (10.3 kcal./mole and −41.7 e.u.)[8] is one more indication that imine formation is taking place.

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CHARLOTTESVILLE, VA.

(8) Unpublished work by C. E. Bell, Jr., and T. I. Crowell.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY]

The Reactions of Carbobenzoxyamino Acid Amides with Carbonyl Compounds

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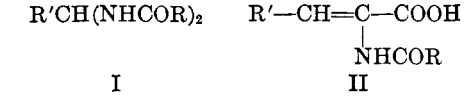
Amides of carbobenzoxyglycine, carbobenzoxyalanine, and carbobenzoxyphenylalanine have been found to react with carbonyl compounds (isobutyraldehyde, benzaldehyde, and cyclohexanone), in the presence of a sulfonic acid catalyst, to give two types of products: 1-carbobenzoxy-4-imidazolidinones (III) and carbobenzoxyamino acid 1-isobutenylamides (IV). The structure of the products is predetermined by the structure of the amide and that of the carbonyl component.

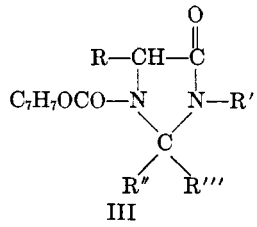
Primary amides and primary urethanes are known to react with aldehydes under acidic conditions to give alkylidenebisamides[3] (I) and alkylidenebisurethans (I,R = OR').[4] In the case of α-keto acids two types of reaction products are known, the bis-adduct (type I) and α-acylaminoacrylic acids (II)[5]:



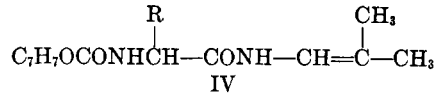
I II

If additional functional groups are present in the amide or urethan component, intramolecular cyclization may occur, leading to cyclic products. Thus, asparagine affords upon treatment with formaldehyde, 6-hydroxytetrahydropyrimidine-4-carboxylic acid,[6] and carbobenzoxyamino acids,[7] or β-hydroxyalkylcarbamates[8] afford on reacting with carbonyl compounds oxazolidine derivatives.

In the present paper the reactions of primary and secondary carbobenzoxyamino acid amides with isobutyraldehyde, benzaldehyde, and cyclohexanone are described. Refluxing benzene solutions of carbobenzoxyglycineamide, carbobenzoxyalanineamide, and carbobenzoxyphenylalanineamide with benzaldehyde or cyclohexanone in the presence of a sulfonic acid catalyst affords crystalline 1-carbobenzoxy-4-imidazolidinone (III. R' = H) under identical experimental conditions the same primary amides react with isobutyraldehyde to give open chain products of the ene-amide type, *i.e.* carbobenzoxyamino acid 1-isobutenylamides (IV):



III



IV

Carbobenzoxyamino acid methylamides (secondary amides) do not react with cyclohexanone and their reactions with isobutyraldehyde and benzaldehyde are much slower than those of the corresponding primary amides. With the methylamides only 1-carbobenzoxy-4-imidazolidinones (III. R' = CH_3) were obtained even with isobutyraldehyde.

The structures assigned to the reaction products are based upon their infrared spectra and chemical behavior. The carbobenzoxyimidazolidinones lack the NH absorptions of the starting materials in the 1500–1600 cm.$^{-1}$ region (cyclic lactams). The two

(1) Presented at the 26th meeting of the Israel Chemical Society, Jerusalem, April, 1960.

(2) From a thesis submitted for the M.Sc. degree by U. Zehavi, Israel Institute of Technology, Haifa, 1960.

(3) W. A. Noyes and D. B. Forman, *J. Am. Chem. Soc.*, **55**, 3493 (1933).

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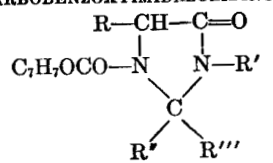
(8) M. Lamin and D. Ben-Ishai, *J. Org. Chem.*, submitted for publication.

