funnel containing 500 ml of diethyl ether. Initially, 75 ml of ether was added to the magnesium and cooled with an ice bath. A few drops of bromine were added to the cooled ether–magnesium mixture; decolorization was immediate. The ether and bromine were added simultaneously while moderating the reaction with the ice bath. After filtration to remove the unreacted magnesium, the reaction product was recrystallized from ether four times to yield white magnesiumb romide etherate. A glpc analysis of a portion of the hydrolyzed material revealed no impurities in the organic layer.

A 500-ml round-bottom flask containing 19.4 g (0.8 g-atom) of triply sublimed magnesium and a stirring bar was connected *via* a Claisen adapter to an addition funnel filled with 101.5 g (0.4 mol) of iodine in 450 ml of diethyl ether and to a water-cooled condenser. After the small initial addition had decolorized, the iodine solution was added to the stirred magnesium at a rate to maintain gentle boiling of the ether. After filtration to remove unreacted magnesium, the reaction product was recrystallized three times from ether to yield white magnesium iodide etherate. A glpc analysis detected no impurities in the hydrolyzed material.

Ether was displaced from magnesium bromide with triethylamine by dissolving a portion of the magnesium bromide etherate (27.1 g, 0.10 mol) in a minimum of diethyl ether in a 200-ml round-bottom flask. The flask was connected to a Claisen adapter fitted with an addition funnel containing 350 ml of triethylamine and a distillation unit with a 5-cm distilling column packed with glass helices. The ether solution was heated to boiling with mixing by a magnetic stirrer. When the ether started to distil, the triethylamine was introduced at a rate to maintain a constant volume of solution in the distilling flask. Addition of the triethylamine was continued until the temperature of the distillate remained constant. The remainder of the solvent was removed by distillation and by drying the solid product on a vacuum manifold overnight. A portion of the tan powder was hydrolyzed, and glpc analysis revealed that displacement of the ether was complete.

Anal. Calcd for $MgBr_2 \cdot NEt_3$: Mg, 8.52; Br, 56.02; Mg/Br, 1.00:2.00. Found: Mg, 8.16; Br, 53.42; Mg/Br, 1.00:1.99. The same treatment of the magnesium iodide etherate followed by a glpc analysis of the hydrolysate indicated that 99.6+% of the ether had been replaced by triethylamine.

Anal. Calcd for $MgI_2 \cdot NEt_3$: Mg, 6.41; I, 66.91; Mg/I, 1.00:2.00. Found: Mg, 6.29; I, 66.44; Mg/I, 1.00:2.02.

Magnesium bromide–TMED was prepared by adding the amine (5.1 g, 0.044 mol) *via* syringe to an ether solution of the halide (0.022 mol) and was not isolated for the redistribution study with dimethylmagnesium–TMED in diethyl ether. A second sample of the compound was prepared in the same manner but was isolated and dried under vacuum for the exchange study in benzene.

Redistribution Studies.—The apparatus and procedure employed was the same for all of the redistribution studies. A 500-ml round-bottomed flask was equipped with a septum cap opening for addition and withdrawal of samples by syringe. The nitrogen was supplied through the top of a water-cooled condenser, and the reaction mixture was mixed by a stirring bar. Thus, a magnesium bromide triethylaminate (0.019 mol)–triethylamine mixture was treated with a triethylamine solution of dimethylmagnesium triethylaminate (0.019 mol), and samples were withdrawn periodically for analysis. Similarly, a triethylamine solution of diethylmagnesium triethylaminate (0.022 mol) was added to a triethylamine–magnesium bromide triethylaminate (0.021 mol) mixture and diethylmagnesium triethylaminate (0.021 mol) in triethylamine was added to magnesium iodide triethylaminate (0.020 mol) in triethylamine. Redistribution of dimethylmagnesium–TMED and magnesium bromide–TMED in diethyl ether was examined by adding 100% excess of TMED to ether solutions of the compounds and then mixing the solution of dimethylmagnesium (0.019 mol) with the magnesium bromide (0.022 mol)–ether mixture. The exchange study in benzene was conducted by adding a benzene solution of dimethylmagnesium–TMED (0.019 mol) to a mixture of magnesium bromide–TMED (0.020 mol) in benzene.

Acknowledgment.—The authors wish to acknowledge the generous support of the Petroleum Research Fund and the National Science Foundation in this investiagtion.

Chemistry of Cyclopropanes. I.[1] Synthesis and Deamination of Spiroamines

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Four spirocyclopropylamines in which the adjacent spiro ring was varied from cyclopropyl to cyclohexyl have been synthesized and deaminated. Three of the amines, 1-aminospirohexane, 1-aminospiro[2.4]heptane, and 1-aminospiro[2.5]octane, were obtained by adding ethyl diazoacetate to the appropriate methylenecycloalkane, and converting the resulting spiro esters by hydrolysis and Curtius rearrangement into the corresponding spiroamines. Similarly spiropentylamine was prepared from ethyl spiropentanecarboxylate. Deamination (aqueous nitrous acid–sodium nitrite) of three of the spirocyclopropylamines (excepting spiropentylamine) gave mixtures of unsaturated alcohols in which the adjacent cycloalkyl moiety remained intact. Spiropentylamine gave predominantly a mixture of 2- and 3-methylenecyclobutanols. These results are discussed in terms of the collapse or rearrangement of an initially formed spirocyclopropyl cation.

