TABLE II

THE SECOND-ORDER RATE CONSTANT AT VARIOUS TEMPERATURES ($10^5\ M^{-1}\ \text{sec}^{-1}$)

	Temp, °C					
Reactants (M)	60	50	45	40	35	30
$ClCH_2COO^-$ (0.1) + NH_3 (5)	...	10.0	6.13	3.25	2.17	...
$ClCH_2COO^-$ (0.055) + $NH_2CH_2COO^-$ (0.15)	209	90.0	...	36.3	...	13.3
$ClCH_2COO^-$ (0.055) + $NH(CH_2COO^-)_2$ (0.15)	223	96.7	...	28.9	...	15.1

TABLE III

pK_a VALUES FOR THE CONJUGATE ACID OF AMINO COMPOUNDS AND ACTIVATION PARAMETERS FOR THE REACTION OF CHLOROACETIC ACID WITH AMINO COMPOUNDS IN AN AQUEOUS SOLUTION AT 30 ± 0.1° AND IONIC STRENGTH 3

Reactants	pK_a[a]	pK_a[b]	$k^c \times 10^5$, $M^{-1}\ \text{sec}^{-1}$	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu
$ClCH_2COO^-$ + NH_3	9.45	9.25	1.12	20.9	−16
$ClCH_2COO^-$ + $NH_2CH_2COO^-$	9.60	9.74	12.2	18.5	−17
$ClCH_2COO^-$ + $NH(CH_2COO^-)_2$	9.15	9.89	11.2	18.7	−17

[a] The acidities of protonated amines were measured at 30° and ionic strength 3. [b] The acidities of protonated amines taken at 30° and lower ionic strength. [c] Second-order rate constant.

apparent from the energy of activation, but not from the entropy of activation which is in the order $NH_2CH_2COO^- \simeq NH(CH_2COO^-)_2 < NH_3$. The observed p$K_a$ values at 30° and ionic strength 3 for conjugate acids of amines are in the order $NH_2CH_2COO^- > NH_3 > NH(CH_2COO^-)_2$, but the basicities and nucleophilicities of these amines at lower ionic strength are in the order: $NH(CH_2COO^-)_2 \simeq NH_2CH_2COO^- > NH_3$. The difference between these values may be due to the difference of ionic strength.

Therefore, the reactivities of these amino compounds depend more on the basicity or nucleophilicity of amino nitrogen. A slight decrease in rate for iminodiacetic acid, compared with the rate for glycine, may have been due to the steric effect. However, the reaction of chloroacetic acid with these amino compounds possesses comparable entropies of activation. Hence, the steric effect of the introduced carboxymethyl group seemed to be negligible.

The rate of reaction is expressed as $v = k[\text{amine}] \times [ClCH_2COO^-]$, where k depends on the basicity (and nucleophilicity) of amino nitrogen. Further, the entropy of activation is *ca.* −16 to −17 eu. These facts suggest that these reactions proceed by the SN2 mechanism.

A mechanism involving carbonium ion or α-lactone is excluded, since the rate did not decrease in spite of the accumulation of chloride ion as the reaction proceeded; *i.e.*, no common ion effect was observed, and the rate of the hydrolysis of substrates compared with ammonolysis is slow.

Registry No.—Chloroacetic acid, 79-11-8; ammonia, 7664-41-7; glycine, 56-40-6; iminodiacetic acid, 142-73-4.

A New Thermal Rearrangement of Allylic Phenylurethans[1]

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On heating to 200–240° with a catalytic amount of sodium hydride, phenylurethans of allylic alcohols rearrange, with expulsion of carbon dioxide, to N-phenylallylamines. Predominant inversion of the allyl moiety occurs and the reaction is considered to proceed by a cyclic electron reorganization process. Rearrangement of optically active Δ^2-cyclohexenylphenylurethan is accompanied by 65% retention of configuration and 35% racemization. Small amounts of imidazolidones are found as by-products and a pathway for their formation, involving base-catalyzed cyclization of N-allylureas, is proposed and supported by testing the presumed intermediates.

Of the thermal reorganization reactions which involve six-membered cyclic transition states,[2] one of the mechanistically most interesting and synthetically most useful families is that whose prototype is the Claisen rearrangement of allyl vinyl ethers (Chart I, reaction a[3]). A number of variations on this theme are known, some of which are listed in Chart I. These include the rearrangement of allylic imidates to amides (b),[4,5] the rearrangement of ketene acetals and their nitrogen analogs to esters and amides (c),[6,7] the pyrolysis of allylic acetoacetates and cyanoacetates (d),[8,9] and the rearrangement of carbanions of allylic esters to α-allyl carboxylic acids (e).[10] Similar rearrangements are observed in reactions which verge on the SNi′ type, such as the thermal isomerization of allyl esters (f),[11,12] and the recently reported conversion of allyl sulfamates into allylamines (g).[13]

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(1) This study was initiated with the support of a Research Fellowship to R. K. H. from the Alfred P. Sloan Foundation and supported by a research grant (GP-3811) from the National Science Foundation, to both of whom the authors express their gratitude.

(2) J. Mathieu and J. Valls, *Bull. Soc. Chim. Fr.*, 1509 (1957).

(3) (a) C. D. Hurd and M. A. Pollock, *J. Amer Chem. Soc.*, **60,** 1905 (1938); (b) W. J. Croxall and J. O. Van Hook, *ibid.*, **72,** 803 (1950); (c) A. W. Burgstahler and I. C. Nordin, *ibid.*, **83,** 198 (1961).

(4) O. Mumm and F. Möller, *Ber.*, **70,** 2214 (1937).

(5) R. M. Roberts and F. A. Hussein *J. Amer. Chem. Soc.*, **82,** 1950 (1960).