TABLE I

CARBOBENZOXYIMIDAZOLIDINONES

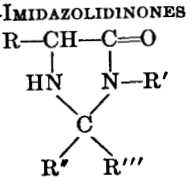


R	R′	R″	R‴	Time of Reaction, Hr.	Yield, %	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	H	H	C_6H_5	1	81	172[d]	$C_{17}H_{16}O_3N_2$	68.90	68.84	5.44	5.46	9.45	9.60
H	H		$(CH_2)_5$	3.5	69	222[d]	$C_{16}H_{20}O_3N_2$	66.64	66.44	6.99	7.05	9.72	9.89
H	CH_3	H	$(CH_3)_2CH$	8.0	64	89[d]	$C_{17}H_{20}O_3N_2$	65.19	65.01	7.30	7.21	10.14	10.33
H	CH_3	H	C_6H_5	48.0	68	116[d]	$C_{18}H_{18}O_3N_2$	69.66	69.56	5.85	5.87	9.03	9.21
CH_3[a]	H		$(CH_2)_5$	2.0	70	236[e]	$C_{17}H_{22}O_3N_2$	67.52	67.49	7.33	7.18	9.25	9.48
C_7H_7[a]	H	H	C_6H_5		22[c]	186[e]	$C_{24}H_{22}O_3N_2$	74.59	74.45	5.74	5.72	7.25	7.28
C_7H_7[a]	H	H	C_6H_5	4.5	34[c]	84[f]	$C_{27}H_{26}O_3N_2$[h]	76.15	75.93	5.88	5.90	6.10	6.38
C_7H_7[a]	H		$(CH_2)_5$	12.0	80	164[f]	$C_{23}H_{26}O_3N_2$	72.99	73.13	6.93	6.95	7.40	7.67
C_7H_7[b]	H		$(CH_2)_5$	11.0	71	146[g]	$C_{23}H_{26}O_3N_2$	72.99	73.03	6.93	6.75	7.40	7.52

[a] *d,l*-Isomer. [b] *l*-Isomer, $[\alpha]_D^{25}$ +169° (*c*, 0.5 in chloroform). [c] One of two isomers obtained in the same reaction. [d] Crystallized from ethyl acetate–hexane. [e] Crystallized from benzene. [f] Crystallized from benzene-methylcyclohexane. [g] Crystallized from methylcyclohexane. [h] This isomer crystallized with benzene in a 2:1 ratio.

TABLE II

4-IMIDAZOLIDINONES



R	R′	R″	R‴	Yield, %	M.P.	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Halogen Calcd.	Halogen Found
H	H	H	C_6H_5	61	105[d]	$C_9H_{10}ON_2$	66.65	66.40	6.22	6.21	17.27	17.10		
H	H		$(CH_2)_5$	84	121[d]	$C_8H_{14}ON_2$	62.30	62.16	9.15	9.00	18.17	17.99		
H	CH_3	H	$(CH_3)_2CH$	74	[c]	$C_7H_{14}ON_2$	59.12	58.87	9.92	9.72	19.70	19.90		
H	CH_3	H	C_6H_5	73	159–162	$C_{10}H_{13}ON_2Cl$					13.18	12.94	16.69	16.56
CH_3[a]	H		$(CH_2)_5$	76	103[e]	$C_9H_{16}ON_2$	64.25	64.42	9.59	9.73	16.65	16.73		
CH_3[a]	CH_3	H	$(CH_3)_2CH$	60	157–160	$C_9H_{17}ON_2Cl$					14.55	14.42	18.44	18.62
C_7H_7[a]	H		$(CH_2)_5$	77	113[e]	$C_{15}H_{20}ON_2$	73.73	73.61	8.25	8.44	11.47	11.35		
C_7H_7[b]	H		$(CH_2)_5$	85	102[f]	$C_{15}H_{20}ON_2$	73.73	73.78	8.25	8.18	11.47	11.16		
C_7H_7[a]	CH_3	H	$(CH_3)_2CH$	45	142–143	$C_{14}H_{21}ON_2Br$					8.95	8.79	25.56	25.36

[a] *d,l*-Isomer. [b] *l*-Isomer, $[\alpha]_D^{25}$ −63° (*c*, 0.5 in chloroform.) [c] B.p. 66°/0.01 mm. [d] Crystallized from benzene-hexane. [e] Crystallized from ethyl acetate–hexane. [f] Crystallized from methylcyclohexane.