Since the initial report of Roberts and Chambers[3] in 1951 that cyclopropyl tosylate gave only allyl acetate upon acetolysis at a rate of 10^{-5} that of cyclohexyl tosylate, a considerable amount of research has been devoted to the carbonium ion chemistry of cyclopropyl systems.[4–7] Although the solvolysis of cyclopropyl derivatives is relatively slow, several investigators have offered strong evidence that these reactions proceed with considerable anchimeric assistance.[4–7] It appears that these solvolyses are a concerted process with ionization and ring opening taking place concurrently.[4,5] Recent studies have further indicated that opening of a cyclopropyl cation is a disrotatory process[8] with the groups *trans* to the leaving group rotating outward.[4,5] The transition state has generally been represented in terms of the delocalized structure

(1) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; Abstracts, p O171.

(2) (a) Abstracted, in part, from the Ph.D. Thesis of L. M. Konzelman, Seton Hall University, 1966. (b) To whom inquiries should be addressed.

(3) J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951).

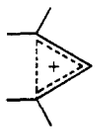
(4) P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966), and references cited therein.

(5) (a) C. H. De Puy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966); (b) C. H. De Puy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965); (c) S. J. Cristol, R. M. Sequeira, and C. H. De Puy, *ibid.*, **87**, 4007 (1965).

(6) J. A. Landgrebe and D. E. Applequist, *ibid.*, **86**, 1536 (1964).

(7) J. A. Landgrebe and L. W. Becker, *ibid.*, **89**, 2505 (1967).

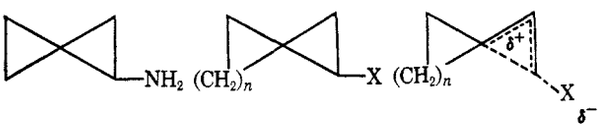
(8) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).



I

I. With the exception of a few cases,[9] carbonium ion reactions of cyclopropyl systems result in the formation of ring-opened allylic products.[3,5a,b,10]

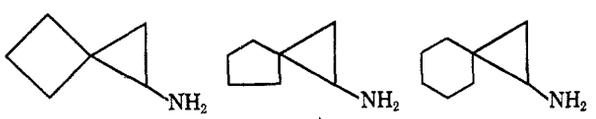
Until recently, little work has been concerned with the reactions of spirocyclopropyl derivatives. Applequist and Fanta[11] obtained 2- and 3-methylenecyclobutanol from the deamination of spiropentylamine (II).



II III, $n = 2,3$; X = Cl, Br IV, $n = 2,3$; X = Cl, Br

More recently Landgrebe and Applequist[6] noted large rate enhancements in the solvolysis of the spirocyclopropyl halides (III) and interpreted their findings in terms of the transition state IV.

In view of the data available on spirocyclopropyl systems we were prompted to investigate the deamination of the spirocyclopropylamines II and V–VII. It

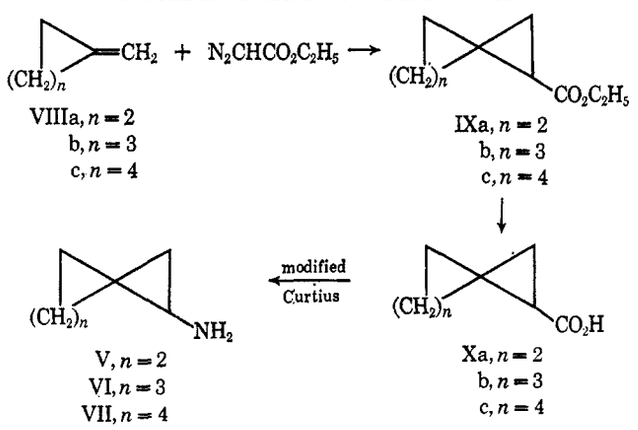


V VI VII

was of particular interest to investigate the effect of the size of the neighboring spiroalkyl ring on the product distributions, especially as to the possibility of obtaining products resulting from expansion of the adjacent spiro ring.

Synthesis.—With the exception of spiropentylamine (II),[11] none of the desired spirocyclopropylamines had been reported previously. A general route found to be applicable for the synthesis of amines V, VI, and VII is outlined in Scheme I.