(6) S. M. McElvain, H. I. Anthes, and S. H. Shapiro, *ibid.*, **64,** 2525 (1942).

(7) (a) H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Ann.*, **641,** 1 (1961); (b) A. E. Wick, D. Felix, K. Steen, and A. Eschenmoser, *Helv. Chim. Acta*, **47,** 2425 (1964).

(8) (a) M. F. Carroll, *J. Chem. Soc.*, 507 (1941); (b) W. Kimel and A. C Cope, *J. Amer. Chem. Soc.*, **65,** 1992 (1943).

(9) E. C. Kooyman, R. Louw, and W. A. M. de Tonkelaar, *Proc. Chem. Soc.*, 66 (1963).

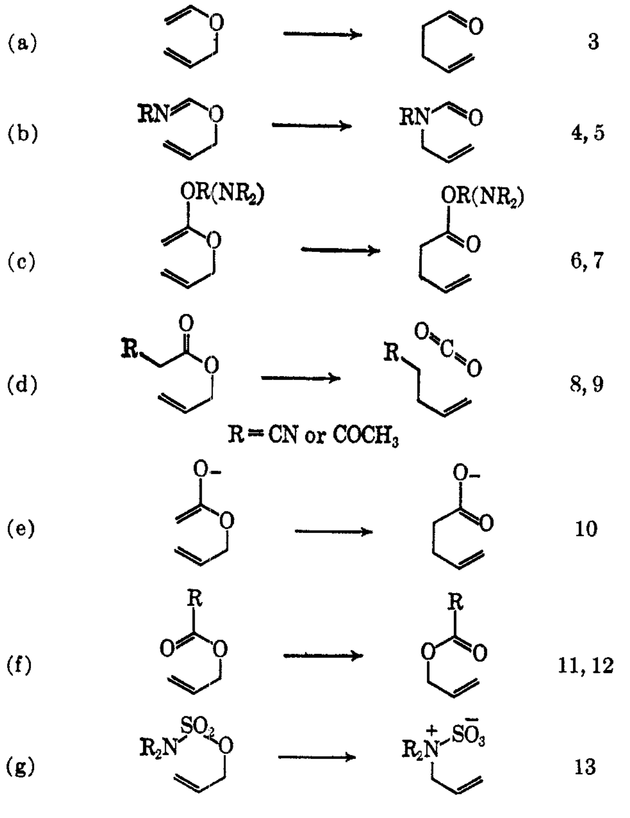
(10) (a) R. T. Arnold and S. Searles, Jr., *J. Amer. Chem. Soc.*, **71,** 1150 (1949); (b) K. C. Brannock, H. S. Pridgen, and B. Thompson, *J. Org. Chem.* **25,** 1815 (1960).

(11) (a) C. S. Marvel and N. O. Brace, *J. Amer. Chem. Soc.*, **70,** 1775 (1948); (b) E. A. Braude, D. W. Turner, and E. S. Waight, *Nature*, **173,** 863 (1954); (c) E. A. Braude and D. W. Turner, *Chem. Ind.* (London), 1223 (1955).

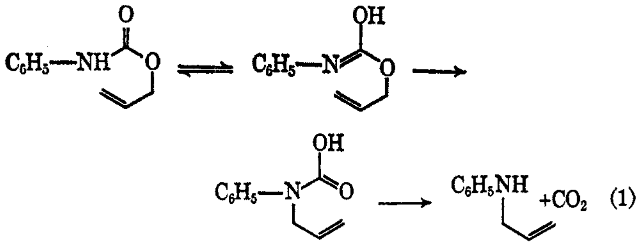
(12) J. Kenyon, S. M. Partridge, and H. Phillips, *J. Chem. Soc.*, 207 (1937).

(13) E. H. White and C. A. Elliger, *J. Amer. Chem. Soc.*, **87,** 5261 (1965).

CHART I
REACTIONS RELATED TO THE CLAISEN REARRANGEMENT

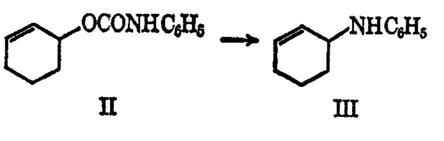


We wish to report a new and practical reaction which belongs in this category, the thermal rearrangement of phenylurethans of allylic alcohols to N-allylanilines. Since urethans are isoelectronic with ester carbanions, it appeared that they might undergo a thermal reaction similar to reaction e in Chart I to produce carbamic acids, which would decarboxylate under the reaction conditions (eq 1).



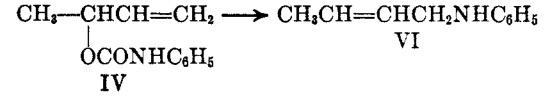
Rearrangement.—Heating the phenylurethans of several allylic alcohols at 200–240° caused the evolution of carbon dioxide and formation of amines. The reaction occurred much more readily when a catalytic amount of sodium hydride was added, and all preparative experiments involved heating the phenylurethan with 1–2% of its weight of a sodium hydride dispersion in mineral oil for 3–12 hr. Under these conditions the phenylurethan (I) of allyl alcohol yielded N-allylaniline in 24% yield. Δ^2-Cyclohexenylphenylurethan (II) afforded N-phenyl-Δ^2-cyclohexenylamine (III) in 34% yield.

$$\underset{\text{I}}{CH_2{=}CHCH_2OCONHC_6H_5} \longrightarrow CH_2{=}CHCH_2NHC_6H_5$$