carbonyl absorptions of the carbobenzoxyamino acid amides at 1675–1690 (amide) and 1710–1720 cm.$^{-1}$ (carbamate)[9] merge to one carbonyl absorption at 1700–1715 cm.$^{-1}$ in the carbobenzoxyimidazolidinones. These displacements are due to a rise in the amide carbonyl frequency due to incorporation into a five-membered lactam ring and to a lowering of the carbamate carbonyl frequency, the secondary carbamate having been converted into a tertiary carbamate.[9] The 1-carbobenzoxy-3-methyl-4-imidazolidinones (III. R′ = CH_3) lack NH absorptions both in the 3420–3460 cm.$^{-1}$ and 1500–1530 cm.$^{-1}$ regions. The imidazolidinones show a strong band in the C—H bonding region (1400–1420 cm.$^{-1}$) which is either absent or very weak in the starting materials.

The carbobenzoxyimidazolidinones (Table I) were converted by catalytic hydrogenation into the free 4-imidazolidinones (Table II). These compounds show carbonyl absorptions at 1690–1710 cm.$^{-1}$, a strong band at 1400–1420 cm.$^{-1}$ and lack the NH absorption band in the 1500–1600 cm.$^{-1}$ region.

The 4-imidazolidinones reported in the literature were prepared by desulfurization of thiohydantoins[10] or by the condensation of α-aminonitriles with carbonyl compounds.[11]

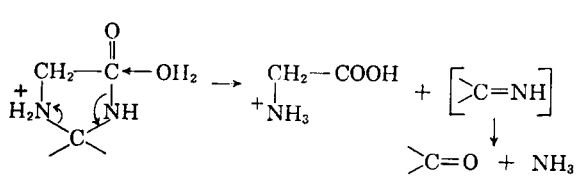
The carbobenzoxyamino acid 1-isobutenylamides (IV) show two carbonyl absorptions at 1670–1690 cm.$^{-1}$ (amide) and 1710–1725 cm.$^{-1}$ (carbamate) and NH absorptions at 3300–3460 cm.$^{-1}$ and 1500–1550 cm.$^{-1}$ They lack the strong band in the 1400 cm.$^{-1}$ region which is present in all the imidazolidinone derivatives. The C=C bands could not be observed probably because of masking by the amide carbonyl absorptions.

Carbobenzoxyglycine 1-isobutenylamide (IV. R = H) decolorizes bromine solution and gives a positive dinitrophenylhydrazone test for isobutyraldehyde. On catalytic hydrogenation it affords glycine isobutylamide which was found to be, after recarbobenzoxylation, identical with carbobenzoxyglycine isobutylamide. Glycine 1-isobutenylamide was obtained by removing the carbobenzoxy group with hydrogen bromide in acetic acid.[12] The hydrobromide could be recarbobenzoxylated to afford the starting materials.

In order to obtain further information concerning formation of the ene-amides, the reaction of phenylacetamide with isobutyraldehyde, benzaldehyde, and cyclohexanone was also investigated. Under the same experimental conditions (boiling benzene) phenylacetamide reacts with benzaldehyde to give benzylidenebisphenylacetamide. Isobutyraldehyde affords in addition to the bis-adduct also *N*-(1-isobutenyl)phenylacetamide in about 50% yield. The latter compound shows NH absorptions at 3410 cm.$^{-1}$ and 1510 cm.$^{-1}$ and a carbonyl absorption at 1660 cm.$^{-1}$ It absorbs one mole of hydrogen and is converted into *N*-isobutylphenylacetamide. Phenylacetamide reacts with cyclohexanone in boiling toluene to give exclusively *N*-(1-cyclohexenyl)phenylacetamide. The properties of these ene-amides are similar to those described above, they decolorize bromine solution and give a positive dinitrophenylhydrazone test for the corresponding carbonyl component.

Carbobenzoxy-*d,l*-phenylalanineamide, on treatment with benzaldehyde, affords two products which can be separated by fractional crystallization. One product melts at 186° and the other at 84°. Their infrared spectra, which are almost identical, suggest that they are isomeric 1-carbobenzoxy-4-imidazolidinones. The lower melting isomer crystallize with benzene in a 2:1 ratio. It loses the solvent upon drying above its melting point and the melt, which solidifies on cooling (m.p. 55–58°), analyses well for the imidazolidinone derivative. A mixed melting point of these isomers is depressed.