SCHEME I
SYNTHESIS OF SPIROCYCLOPROPYLAMINES



Ethyl diazoacetate was added to the appropriate methylenecycloalkane.[12] The physical properties of the spirocyclopropyl esters agreed well with the literature.[12] The presence of the cyclopropyl ring was apparent from the ir spectra of IX, all displaying the characteristic cyclopropyl carbon–hydrogen stretching band around 3070 cm^{-1} as well as the cyclopropyl ring-deformation band in the 1000–1050-cm^{-1} region.[13] Hydrolysis of the esters IX readily afforded the corresponding spirocyclopropylcarboxylic acids X.

Of the three general methods for the conversion of acids (and/or their derivatives) into amines,[14] the Curtius rearrangement has been the most widely used for small-ring amines.[15] Applications of the modified Curtius reaction as described by Weinstock[16] to the acids X resulted in an excellent yield of the desired spirocyclopropylamines V, VI, and VII. The amines V, VI, and VII were found to be quite stable[17] and were readily characterized. The ir spectrum of V–VII displayed the two cyclopropyl carbon–hydrogen stretching bands around 3060 and 2980 cm^{-1} and at least one absorption in the ring-deformation region.[13] The nmr spectra of the amines and their derivatives confirmed the spirocyclopropyl structure. The cycloalkyl protons were found to occur from τ 7.99 for V to 8.53 for VII. The cyclopropyl protons generally appeared as an ABX pattern with the proton on the carbon bearing the substituent always appearing at the lowest field. The protons of the cyclopropyl methylene carbon appeared at higher fields, with the proton *cis* to the amino or substituted amino group being found at the highest field. This assignment was based on the well-documented observation that $J_{cis} > J_{trans}$ in cyclopropanes.[6,18]

Spiropentylamine had been previously prepared by Applequist and Fanta[11] using a series of reactions beginning with the conversion of chlorospiropentane[19] into ethyl spiropentanecarboxylate (XII). Ullman and Fanshawe[20] later reported the synthesis of ethyl spiropentanecarboxylate (eq 1) by treating the olefinic ester XI with methylene iodide zinc–copper couple.[21]

(9) (a) P. Lipp and C. Padberg, *Ber.*, **54B**, 1316 (1921); (b) R. Pettit, *J. Amer. Chem. Soc.*, **82**, 1972 (1960); (c) H. Hart and R. H. Martin, *ibid.*, **82**, 6362 (1960).

(10) (a) See footnote 1 of ref 4. (b) G. Gustavson [*J. Prakt. Chem.*, **43** [2], 396 (1891)] first noted the solvolytic inertness of cyclopropyl chloride.

(11) D. E. Applequist and G. F. Fanta, *J. Amer. Chem. Soc.*, **82**, 6393 (1960).

(12) (a) G. Chiurdoglu, J. Loune, and M. Poelmans, *Bull. Soc. Chim. Belges*, **65**, 257 (1956). (b) For a review on the reactions of carboethoxycarbene, see W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, pp 95–114.

(13) (a) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966), and references cited therein; (b) S. A. Liebman and B. J. Gudzinowicz, *Anal. Chem.*, **33**, 931 (1961); (c) S. E. Wiberley, S. C. Bunce, and W. H. Bauer, *ibid.*, **32**, 217 (1960); (d) S. E. Wiberley and S. C. Bunce, *ibid.*, **24**, 623 (1952); (e) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1959, pp 13, 18, 29, 30; (f) A. T. Blomquist and D. T. Longone, *J. Amer. Chem. Soc.*, **81**, 2012 (1959); (g) V. A. Slabey, *ibid.*, **76**, 3604 (1954).

(14) R. Adams, Ed., "Organic Reactions," Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1946, pp 267–449.

(15) D. E. McKay, Jr., Ph.D. Thesis, University of Illinois, Urbana, Ill., 1966.

(16) (a) J. Weinstock, *J. Org. Chem.*, **26**, 3511 (1961); (b) C. Kaiser, B. M. Lester, C. L. Zirkle, A. Burger, C. S. Davis, T. J. Delia, and L. Zirngibl, *J. Med. Pharm. Chem.*, **5**, 1243 (1962).

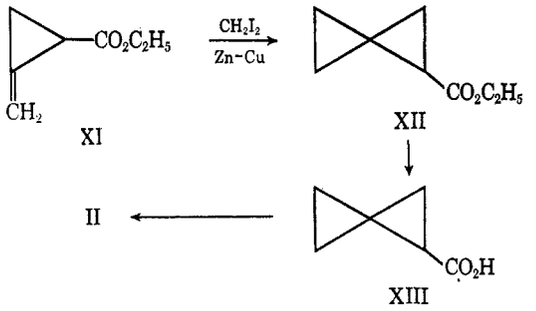
(17) 1-Aminospirohexane (V), although stable to distillation, underwent decomposition upon vpc analysis.

(18) (a) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963); (b) K. B. Wiberg and B. J. Nist, *ibid.*, **85**, 2788 (1963); (c) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *ibid.*, **86**, 762 (1964); (d) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962); (e) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962).

(19) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Amer. Chem. Soc.*, **82**, 2368 (1960).

(20) E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961).