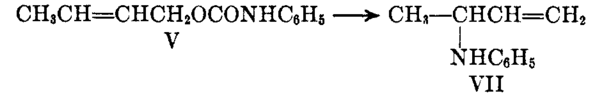


II III

A cyclic rearrangement mechanism requires inversion of the allyl moiety; this was tested with the phenylurethans (IV and V) of α-methallyl and crotyl alcohol. The amine formed in 60% yield by pyrolysis of IV was shown by vpc analysis to be essentially pure N-crotylaniline (VI), accompanied by 1–2% each of aniline and N-phenyl-α-methallylamine (VII). The butenylaniline formed in yields of 56–64% from V was similarly shown to be an 85:15 mixture of VII and VI. The two isomeric amines could be separated by careful distillation through a spinning-band column. Their structures were established unambiguously from infrared and nmr spectra and by hydrogenation of VII to N-*sec*-butylaniline. The predominant product of each rearrangement is consequently the amine in which the allyl group has inverted.



$$\underset{\text{IV}}{CH_3\underset{|\atop OCONHC_6H_5}{C}HCH{=}CH_2} \longrightarrow \underset{\text{VI}}{CH_3CH{=}CHCH_2NHC_6H_5}$$



$$\underset{\text{V}}{CH_3CH{=}CHCH_2OCONHC_6H_5} \longrightarrow \underset{\text{VII}}{CH_3\underset{|\atop NHC_6H_5}{C}HCH{=}CH_2}$$

Amines VI and VII are thermally stable. The small amount of allylic isomer which accompanies each in the pyrolysis may have two possible origins: (a) decomposition of the phenylurethan without allylic rearrangement or (b) partial isomerization of the phenylurethan to its allylic isomer prior to decomposition to amine. The latter alternative may be more likely in view of the report[12] of thermal isomerization of arylurethans to allylic isomers. We were unable to recover any phenylurethans from the pyrolysis mixture to test directly the possibility of phenylurethan isomerization in this case.

Though the yields of amines produced in this rearrangement are only moderate, the yields reported here are all for redistilled products, and the ease of preparation of the starting materials and simplicity of the reaction conditions make this a valuable method for the preparation of N-phenylallylamines. It may prove to be of particular utility when one unsymmetrical allylamine, such as VI or VII, is desired, since the most common present method of preparation, the displacement of allyl halides by amines, leads invariably to mixtures of allylic isomers.[14]

A single attempt to rearrange the *n*-butylurethan of crotyl alcohol under similar conditions gave no amine.

By-products.—Small amounts of aniline and, in some cases, *sym*-diphenylurea, resulting from decomposition of the phenylurethans, were isolated in most runs. From the rearrangement of allylphenylurethan there was isolated, in addition to N-allylaniline, about 5% of a neutral solid, $C_{16}H_{16}N_2O$, mp 122–123°. The infrared spectrum revealed the absence of N–H bands and showed aromatic absorption as well as a strong carbonyl band at 5.87 μ. The nmr spectrum showed a multiplet in the aromatic region centered about 7.3, a multiplet at 3.1–4.4, and a doublet at 1.2 ppm; the three groups of protons were in the ratio 10:3:3. These data led to the suggestion that the compound might be 1,3-diphenyl-4-methylimidazolidone-2 (VIII).

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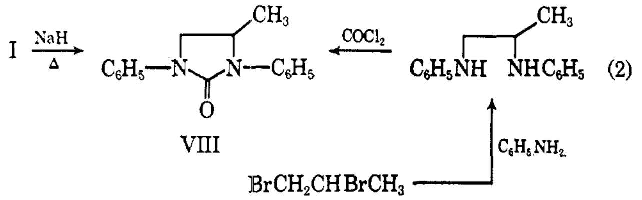
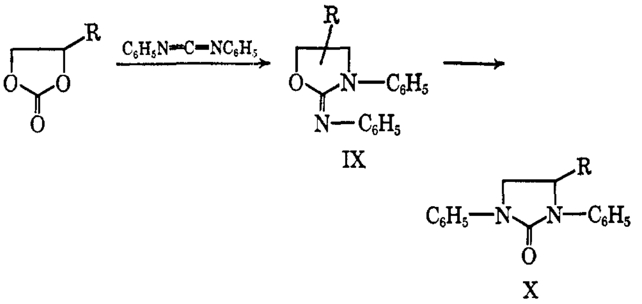
[14] For example, the reaction of α-methallyl chloride with N-methylanilines gives less than 10% of the S_N2 displacement product: D. C. Dittmer and A. F. Marcantonio, *J. Amer. Chem. Soc.*, **86**, 5621 (1964).

However, a compound of this structure was reported a few years ago by Gulbins and Hamann,[15] with mp 76–77°. Gulbins and Hamann prepared their compound by reaction of propylene carbonate with diphenylcarbodiimide, and assigned the structure by analogy with the corresponding product from ethylene carbonate, which they showed to be the known 1,3-diphenylimidazolidone-2 (X, R = H).

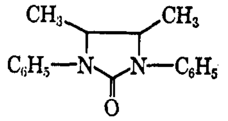
A sample kindly furnished by Professor Hamann confirmed the nonidentity of the propylene carbonate–diphenylcarbodiimide product with the by-product from the allyl phenylurethan rearrangement. Though the nmr and infrared spectra showed certain similarities, they were distinctly different. In order to decide which substance is the imidazolidone VIII a sample of VIII was prepared by the unambiguous method of Hanssen.[16] 1,2-dibromopropane was heated with aniline and the resulting diamine treated with phosgene (eq 2). Authentic VIII prepared in this way melted at 122–123° and was identical with the allylphenylurethan rearrangement product. The structure of the Gulbins–Hamann compound remains in doubt. These authors had suggested that the reaction of carbonates with diphenylcarbodiimide proceeds *via* the intermediates IX which then thermally isomerize to imidazolidones X, and it may be that their compound is one of the methyl derivatives (R = CH_3) of IX, but we have no further information on this subject.