The acid hydrolysis of the free imidazolidinones was studied qualitatively and compared with the rate of hydrolysis of α-benzylideneaminoacetamide,[11] glycine 1-isobutenylamide, and glycineamide itself. The hydrolysis was followed by paper chromatography. In 5*N* hydrochloric acid at room temperature both α-benzylideneaminoacetamide and glycine 1-isobutenylamide hydrolyze completely after twelve hours to give glycineamide and glycine. Under the same conditions glycineamide is partly hydrolyzed to glycine. 2-Phenyl-4-imidazolidinone and 2-spirocyclohexano-4-imidazolidinone are much more stable to hydrolysis. After 100 hours spots of the unhydrolyzed imidazolidinones could be observed on the chromatogram. The only hydrolytic product detected was glycine; no glycineamide was observed at any time during the hydrolysis. 2-(*p*-Nitrophenyl)-4-imidazolidinone hydrolyzes to give glycine much faster (twenty-four hours) than 2-phenyl-4-imidazolidinone or glycineamide itself. These observations suggest that under acidic conditions (5*N* hydrochloric acid) a *direct* hydrolysis of the imidazolidinone to the amino acid, without passing through the amino acid amide, occurs:



(9) S. Pinchas and D. Ben-Ishai, *J. Am. Chem. Soc.*, **79**, 4099 (1957).

(10) J. T. Eduards and E. F. Matlem, *Chemistry and Industry*, 193 (1954), K. Freter, J. Rabinowitz, and B. Witkop, *Ann.*, **607**, 174 (1957).

(11) A. C. Davis and A. L. Levy, *J. Chem. Soc.*, 3479 (1951).

(12) D. Ben-Ishai and A. Berger, *J. Org. Chem.*, **17**, 1564 (1952).

TABLE III

CARBOBENZOXYAMINO ACID AMINES

$$C_7H_7OCONHCHCONHR'$$
(with R on the CH)

R	R'	M.P.	Yield, %	Formula	Carbon		Hydrogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
H	CH_3	105	47	$C_{11}H_{14}O_3N$	59.45	59.63	6.35	6.16	12.60	12.80
CH_3[a]	H	123	51	$C_{11}H_{14}O_3N$	59.45	59.69	6.35	6.57	12.60	12.45
CH_3[a]	CH_3	114	48	$C_{12}H_{16}O_3N$	61.00	60.95	6.83	6.64	11.86	11.79
C_7H_7[a]	H	183	48	$C_{17}H_{18}O_3N$	68.44	68.28	6.08	5.95	9.39	9.33
C_7H_7[a]	CH_3	152	53	$C_{18}H_{20}O_3N$	69.21	69.27	6.45	6.43	8.97	8.95
C_7H_7[b]	H	167	71							

[a] *d,l*-Isomer. [b] *l*-Isomer, Ref. 7, m.p. 167°.

In neutral solutions (*p*H = 7) at room temperature, 2-phenyl- and 2-spirocyclohexano-4-imidazolidinones hydrolyze slowly to give glycineamide. In boiling water hydrolysis to glycineamide of the above imidazolidinones is completed within twenty minutes.

EXPERIMENTAL[13]

Carbobenzoxyamino acid amides. A solution of carbobenzoxyamino acid (0.25 mole), methanol (30 ml.), and concentrated sulfuric acid (2.5 ml.) in 1,2-dichloroethane was refluxed for 12 hr. according to the procedure of Clinton and Laskowski.[14] The oily methyl ester obtained was dissolved in 250 ml. of ethanol saturated with ammonia[15] or methylamine and the solution was left at room temperature for 5 days. The ethanol was removed *in vacuo* and the solid amide obtained was dissolved in ethyl acetate. The ethyl acetate solution was washed with water and 5% hydrochloric acid and dried over sodium sulfate. The carbobenzoxyamino acid amide crystallized on concentration of the ethyl acetate solution (Table III).