(21) (a) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964); (b) E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964); (c) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).



This sequence, coupled with the facile conversion of spirocyclopropyl esters into their corresponding amines (Scheme I), made this approach more desirable than the initial synthesis of II.[11]

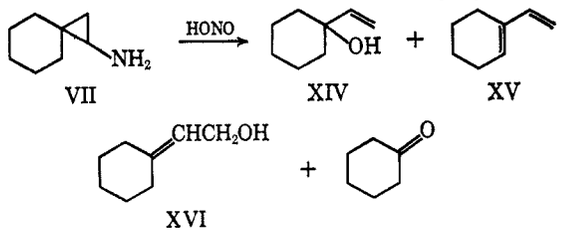
Application of the Simmons–Smith reaction[20,21] to XI resulted in a low conversion (27%) into XII. This difficulty was overcome by recycling the crude product mixture twice with fresh methylene iodide zinc–copper couple. The structure of XII was confirmed by its ir spectrum being in excellent agreement with the literature.[13a] Treatment of XII according to Scheme I gave spiropentylamine (II). The presence of the spiropentyl ring system in XIII and its derivatives was confirmed by the occurrence of only cyclopropyl C–H stretching bands in the 3100–2900-cm^{-1} region in the spectra of the amide and hydrazide and from the nmr spectra. The protons of the unsubstituted cyclopropyl ring appeared at the highest field (τ 9.0–9.1) with the proton α to the substituent appearing at lowest field (τ 7.9–8.2) in complete agreement with the literature.[11,19,20,22] Curtius rearrangement on XIII gave spiropentylamine as the hydrochloride. This salt was very hygroscopic and could not be crystallized. The free amine likewise did not lend itself to purification, discoloring rapidly even at 0° under a nitrogen atmosphere. That II was indeed isolated was verified from its phenylthiourea[11] and benzamide derivatives.

Results and Discussion

The deaminations of amines II and V–VII were carried out in an aqueous nitrous acid–sodium nitrite medium employing the free amines of VI and VII and the hydrochlorides of II and V. The product mixtures were separated into their components by vpc (utilizing a Dowfax column[23] for amines V, VI, and VII and a Ucon column for amine II). The products were identified for the most part by trapping the major components and spectrally (ir and nmr) comparing them with authentic samples.

Amines V–VII.—Deamination of 1-aminospiro[2.5]-octane (VII) (Scheme II) gave a crude product mixture

SCHEME II
DEAMINATION PRODUCTS OF 1-AMINOSPIRO[2.5]OCTANE



(22) C. L. Bumgardner, *J. Org. Chem.*, **29**, 767 (1964).
(23) J. F. O'Donnell and C. K. Mann, *Anal. Chem.*, **36**, 2097 (1964).

(accounting for 95% of the amine) whose infrared spectrum was indicative of a mixture of unsaturated alcohols.[24] A carbonyl band at 1712 cm^{-1} was suggestive of a saturated cyclic ketone. Vpc indicated the presence of four components (Table I).

TABLE I
DEAMINATION PRODUCTS OF 1-AMINOSPIRO[2.5]OCTANE

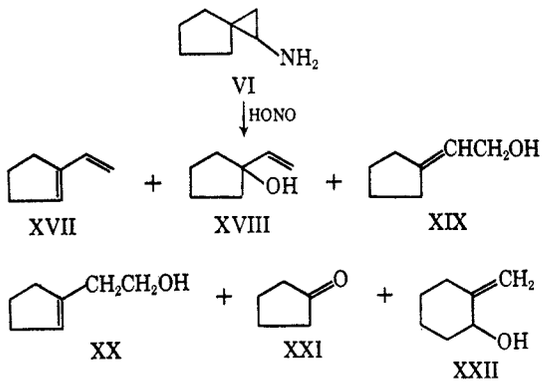
Component[a]	% relative abundance[b]	Identification
1	0.9	1-Vinylcyclohexene (XV)
2	5.6	Cyclohexanone
3	91.2	1-Vinylcyclohexanol (XIV)
4	2.3	Cyclohexylidenethanol (XVI)

[a] Listed in order of increasing retention time. [b] Value represents a percentage of the product mixture.

Component 1 was identified as 1-vinylcyclohexene (XV) by comparison of its retention time (peak enhancement) with that of an authentic sample. Component 2 was shown to be cyclohexanone by comparison of its infrared spectrum with known material. The third and fourth components were similarly identified as 1-vinylcyclohexanol (XIV) and cyclohexylideneethanol (XVI). The complete absence of 2-methylenecycloheptanol and 1-cycloheptenylmethanol (likely products of cyclohexyl ring expansion) was definitely shown by vpc as was the absence of 2-(1-cyclohexenyl)-ethanol, the *endo* isomer of XVI.