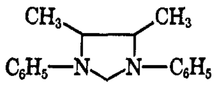
(2)



A homolog of VIII, 1,3-diphenyl-4,5-dimethylimidazolidone-2 (XI), was isolated in 2–3% yield as a mixture of stereoisomers from the rearrangement of crotylphenylurethan (V). Neither fractional crystallization nor chromatography effected more than partial separation of the isomers. In one run it was possible to isolate small amounts of two fairly sharp-melting substances, mp 145–146° and 152–153°, but their nmr spectra showed clearly that neither was a pure stereoisomer. The nmr spectrum of the mixture showed aromatic protons (10 H) at 7.0–7.7, overlapping quartets (2 H) centered about 4, and a doublet (6 H) at 1.4 ppm. Synthesis of XI from 2,3-dibromobutane (mixture of stereoisomers) and aniline, followed by ring closure with phosgene, gave a mixture with the same melting point behavior and identical infrared and nmr spectra. Lithium aluminum hydride reduction of XI gave the imidazolidine XII, whose nmr spectrum showed aromatic absorption at 6.5–7.4 (10 H), a singlet at 4.65 (2 H), a quartet at 3.9 (2 H), and a doublet at 1.2 ppm (6 H).



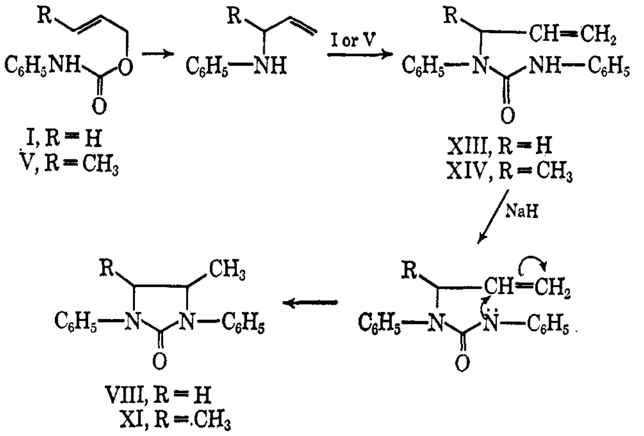
XI



XII

A plausible mechanism for the formation of the imidazolidones VIII and XI is suggested in Scheme I.

SCHEME I



Nucleophilic attack of amine (N-allylaniline or VII) on the carbonyl group of unreacted phenylurethan would lead to the unsymmetrical ureas XIII and XIV. Intramolecular addition of the urea N-H group to the double bond, catalyzed by sodium hydride, could then form VIII and XI. The addition of alkali metal derivatives of organic compounds to unconjugated olefins is a well-documented process.[17]

An obvious test of this proposal is to determine whether the presumed intermediates, ureas XIII and XIV, do in fact cyclize to imidazolidones. The ureas were prepared from the amines and phenyl isocyanate and separately heated with sodium hydride for a few minutes, resulting in the formation of VIII and XI in low yields. In the absence of sodium hydride, only *sym*-diphenylurea resulted from heating XIV.

Stereochemistry.—A stereochemical characteristic of the cyclic mechanism by which the reactions in Chart I take place is the ability to transmit asymmetry from one site on the cycle to another through a transition state of fairly rigid geometric requirements. This sort of internal asymmetric induction has been observed for the reactions a,[18] c,[7b] d,[19] and f.[12] In order to make

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[15] K. Gulbins and K. Hamann, *Chem. Ber.*, **94**, 3287 (1961).

[16] A. Hanssen, *Ber.*, **20**, 784 (1887).

[17] (a) J. G. Welch and R. M. Magid, *J. Amer. Chem. Soc.*, **89**, 5300 (1967); (b) H. Pines, J. Veseley, and V. Ipatieff, *ibid.*, **77**, 554 (1955); (c) P. D. Bartlett, S. Friedman, and M. Stiles, *ibid.*, **75**, 1771 (1953); (d) G. G. Eberhardt, *J. Org. Chem.*, **29**, 643 (1964). For a particularly close analogy, see (e) R. F. Brown and N. M. van Gulick, *J. Amer. Chem. Soc.*, **77**, 1092 (1955).

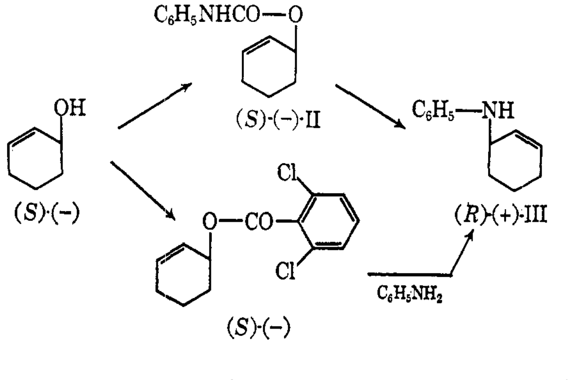
[18] R. K. Hill and A. G. Edwards, *Tetrahedron Lett.*, 3239 (1964). Asymmetric induction has also been observed in the Claisen rearrangement of aryl allyl ethers: E. R. Alexander and R. W. Kluiber, *J. Amer. Chem. Soc.*, **73**, 4304 (1951); H. L. Goering and W. I. Kimoto, *ibid.*, **87**, 1748 (1965).

[19] R. K. Hill and M. E. Synerholm, *J. Org. Chem.*, **33**, 925 (1968).

this stereochemical test in the rearrangement of allylic phenylurethans, we have studied the pyrolysis of optically active Δ^2-cyclohexenylphenylurethan (II). If the rearrangement involves dissociation of the starting material into discrete radicals or ions, then any delocalized intermediate from the cyclohexenyl moiety would be symmetrical and the product racemic.