Reaction of carbobenzoxyamino acid amides with carbonyl compounds. General procedure. A solution of the amide (0.025 mole), carbonyl compound (0.050 mole), and β-naphthalene sulfonic acid (0.25 g.) in benzene (200 ml.) was refluxed and the water was distilled and collected in a water separator as soon as it was formed. The reaction time is recorded in Table I. Ethyl acetate (200 ml.) was added and the combined benzene–ethyl acetate solution was washed with 10% aqueous sodium carbonate solution and water and dried over sodium sulfate. The product obtained after the removal of the organic solvent *in vacuo* was crystallized from a suitable solvent (Table I). The oily products which did not crystallize were hydrogenated catalytically without further purification and were characterized as the imidazolidinone hydrochlorides (Table II).

1-Carbobenzoxy-2-(p-nitrophenyl)-4-imidazolidinone. A mixture of carbobenzoxy-glycineamide (5.2 g., 0.025 mole), *p*-nitrobenzaldehyde (3.78 g., 0.025 mole), and β-naphthalenesulfonic acid (0.2 g.) in benzene (200 ml.) was refluxed for 2 hr. as described above (general procedure). After cooling to room temperature the solid material was filtered and crystallized from methanol–ethyl acetate. The yield was 4.14 g. (48%), m.p. 222°.

Anal. Calcd. for $C_{17}H_{15}O_5N_3$: C, 59.82; H, 4.43; N, 12.31. Found: C, 59.69; H, 4.33; N, 12.20.

1-Carbobenzoxy-2-phenyl-5-benzyl-4-imidazolidinone. A solution of carbobenzoxy-*d,l*-phenylalanine (3.75 g., 0.0125 mole), benzaldehyde (2.5 ml.) and β-naphthalene sulfonic acid (0.1 g.) in benzene (100 ml.) was refluxed as described above (general procedure). The residue obtained after removal of the solvent was crystallized from benzene-methylcyclohexane to give a product (1.4 g.) which melted at 170–174°. The addition of hexane to the mother liquor precipitated a second product (2.3 g.) which melted at 79–81°. The melting points of the products were raised to 186° and 84°, respectively, after recrystallization (Table I) and a mixed melting point was depressed. The infrared spectra of the two products which were almost identical showed carbonyl absorptions at 1710–1720 cm.$^{-1}$, NH absorptions at 3420 cm.$^{-1}$, and a strong band at 1400 cm.$^{-1}$ They lack the NH absorptions of the starting material in the 1500–1600 cm.$^{-1}$ region. The lower melting isomer crystallizes with benzene in a 2:1 ratio. It loses 10% of its weight on drying at 140°/0.01 mm. for 3 hr. and the melt which solidifies on cooling (m.p. 55–58°) has an analysis which agrees well for 1-carbobenzoxy-2-phenyl-5-benzyl-4-imidazolidinones.

Anal. Calcd. for $C_{24}H_{22}O_3N_2$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.29; H, 5.66; N, 7.35.

4-Imidazolidinones. 1-Carbobenzoxy-4-imidazolidinone (0.01 mole) was hydrogenated catalytically in ethanol (100 ml.) under 4 atm. pressure and in the presence of 5% palladized charcoal (0.1 g.). After 5 hr. the solution was filtered from the catalyst and evaporated *in vacuo* to dryness. The solid 4-imidazolidinone thus obtained was crystallized from a suitable solvent (Table II). The oily imidazolidinones were dissolved in dry ether and the solution was saturated with dry hydrogen chloride. The hydrochlorides were filtered and crystallized from absolute ethanol and dry ether (Table II).

2-p-Nitrophenyl-4-imidazolidinone hydrobromide. 1-Carbobenzoxy-2-*p*-nitrophenyl-4-imidazolidinone (1.7 g.) was dissolved in a solution of hydrogen bromide in glacial acetic acid (25%; 4 g.). After 1 hr., dry ether (50 ml.) was added and the hygroscopic hydrobromide which precipitated was washed three times with 50-ml. portions of dry ether. The hydrobromide was then suspended in ethyl acetate (100 ml.) and anhydrous potassium carbonate (3 g.) was added. After stirring for 3 hr. the solution was filtered and evaporated to dryness *in vacuo*. The free imidazolidinone thus obtained was crystallized from ethyl acetate–hexane. The yield was 0.34 g. (33%), m.p. 127°.

Anal. Calcd. for $C_9H_9O_3N_3$: C, 52.17; H, 4.38; N, 20.28. Found: C, 52.40; H, 4.53; N, 20.29.