When 1-aminospiro[2.4]heptane (VI) was deaminated (Scheme III) a mixture of nine components (94%

SCHEME III
PRODUCTS OF 1-AMINOSPIRO[2.4]HEPTANE DEAMINATION



material balance) was obtained whose infrared spectrum was again indicative of a mixture of unsaturated alcohols.[24] A weak carbonyl band at 1730 cm^{-1} was also present. The products and their identification are listed in Table II. Three of the components remained unidentified. With the exception of a small amount of 2-methylenecyclohexanol, no products resulting from expansion of the neighboring cyclopentyl ring were identified. Other possible products of adjacent ring expansion shown by vpc to be definitely absent from the product mixture were 1-cyclohexenylmethanol, 2-methyl-2-cyclohexen-1-ol, and 2-(2-cyclopentenyl)ethanol, a double-bond isomer of XIX and XX. As in the deamination of VII, a cyclic ketone, cyclopentanone, was found among the products.

(24) (a) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, pp 95–102, 118–127; (b) see ref 13e, Chapters 3 and 6.

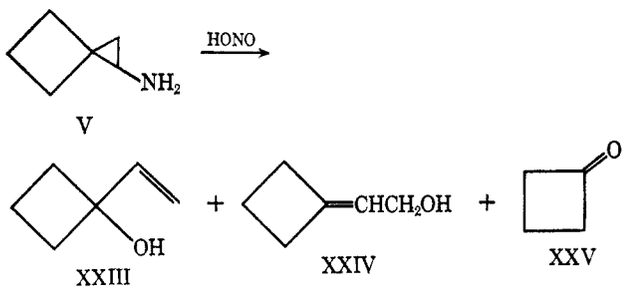
TABLE II

PRODUCTS OF DEAMINATION OF 1-AMINOSPIRO[2.4]HEPTANE

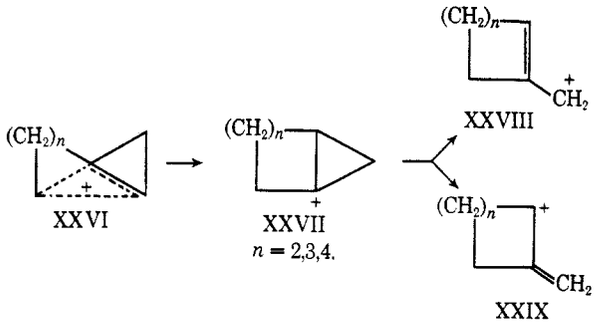
Component[a]	% relative abundance[b]	Identification	Method of identification
1	0.6	*c*	
2	1.1	1-Vinylcyclopentene (XVII)	*d*
3	1.0	Cyclopentanone (XXI)	*d*
4	79.0	1-Vinylcyclopentanol (XVIII)	*e*
5	1.2	2-Methylenecyclohexanol (XXII)	*d*
6	1.8	*c*	
7	3.1	2-(1-Cyclopentenyl)ethanol (XX)	*d*
8	0.7	*c*	
9	11.5	Cyclopentylideneethanol (XIX)	*e*

[a] In order of increasing retention time. [b] Value represents a percentage of the product mixture. [c] Unknown. Component 1 was found to have the same retention time as a minor component in the vpc of 1-vinylcyclopentene. [d] Comparison with an authentically synthesized sample by retention time and peak enhancement. [e] Trapped from the vpc and spectral comparison (ir and nmr) with authentic samples.

The deamination mixture from 1-aminospirohexane (V) followed the same general pattern as amines VI and VII giving a four-component mixture which again from its ir spectrum[24] appeared to be a mixture of unsaturated alcohols and was very similar to 1-vinylcyclobutanol.[25] A weak carbonyl band (1780 cm^{-1}) was also present. Indeed, 1-vinylcyclobutanol (XXIII) was found to be the major component (84.6% of the product mixture) with cyclobutylideneethanol (XXIV) also being present to the extent of 9.8%, as confirmed by spectral (ir and nmr) comparison of these alcohols and their *p*-nitrobenzoates with the authentic materials. Of the two other components, one remained unidentified. The first component (2.4%) was found to be cyclobutanone. It was shown (vpc) that the remaining component (3.2%) was not any of the possible products of cyclobutyl ring expansion, *viz.*, 2-methylenecyclopentanol, 1-cyclopentenylmethanol, and 2-methyl-2-cyclopenten-1-ol.