Pyrolysis of the phenylurethan of (*S*)-(−)-Δ^2-cyclohexenol[20] yielded an amine (III) whose hydrochloride showed no detectable rotation at the D line, but a clear, though small, positive rotation at 300 mμ. To obtain an estimate of the optical purity of III and to establish at the same time its absolute configuration, III was prepared independently from Δ^2-cyclohexenol as shown in Scheme II. The (*S*)-(−) alcohol was converted into the 2,6-dichlorobenzoate and heated with aniline to afford the (*R*)-(+)-hydrochloride of III. The optical rotation of the amine III prepared by the phenylurethan rearrangement was 65% of that of the amine prepared by displacement. Consequently the rearrangement is accompanied by a minium of 35% racemization; if any racemization occurs in the displacement reaction this figure will, of course, be higher.

SCHEME II



It may be noted that regardless of whether the displacement of the allylic dichlorobenzoate is an SN2 or SN2′ process the result is inversion of configuration;[21] the amine prepared in this way from the (*S*) alcohol[22] must have the (*R*) configuration. Amine prepared from phenylurethan rearrangement has the same sign and consequently is also formed with inversion of configuration, a result demanded by the cyclic transition state.

These experiments thus show that the thermal rearrangement of allylic phenylurethans displays the characteristic inversion of the allyl double bond and induction of asymmetry which are typical of concerted cyclic electron-reorganization reactions. The partial racemization accompanying the formation of III may be due to a small degree of nonconcerted rearrangement, or it may be an artifact caused by partial racemization of the starting phenylurethan by allylic isomerization. These alternatives could be distinguished by the use of a suitable unsymmetrical optically active phenylurethan.

Experimental Section

Preparation of Phenylurethans.—The allylic alcohol was treated with an equimolar amount of phenyl isocyanate. When the initial reaction had subsided, the mixture was heated on the steam bath for 1 hr. Dilution with 1:1 benzene-petroleum ether (60–70°) and cooling gave the phenylurethan in high yield and purity. Phenylurethans obtained were allylphenylurethan, mp 68–69° (lit.[23] mp 70°); α-methallylphenylurethan, mp 50–52° (lit.[24] mp 50–51°); crotylphenylurethan, mp 78.5–80° (lit.[25] mp 79.4–80.0°); Δ^2-cyclohexenylphenylurethan, mp 107–108° (lit.[26] mp 107°).

Rearrangement of Allylphenylurethan.—The phenylurethan (100 g) was mixed with 2 g of a 55% dispersion of sodium hydride in mineral oil and heated under reflux in a Woods' metal bath at 210–230° for 12 hr. After cooling, the mixture was diluted with an equal volume of ether and kept at 5° overnight. The solid which had precipitated was collected (see below) and the filtrate extracted with 125 ml of 6 *N* hydrochloric acid in several portions. The acidic extracts were made strongly alkaline with sodium hydroxide and extracted with ether. After drying over magnesium sulfate, the ether solution was distilled through a Vigreux column, affording 26 g (35%) of amine, bp 100–115° (15 mm). Careful redistillation through an 18-in. spinning-band column gave 18 g (24%) of **N-allylaniline**, bp 85–87° (3 mm), lit.[27] bp 68–70° (1.3 mm). The **hydrochloride**, after recrystallization from ethanol–ether, melted at 118–119° (lit.[5] mp 110°); no melting point depression was observed when the hydrochloride was mixed with an authentic sample prepared from aniline and allyl bromide.

N,N′-Diphenyl-N-allylurea (XIII), prepared from the amine and phenyl isocyanate, melted at 84–85° after recrystallization from benzene–petroleum ether.

Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 75.96; H, 6.48; N, 11.28.

The solid (4.0 g) which had crystallized from the ether solution of the reaction mixture was recrystallized from alcohol to give **1,3-diphenyl-4-methylimidazolidone-2 (VIII)**, mp 122–123°.

Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.21; H, 6.42; N, 11.06.

Preparation of VIII. A. From 1,2-Dibromopropane.—A mixture of 20 g of 1,2-dibromopropane and 50 g of aniline was heated under reflux for 2 hr, poured into a mixture of ice and hydrochloric acid, and extracted with ether. The acidic solution was made alkaline and extracted with ether, and the extracts dried over magnesium sulfate and distilled, yielding 13.9 g (62%) of 1,2-dianilinopropane, bp 220–225° (0.5 mm).

To a cooled, stirred solution of this diamine in benzene was slowly added a benzene solution of 6.2 g of phosgene, followed by 10 g of pyridine in benzene, and the mixture was stirred 30 min at room temperature. The solution was filtered and the filtrate evaporated to dryness. Three recrystallizations of the residue from ethanol gave VIII, mp 123–124°. Infrared and nmr spectra were identical with those of the sample obtained from the allylphenylurethan rearrangement, and the mixture melting point was not depressed.

B. From N,N′-Diphenyl-N-allylurea (XIII).—A mixture of 3.0 g of XIII and 0.2 g of sodium hydride dispersion was heated for a few minutes at 160–180°, cooled, and extracted with boiling cyclohexane. The extracts were filtered hot and concentrated at reduced pressure, and the residual yellow oil crystallized from ethanol, affording 0.1 g of VIII. After four recrystallizations from ethanol it melted at 123–124°, alone or mixed with the product of part A.

Rearrangement of crotylphenylurethan (100 g) was accomplished by heating with sodium hydride as described above for the allyl derivative. From the ether solution of the reaction mixture, on standing overnight at 5°, 1–2 g of a solid (XIa) precipitated and was filtered. The filtrate was extracted with 6 *N* hydrochloric acid; evaporation of the ethereal solution left a mixture of oil and a solid (XIb).

The aqueous acid extracts were made basic with sodium hydroxide and extracted with ether. The combined extracts

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[20] D. B. Denney, R. Napier, and A. Cammarata, *J. Org. Chem.*, **30**, 3151 (1965). We are grateful to Professor Denney for furnishing us with the details of his elegant synthetic procedure before publication.