Carbobenzoxyglycine-1-isobutenylamide. A mixture of carbobenzoxyglycineamide (0.025 mole), isobutyraldehyde (0.050 mole), and β-naphthalenesulfonic acid in benzene (200 ml.) was refluxed for 2 hr. as described above (general procedure). The product obtained after the evaporation of the solvent *in vacuo* was crystallized from ethyl acetate. The yield was 73%; m.p. 136°.

(13) Melting points were taken on a Fisher-Johns block and are uncorrected.

(14) R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3135 (1948).

(15) S. W. Fox and H. Wax, *J. Am. Chem. Soc.*, **73**, 2936 (1951).

Anal. Calcd. for $C_{14}H_{18}O_3N_2$: C, 64.10; H, 6.92; N, 10.68; mol. wt., 262. Found: C, 63.91; H, 6.71; N, 10.75; mol. wt., 242.

Carbobenzoxyglycineisobutylamide. Carbobenzoxyglycine-1-isobutenylamide (0.15 g.) was catalytically hydrogenated in ethanol (50 ml.) under 4 atm. pressure in the presence of 5% palladized charcoal (0.1 g.). After 4 hr. the solution was filtered from the catalyst and evaporated *in vacuo* to dryness. The glycine isobutylamide thus obtained was dissolved in 10% sodium bicarbonate solution (10 ml.) and carbobenzoxylated in an ice water bath with carbobenzoxy chloride (0.5 g.). The product was extracted with ether (100 ml.) and the ethereal solution was washed with water and 10% hydrochloric acid and dried over sodium sulfate. The residue obtained after the evaporation of the ether was crystallized from ethyl acetate–hexane. The yield was 0.42 g. (64%), m.p. 71°.

Anal. Calcd. for $C_{14}H_{20}O_3N_2$: C, 63.61; H, 7.63; N, 10.60. Found: C, 63.78; H, 7.72; N, 10.49.

This compound was found to be identical, through infrared spectra and mixed melting point, with carbobenzoxyglycineisobutylamide prepared from carbobenzoxyglycine and isobutylamide in the presence of dicyclohexylcarbodiimide.[16]

Glycine 1-isobutenylamide hydrobromide. Carbobenzoxyglycine-1-isobutenylamide (1.3 g.) was dissolved in a 25% solution of hydrogen bromide in glacial acetic acid (4.0 g.).[12] After 30 min. dry ether (50 ml.) was added and the solid precipitate was filtered and washed with dry ether. The hydrobromide melted at 173–175° after crystallization from absolute ethanol and dry ether; yield 1.0 g. (96%).

Anal. Calcd. for $C_6H_{13}ON_2Br$: N, 13.41; Br, 38.22. Found: N, 13.21; Br, 38.10.

Carbobenzoxy-d,l-alanine 1-isobutenylamide. A mixture of carbobenzoxy-*d,l*-alanineamide (0.025 mole), isobutyraldehyde (0.050 mole), and β-naphthalenesulfonic acid (0.2 g.) in benzene (200 ml.) was refluxed for 1 hr. as described above (general procedure). The product obtained after the evaporation of the solvent *in vacuo* was crystallized from ethyl acetate–hexane and melted at 113°; yield 80%.

Anal. Calcd. for $C_{15}H_{20}O_3N_2$: C, 65.19; H, 7.30; N, 10.14. Found: C, 65.36; H, 7.11; N, 9.95.

Carbobenzoxy-d,l-phenylalanine 1-isobutenylamide. A mixture of carbobenzoxy-*d,l*-phenylalanineamide (0.025 mole), isobutyraldehyde (0.050 mole), and β-naphthalenesulfonic acid (0.2 g.) in benzene (200 ml.) was refluxed for 1 hr. as described above (general procedure). The product melted at 127° after crystallization from benzene; yield 93%.

Anal. Calcd. for $C_{21}H_{24}O_3N_2$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.56; H, 6.67; N, 8.07.