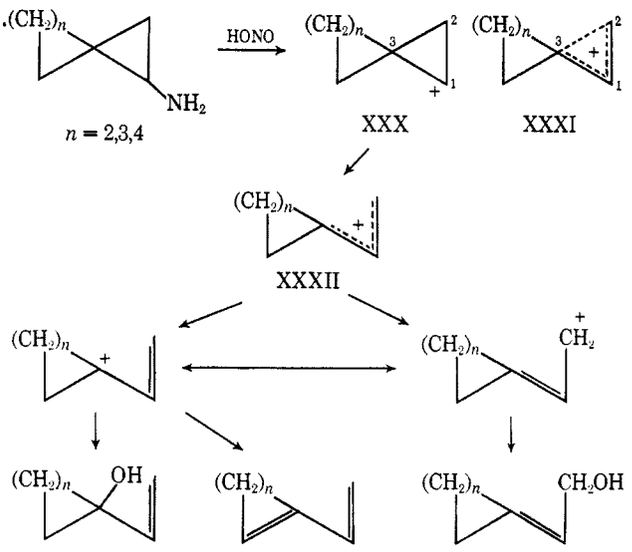
The products from the deamination of amines V–VII appear to result almost exclusively from rupture of the cyclopropyl ring. The adjacent spiro ring does not seem to have any significant effect upon the product distributions.[26] The complete absence (except for 1.2% XXII from VI) of ring-expanded products argues heavily against the intervention of an intermediate of the type XXVI[27] or its classical counterpart, XXVII, since no products derived from cations XXVIII and XXIX were detected.



The product distributions from the deamination of amines V–VII are best explained in terms of the scheme outlined in Scheme IV.[28] The initial spirocyclopropyl cation, XXX, probably exhibits appreciable 2,3-bond delocalization and may well be better represented by cation XXXI.[4,5] However, such a distinction cannot be made on the basis of the data presented here.[29] Complete rupture of the 2,3 bond, a process known to be operative in carbonium ion reactions of cyclopropyl derivatives[3–5,10b] and especially in amine deaminations,[30] gives rise to the tertiary allylic cation XXXII from which the products are formed by either proton loss or solvent attack.[31] Although Scheme IV explains well

SCHEME IV

DEAMINATION OF AMINES V–VII



(25) G. Fontaine, C. Andre, C. Jolivet, and P. Moitte, *Bull. Soc. Chim. Fr.*, 1444 (1963).

(26) Deamination of cyclobutylmethylamine [N. J. Demjanow, *Ber.*, **40**, 4959 (1907)], cyclopentylmethylamine [P. A. S. Smith, D. R. Baer, and S. N. Ege, *J. Amer. Chem. Soc.*, **76**, 4564 (1954)], and cyclohexylmethylamine [L. Ruzicka and W. Brugger, *Helv. Chim. Acta*, **9**, 399 (1926)] gave the ring-expanded secondary alcohol as the principal product.

(27) Cation XXVI may be considered a type of bicyclobutonium ion: R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 4390 (1959).

(28) For general reviews of amine deaminations, see (a) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. I, W. A. Benjamin, Inc., New York, N. Y., 1965, pp 35–45; (b) J. H. Kidd, *Quart. Rev.* (London), **15**, 418 (1961); and (c) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961, pp 93–137.

(29) W. Kirmse and H. Schütte, *J. Amer. Chem. Soc.*, **89**, 1285 (1967); N. J. Turro and W. B. Hammond [*ibid.*, **89**, 1028 (1967)] and J. A. Landgrebe and L. W. Becker[7] have recently offered evidence for the intervention of a cyclopropyl cation in carbonium ion forming reactions of cyclopropyl derivatives.

(30) (a) E. J. Corey and R. F. Atkinson, *J. Org. Chem.*, **29**, 3707 (1964); (b) J. E. Hodgkins and R. F. Flores, *ibid.*, **28**, 3356 (1963); (c) R. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, **499**, 1 (1932).

(31) Alcohol XX (Scheme III) is probably formed by isomerization of XIX.

over 90% of the product mixtures, it does not account for the formation of cyclohexanone (from VII), cyclopentanone (from VI), and cyclobutanone (from V). The formation of these ketones presently evades adequate explanation. It was thought that perhaps they may have been formed during the vpc by the pyrolytic elimination of ethylene from the corresponding 1-vinylcycloalkanols. The absence of any cyclopentanone (XXI) in the vpc of either pure 1-vinylcyclopentanol (XVIII) or the product mixture from VI at three different injection block temperatures (195, 305, and 450°) eliminated this possibility.

Spiropentylamine.—Because of the difficulty of purifying spiropentylamine and its hydrochloride, the amount of amine present in a sample to be deaminated had to be determined with reasonable accuracy. This was readily accomplished by titration of a methanol solution of spiropentylamine hydrochloride with standardized methanolic sodium methoxide.[32]

Deamination of spiropentylamine as the hydrochloride gave (75% material balance) a complex ten component mixture, six of which amounted to less than 1% each, and which were not investigated. The four remaining components amounted to 5.1, 16.9, 69.9, and 4.7%. The major components (16.9 and 69.9%) were identified as 2- and 3-methylenecyclobutanol, respectively, by comparison of their ir and nmr spectra with those previously described by Applequist and Fanta.[11] The 4.7% component was assumed to be a polymeric alcohol from its long retention time and the absence of olefinic bands in its ir and nmr spectrum. The ir spectrum of the 5.1% component displayed bands attributable to an alcohol containing a vinyl group.[24] The nmr spectrum had to be run in a very dilute solution at maximum spectrum amplitude. The low signal to noise level made an accurate integration of the peak areas impossible. However, the spectrum did indicate the presence of a vinyl group and a cyclopropyl ring. From these data, this component was tentatively identified as 1-vinylcyclopropanol.