[21] SN2′ displacement on cyclohexenol derivatives involves a *cis* relation of nucleophile and leaving group; see G. Stork and W. N. White, *J. Amer. Chem. Soc.*, **78**, 4609 (1956).

[22] J. A. Mills, *J. Chem. Soc.*, 4976 (1952).

[23] H. Pariselle, *Ann. Chim.* (Paris), [8] **24**, 339 (1911).

[24] A. F. Dobrjanski, R. Gutner, and M. Schtschigelskaja, *Zh. Obshch. Khim.*, **7**, 1319 (1937).

[25] E. Galand, *Bull. Soc. Chim. Belges*, **39**, 529 (1930).

[26] R. Willstäter and E. Sonnenfeld, *Ber.*, **46**, 2957 (1913).

[27] J. E. Hyre and A. R. Bader, *J. Amer. Chem. Soc.*, **80**, 437 (1958).

were dried and concentrated; vpc analysis[28a] showed that the amine mixture consisted of 8% aniline, 76% **N-phenyl-α-methallylamine** (VII), and 16% N-crotylaniline (VI). Distillation through a Vigreux column gave a small forerun, bp below 100° (15 mm), identified as aniline by its infrared spectrum and the formation of the hydrochloride, mp and mmp 197–198°. The main fraction, bp 100–115° (15 mm), weighed 43–49 g (56–64%). Vpc analysis[28b] showed this to be a mixture of 85% VII and 15% VI. Redistillation through an 18-in. spinning-band column gave pure VII, bp 107–111° (10 mm), 55–56° (0.35 mm) (lit. bp 130° (20 mm),[5] 63–65° (2 mm)[29]) in 34–45% yield. The infrared spectrum (neat) had N–H absorption at 2.88 and vinyl bands at 6.05, 10.02, and 10.80 μ. The nmr spectrum showed complex aromatic splitting at 6.3–7.2 (5 H), the characteristic vinyl pattern at 4.8–6.1 (3 H), a multiplet at 3.9 overlapping a broad N–H signal at 3.3 (total 2 H), and a doublet ($J = 7$ cps) at 1.2 ppm (3 H).

Anal. Calcd for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.64; H, 8.88.

The **hydrochloride** melted at 149–151° (lit.[5] mp 150°).

Anal. Calcd for $C_{10}H_{14}NCl$: C, 65.38; H, 7.68; N, 7.63. Found: C, 65.46; H, 7.68; N, 7.57.

The *p*-**nitrobenzoyl derivative**, recrystallized from heptane, melted at 67.5–68°.

Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.90; H, 5.44; N, 9.45. Found: C, 68.50; H, 5.65; N, 9.58.

N,N′-Diphenyl-N-(α-methallyl)urea (XIV), prepared from VII and phenyl isocyanate, had mp 56–57° (recrystallized from ligroin).

Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.58; H, 6.88; N, 10.67.

The minor component of the amine mixture from the rearrangement was identified as **N-crotylaniline** (VI) from the nmr spectrum of a pure sample separated by preparative vpc. The spectrum (in $CDCl_3$) showed a doublet of triplets (3 H) at 1.66 ppm (olefinic methyl), two vinyl protons at 5.5–5.7, five aromatic protons at 6.4–7.2, and overlapping bands due to N–H and $-CH_2-$ (3 H) at 3.5–3.6 ppm. The infrared spectrum showed an N–H band at 2.94 μ and double-bond absorption at 6.2 and 10.4 μ.

Hydrogenation of amine VII by catalysis in ethanol resulted in extensive hydrogenolysis. In benzene, however, hydrogenation over palladium–charcoal gave **N-phenyl-*sec*-butylamine, hydrochloride** mp and mmp 137–140° (lit.[5] mp 136°).

1,3-Diphenyl-4,5-dimethylimidazolidone-2 (XI). Formation of XIa.—The solid which precipitated from the ether solution of the reaction mixture was recrystallized several times from ethanol to give colorless crystals, mp 152–153°.

Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.27; H, 6.66; N, 10.37.

Formation of XIb.—The solid left by evaporation of the ether solution after extraction with acid was triturated with ether and recrystallized several times from ethanol, giving 1.0 g of crystals, mp 145–146°. A mixture of XIa and XIb melted at 137–139°.

Anal. Found: C, 76.39; H, 6.63; N, 10.55.

In all other runs than the one described, the imidazolidone isolated was a mixture of XIa and XIb and could not be separated into pure components by repeated recrystallization from ethanol or by chromatography on alumina.

Preparation of XI. A. From 2,3-Dibromobutane.—Using the procedure described above, 21.6 g of 2,3-dibromobutane (Eastman, mixture of stereoisomers) was treated with 50 g of aniline to yield 12.1 g (83%) of 2,3-dianilinobutane, bp 190–195° (1 mm). To a stirred, cooled solution of 5 g of this diamine in 50 ml of benzene was added dropwise a solution of 4 g of phosgene in 12 ml of benzene, followed by 3 ml of pyridine. The mixture was stirred for 30 min at room temperature, filtered, and evaporated to dryness. The residue (3.6 g) was recrystallized twice from alcohol to yield a mixture of XIa and XIb, mp 140–143°. The infrared and nmr spectra were identical with those of the mixture obtained from the rearrangement of crotylphenylurethan.

Anal. Found: C, 76.75; H, 6.96; N, 10.37.