Reaction of phenylacetamide with isobutyraldehyde. A mixture of phenylacetamide (3.4 g., 0.025 mole), isobutyraldehyde (2.8 g., 0.050 mole), and β-naphthalenesulfonic acid (0.25 g.) in benzene (250 ml.) was refluxed for 1.5 hr. as described above (general procedure). The solvent was removed *in vacuo* and the residue was chromatographed over 100 g. of basic aluminum oxide (Merck). The *N*-(1-isobutenyl)phenylacetamide was eluted first with benzene-chloroform (1:2) followed by isobutylenebisphenylacetamide. The *N*-(1-isobutenyl)phenylacetamide melted at 102° after crystallization from ethyl acetate–hexane; yield 2.54 g. (52%).

(16) J. C. Sheehan and G. P. Hess, *J. Am. Chem. Soc.*, **77**, 1067 (1955).

Anal. Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.35; H, 7.96; N, 7.37.

The isobutylenebisphenylacetamide melted at 223° after crystallization from aqueous ethanol; yield 1.80 g. (43%).

Anal. Calcd. for $C_{20}H_{24}O_2N_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 74.21; H, 7.24; N, 8.62.

N-Isobutylphenylacetamide. *N*-(1-Isobutenyl)phenylacetamide (0.79 g.) was hydrogenated catalytically in ethanol (20 ml.) under atmospheric pressure and in the presence of 5% pallidized charcoal (0.1 g.). After 1 mole of hydrogen was absorbed (7 hr.) the solution was filtered from the catalyst and evaporated to dryness *in vacuo*. The residue was crystallized from ethyl acetate–hexane and melted at 76°; yield 0.67 g. (84%).

Anal. Calcd. for $C_{12}H_{17}ON$: C, 75.35; H, 8.96; N, 7.39. Found: C, 75.53; H, 8.76; N, 7.30.

This compound was found to be identical, through mixed melting point and infrared spectra, with *N*-isobutylphenylacetamide prepared from phenylacetyl chloride and isobutylamine by the Schotten-Baumann procedure.

N-(1-Cyclohexenyl)phenylacetamide. A mixture of phenylacetamide (3.4 g., 0.025 mole), cyclohexanone (4.0 g., 0.050 mole and β-naphthalenesulfonic acid (0.2 g.) in toluene (250 ml.) was refluxed for 24 hr. as described above (general procedure). The product melted at 106° after crystallization from benzene-hexane; yield 3.19 g. (59%).

Anal. Calcd. for $C_{14}H_{17}ON$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.22; H, 7.70; N, 6.62.

N-Cyclohexylphenylacetamide. *N*-(1-Cyclohexenyl)phenylacetamide (2.15 g.) was hydrogenated catalytically in ethanol (20 ml.) under atmospheric pressure in the presence of 5% palladized charcoal (0.2 g.). After 1 mole of hydrogen was absorbed (8 hr.) the solution was filtered from the catalyst and evaporated to dryness *in vacuo*. The residue was crystallized from ethyl acetate and melted at 139°; yield 1.79 g. (82%).

Anal. Calcd. for $C_{14}H_{19}ON$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.29; H, 8.65; N, 6.49.

This compound was found to be identical, through mixed melting point and infrared spectra, with *N*-cyclohexylphenylacetamide prepared from phenylacetyl chloride and cyclohexylamine by the Schotten-Baumann procedure.

Benzylidenebisphenylacetamide. A mixture of phenylacetamide (3.4 g., 0.025 mole), benzaldehyde (5.3 g., 0.050 mole), and β-naphthalenesulfonic acid (0.25 g.) in benzene (300 ml.) was refluxed for 5 hr. as described above (general procedure). The solution was cooled to room temperature and the product which had precipitated was filtered and crystallized from ethanolwater. The yield was 4.3 g. (94%), m.p. 238°.

Anal. Calcd. for $C_{23}H_{22}O_2N_2$: C, 77.07; H, 6.19; N, 7.82. Found: C, 77.15; H, 6.16; N, 7.86.

Acid hydrolysis of 4-imidazolidinones. 4-Imidazolidinone (5×10^{-5} mole) was dissolved in 5*N* hydrochloric acid (1 ml.) and the solution was left at room temperature. Samples were taken out at various intervals of time and were put on the chromatogram. The paper chromatograms (ascending) were run overnight on Whatman No. 1 paper, with *n*-propyl alcohol–acetic acid–water (10:1:9) or methanol-pyridine-water (80:40:20) as developing solvent systems. Spots were detected with ninhydrin.

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