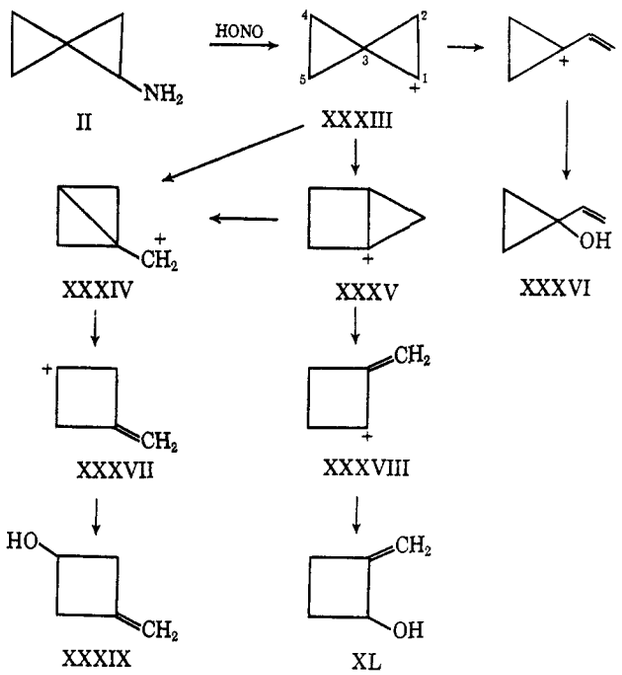
It is felt that these results presently can be best explained in terms of Scheme V, which embodies parts of the schemes proposed by Applequist and Fanta,[11] and Kiefer and Roberts.[33] The initially formed spiropentyl cation XXXIII can decompose in three different ways. Collapse of the 2,3 bond and solvent attack on the 1-vinylcyclopropyl cation gives 1-vinylcyclopropanol (XXXVI). Scission of the 3,5 bond yields the tertiary cation XXXV which can collapse to XXXVIII or rearrange to the bicyclobutylmethyl cation XXXIV. Isomerization of XXXIV to XXXVII and reaction with water gives the major product, 3-methylenecyclobutanol (XXXIX). Cation XXXIV might possibly also be formed by migration of the 4,5 bond of XXXIII. Applequist and Fanta[11] have postulated the formation of XXXVII from XXXVIII, thereby attributing an unusual measure of stability to XXXVII, a conclusion in disagreement with the kinetic data of Kiefer and Roberts.[33,34]

(32) Private communication, A. G. Mohan, Seton Hall University, South Orange, N. J., 1966.

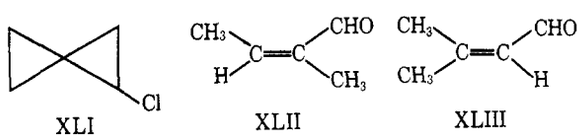
(33) E. F. Kiefer and J. D. Roberts, *J. Amer. Chem. Soc.*, **84**, 784 (1962).

(34) However, Kiefer and Roberts[33] did report the preparation of 3-methylenecyclobutanol by deamination of 3-methylenecyclobutylamine, whereas deamination of 3-methylcyclobutylamine [M. S. Silver, M. C. Caserio, and J. D. Roberts, *ibid.*, **83**, 3671 (1961)] gave rise to extensive rearrangement.

SCHEME V
DEAMINATION OF SPIROPENTYLAMINE

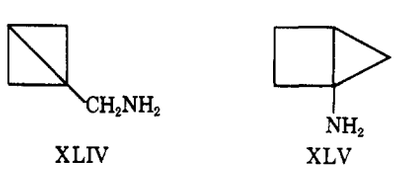


Interestingly, spiropentyl chloride (XLI) gave tiglaldehyde (XLII) when treated with aqueous silver nitrate at 100° for 6 days in a sealed tube.[6] It was suggested that possibly the methylenecyclobutanols XXXIX and XL were initially formed and isomerized



to XLII. However, treatment of XXXIX with either acid or base yields β-methylcrotonaldehyde (XLIII),[33] thus casting some doubt on the possibility of XXXIX being a precursor to the formation of XLII from the solvolysis of XLI.

Additional information concerning the nature of the cations generated from spiropentyl system could be gained by the deamination of amines XLIV and XLV. Deamination of XLIV should give XXXIV directly and result in the formation of 3-methylenecyclobutanol (XXXIX) as the major product according to Scheme V. Likewise, deamination of XLV should result in



the formation of XXXIX and XL. The synthesis and deamination of XLIV and XLV, as well as other experimentation designed to shed light on the reaction sequence proposed in Scheme V, are currently in progress in these laboratories. In addition, the solvolysis of alcohol derivatives corresponding to amines V through VII[35] will be reported in the near future.

(35) S. Lazarus, Ph.D. Thesis, Seton Hall University, 1967.