B. From Urea (XIV).—A mixture of 5 g of XIV and 0.1 g of sodium hydride dispersion in mineral oil was heated to 100°. The mixture foamed and the temperature rose to 140°, where it was held for a few minutes. On cooling and dilution with alcohol a solid separated, which was filtered and recrystallized from alcohol. The yield was 0.9 g (18%) of a mixture of XIa and XIb, mp 136–139°, with nmr and infrared spectra identical with those of the product from part A. In the absence of sodium hydride, the only product isolated from heating XIV was *sym*-diphenylurea, mp and mmp 239–240°.

Reduction of XI.—A mixture of 650 mg of the imidazolidone (XI, mixture of isomers) and 500 mg of lithium aluminum hydride in 5 ml of tetrahydrofuran was stirred at room temperature for 6 hr and the excess hydride destroyed by the addition of ethyl acetate. When dilute hydrochloric acid was added to dissolve the salts a solid separated (350 mg), which was collected and recrystallized from ethanol to afford 1,3-diphenyl-4,5-dimethylimidazolidine (XII), mp 98–99°, apparently a single stereoisomer.

Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.72; H, 7.97; N, 11.07.

Rearrangement of α-Methallylphenylurethan.—The phenylurethan (IV) was rearranged as described above for V, heating the mixture for 3 hr at 240°. Vpc analysis of the crude basic product showed it to be almost completely N-crotylaniline (VI), contaminated with 1–2% each of aniline and N-phenyl-α-methallylamine (VII). Distillation gave pure VI, bp 58–59° (0.1 mm) (lit.[30] bp 89–90° (3 mm)), in 60% yield. The infrared and nmr spectra were identical with those of the sample of VI obtained as the minor product of rearrangement of V.

Rearrangement of Δ^2-Cyclohexenylphenylurethan.—A mixture of 7 g of the phenylurethan II and 0.15 g of a 55% sodium hydride dispersion in mineral oil was heated at 210–220° for 3 hr and worked up as described above. Small amounts of *sym*-diphenylurea, mp and mmp 239–240°, crystallized from the ether solution of the reaction mixture. Distillation of the basic fraction gave 0.5 g of aniline, bp 83–100° (25 mm), and 1.9 g (34%) of **N-phenyl-Δ^2-cyclohexenylamine (III)**, bp 153–158° (25 mm). The hydrochloride, mp 172°, did not depress the melting point of an authentic sample prepared by the reaction[31] of Δ^2-cyclohexenyl bromide with aniline.

Rearrangement of Optically Active II.—Optically active Δ^2-cyclohexenol was prepared by the method of Denney, Napier, and Cammarata.[20] The alcohol, bp 92–97° (50 mm) and $[\alpha]^{23}\mathrm{D}$ −5.88° (neat, 5-cm tube), furnished a phenylurethan, mp 107–108° and $[\alpha]^{23}\mathrm{D}$ −7.52° (*c* 9.85, chloroform).

Rearrangement of the levorotatory phenylurethan was carried out just as described for the racemic compound and afforded the hydrochloride of III, mp 172°, $[\alpha]^{23}\mathrm{D}$ 0°, and $[\alpha]^{23}{}_{300}$ +2.6° (*c* 1.84, chloroform).[32] The amine was regenerated from the hydrochloride and converted into N,N′-diphenyl-N-(Δ^2-cyclohexenyl)-urea by treatment with phenyl isocyanate. The urea had mp 122–123° and $[\alpha]^{23}\mathrm{D}$ −0.85 ± 0.57° (*c* 2.8, chloroform).[32]

Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.90; N, 9.58. Found: C, 77.87; H, 6.79; N, 9.44.

Alternate Preparation of III.—Following the procedure of Stork and White,[21] a solution of 2.1 g of Δ^2-cyclohexenol, $[\alpha]^{25}\mathrm{D}$ −15.2° (*c* 5.32, chloroform), in 10 ml of pyridine was treated with 5.0 g of 2,6-dichlorobenzoyl chloride and heated on the steam bath for 3 hr. After cooling, the mixture was saturated with gaseous ammonia, poured into 150 ml of 5% hydrochloric acid, and extracted with ether. The ether extracts were washed with dilute acid, water, and aqueous sodium bicarbonate, dried over potassium carbonate, concentrated, and diluted with 100 ml of petroleum ether (bp 30–60°). After standing 2 hr, the mixture was filtered through Celite, then through a short column of alumina, and distilled to afford 3.0 g of the dichlorobenzoate, bp 138–140° (0.5 mm) (lit.[21] bp 163–164° (1.6 mm)) and $[\alpha]^{22}\mathrm{D}$ −14.6° (*c* 9.2, chloroform).

A mixture of 3.0 g of the dichlorobenzoate and 5.2 g of aniline was heated to 110° for 46 hr, cooled, and distributed between ether and 10% hydrochloric acid. The acidic aqueous layer was made basic with 6 *N* sodium hydroxide solution and extracted with ether. After the ether extracts were dried (potassium carbonate), fractional distillation gave 1.4 g of amine III,

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(28) (a) On a 10-ft column of 15% Carbowax 20M (column temperature, 215°; flow rate, 110 cc of helium/min) the retention times were 3.6 min (aniline), 4.3 min (VII), and 7.2 min (VI). (b) With a 20-ft column of 30% SDC 710 on Chromosorb W, 45–60 mesh (column temperature, 220°; flow rate, 250 cc of helium/min), the retention times were 15 min (VII) and 23 min (VI).

(29) V. Wolf and D. Ramin, *Ann.*, **626**, 47 (1959).

(30) Y. A. Arbuzov, *Dokl. Akad. Nauk SSSR*, **63**, 531 (1948); *Chem. Abstr.*, **43**, 5403 (1949).

(31) Y. A. Arbuzov and T. A. Mastryukova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 665 (1952); *Chem. Abstr.*, **47**, 10493 (1953).

(32) We thank Dr. P. Laur and Mr. G. R. Krow for measuring these rotations on a Cary spectropolarimeter.

bp 88–90° (0.5 mm), which furnished a crystalline hydrochloride, mp 171–174°. The hydrochloride had rotations of $[\alpha]^{23}\text{D}$ +1.62° and $[\alpha]^{23}_{300}$ +10.8° (*c* 0.283, chloroform).[32] The infrared spectra of the free base and its hydrochloride were identical with those of authentic III and its hydrochloride.

Calculation of Asymmetric Induction.—The cyclohexenol sample, $[\alpha]\text{D}$ −5.88° (neat), used for the phenylurethan rearrangement is calculated to have $[\alpha]^{24}\text{D}$ −5.66° (*c* 5.54, chloroform), by comparing the rotation of its phenylurethan with that reported by Denney.[20] If no racemization occurred in the preparation and displacement of the allylic dichlorobenzoate, a sequence in which alcohol of $[\alpha]\text{D}$ −15.2° gave amine of $[\alpha]_{300}$ +10.8°, alcohol of $[\alpha]\text{D}$ −5.66° should have given amine of $[\alpha]_{300}$ +4.02° if asymmetric induction were quantitative. The experimental amine rotation of $[\alpha]_{300}$ +2.6° corresponds to 65% asymmetric induction.

Registry No.—(*S*)-(−)-Δ^2-Cyclohexenol, 6426-24-2; II, 15619-41-7; III, 15619-43-9; III hydrochloride, 15619-44-0; N,N′-diphenyl-N-(Δ^2-cyclohexenyl) urea, 15717-36-9; (*S*)-(−)-Δ^2-cyclohexenol dichlorobenzoate, 15717-37-0; VI, 6246-96-4; VII, 15645-60-0; VII *p*-nitrobenzoyl derivative, 15717-39-2; VIII, 15645-61-1; XI, 15645-62-2; 1,2-dianilinopropane, 15717-40-5; XII, 15645-63-3; XIII, 15645-64-4; XIV, 15717-41-6.

Phenylcyclohexadienes

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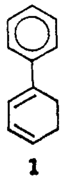
A detailed examination of the published methods for the reduction of biphenyl, *via* the alkali metal adducts, has shown that the phenylcyclohexadienes **3** and **4** may be formed depending on the conditions employed. The more reduced compounds, phenylcyclohexene and phenylcyclohexane, may also be produced. Dienes **1** and **2** can be prepared by the elimination of certain groups from the substituted 1-phenylcyclohexenes (**6**). Dienes **1–4** were isolated by glpc and the structures assigned on the basis of ultraviolet, mass, and nuclear magnetic resonance spectroscopic measurements.

During a study of the photochemistry of sodium tetraphenylborate[1] we isolated a compound the analytical data for which indicated that it was one of the phenylcyclohexadienes **1–5** and probably **2**.



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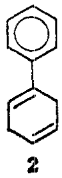

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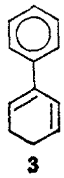

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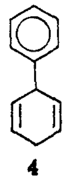

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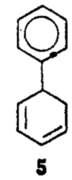

5

In the last 40 years, reports of compounds **1–4** have appeared but conclusive evidence for the structural assignments has been lacking. Although calculations predict **4** as the product resulting from the addition of alkali metals to biphenyl,[2] the Russian workers,[3] on the basis of spectral evidence, have reported **2** as the product. Their report was claimed as a correction of the earlier work of Schlenk and Bergmann[4] on the addition of lithium to biphenyl. These authors, on the basis of chemical evidence, assigned the structure **4** to the diene which they obtained. In 1939, Hückel and Bretschneider[5] studied the reaction between sodium and biphenyl in liquid ammonia at −70°. The adduct was decomposed with methanol and the diene **3** was claimed as the product on the basis of chemical evidence. In 1956, a further study was conducted[6] and, under conditions that the authors state are not appreciably different from those used previously, a diene was isolated to which the structure **4** was assigned. In this latter reaction the adduct was decomposed with ammonium chloride after a much shorter reaction time More recently, this preparation has been repeated by DeTar and Long[7] to provide an authentic sample of **4** to compare with the product obtained by the thermal decomposition of benzoyl peroxide in benzene. In an unrelated study,[8] isomer **1** has been reported to be formed by the dehydration of 3-phenyl-2-cyclohexen-1-ol over alumina at 350°. It was pointed out, however, that rearrangement under these conditions was possible.

Our unknown diene (A) had *m/e* 156, mp 89°, λ_{max} 249 mμ (ε 9300), which suggested a phenylcyclohexadiene type **2**. However, the Russian workers[3] claim **2** as a liquid with λ_{max} 250 mμ (ε 12,000). In addition the melting point and ultraviolet spectrum of the unknown compared favorably with the physical data reported for **1**—mp 85°, λ_{max} 248 mμ (ε 9000).[8] We have therefore repeated the earlier preparations of these dienes. In view of the contradictions mentioned earlier, we have isolated *all* the products from the diene syntheses by preparative glpc and examined each peak by mass and ultraviolet spectrometry. Peaks with *m/e* values of 156 were then examined by high-resolution mass spectrometry and elemental analyses were carried out on the more stable compounds. The homogeneity of each diene was tested on a second glpc column. Assignments were made on the basis of the spectroscopic data and in some cases deuterium tagging facilitated the interpretation. By avoiding chemical methods, we hoped to eliminate the possibilities of isomerization and oxidation to biphenyl.

For the reduction of biphenyl, the method of Egerov, *et al.*,[3] yielded phenylcyclohexane, a phenylcyclohexadiene (B), and 1-phenylcyclohexene; the method of Hückel and Bretschneider[5] yielded a similar mixture, together with another phenylcyclohexadiene (C), and the method of Hückel and Schwen[6] yielded the phenylcyclohexadiene (B). Biphenyl was recovered in each

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(2) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 425.

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