Experimental Section

Melting and boiling points are uncorrected. Microanalyses were performed by Bernhardth Mikroanalytisches Laboratorium, Mulheim, Germany. Ir spectra were obtained with a Beckman IR-10 grating spectrophotometer. Nmr spectra were determined on either a Varian A-60 or A-60A in deuteriochloroform or carbon tetrachloride, and are referred internally to tetramethylsilane. Vpc was performed on a F & M Model 720 gas chromatograph using 0.25 in. columns as follows: 6-ft 10% Apiezon L on potassium hydroxide treated Chromosorb W (Apiezon); 6-ft 10% silicone rubber SE-30 on Chromosorb P (silicone rubber); 6-ft 20% Carbowax 20M on Chromosorb P with 0.5% sodium hydroxide (Carbowax);[23] 6- and 11-ft 20% Dowfax 9N9 on Chromosorb P with 2.5% sodium hydroxide (Dowfax);[23] 10-ft 20% Ucon LB 550X Diatoport W (Ucon). Almost all vpc analyses were programmed 5°/min from 100 to 190° at a helium flow rate of 60 cm³/min.

Ethyl 1-Spiro[2.5]octanecarboxylate (IXc).—Ethyl diazoacetate[36] (137 g, 1.2 mol) was added dropwise over an 8-hr period to a refluxing stirred mixture of 96.0 g (1.0 mol) of methylenecyclohexane,[37] 150 ml of methylcyclohexane, and 10.0 g of freshly prepared copper-bronze.[30b] After stirring at room temperature for 16 hr, the catalyst was removed by filtration and the methylcyclohexane was stripped by atmospheric distillation. Fractionation of the residue gave 146 g (80%) of ethyl 1-spiro[2.5]octanecarboxylate: bp 100–102° (14 mm); $n^{20}D$ 1.4620 [lit.[12a] bp 123–125° (33 mm); $n^{20}D$ 1.4614].

1-Spiro[2.5]octanecarboxylic Acid (Xc).—A stirred mixture of 370 g (2.0 mol) of IXc in 1400 ml of water containing 120 g (3.0 mol) of sodium hydroxide was slowly brought to reflux and stirred at reflux for 5 hr. The cooled solution was extracted with two 100-ml portions of ether, acidified with hydrochloric acid (cooling), and extracted with four 300-ml portions of ether. The ether extracts were dried ($MgSO_4$) and concentrated, and the residue was distilled giving 295 g (94%) of 1-spiro[2.5]octanecarboxylic acid: bp 148–150° (14 mm); $n^{20}D$ 1.4859. Analysis by vpc (silicone rubber) indicated the sample was homogeneous.

Anal.[38] Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.96; H, 9.25.

The amide obtained in the usual manner[39] had mp 192–193° (aqueous methanol).

Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.76; H, 9.77; N, 9.17.

The anilide, after several recrystallizations from aqueous methanol, had mp 96–97°.

Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.49; H, 8.49; N, 6.23.

1-Aminospiro[2.5]octane (VII).—The modified Curtius procedure as described by Weinstock[16a] was employed. From 26.6 g (0.17 mol) of Xc, 20.5 g (0.20 mol) of triethylamine, 24.2 g (0.22 mol) of ethyl chloroformate and 17.0 g (0.26 mol) of sodium azide there was obtained 20.0 g (72%) of crude 1-aminospiro[2.5]octane hydrochloride (slightly hygroscopic). The free amine was obtained by adding 20.0 g of the hydrochloride to a solution of 12.0 g of potassium hydroxide in 70 ml of water, followed by extraction with four 40-ml portions of methylene chloride. After drying over $MgSO_4$ and removing the methylene chloride, distillation of the residue gave 7.5 g of amine [bp 75° (29 mm) and 98–100° (70 mm); $n^{20}D$ 1.4782], which was homogeneous by vpc (Dowfax).

Anal.[38] Calcd for $C_8H_{15}N$: C, 76.74; H, 12.07; N, 11.19. Found: C, 76.67; H, 11.93; N, 11.12.

1-Aminospiro[2.5]octane hydrochloride for spectral and elemental analyses was obtained by several crystallizations (Norit) of the crude hydrochloride from methanol–ethyl acetate, mp 183–184°.

Anal. Calcd for $C_8H_{16}ClN$: C, 59.43; H, 9.98; N, 8.66; Cl, 21.93. Found: C, 59.43; H, 9.85; N, 8.80; Cl, 21.82.

The benzamide[40] had mp 121–122° (methylene chloride–hexane).

Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.68; H, 8.55; N, 6.16.

The phenylthiourea was obtained by stirring a solution of 0.30 g of crude VII hydrochloride, and 0.35 g of phenylisothiocyanate in 5 ml of saturated sodium bicarbonate and 8 ml of isopropyl alcohol for 16 hr at room temperature. After drowning in water, the product was extracted into chloroform. Removal of the chloroform after drying ($MgSO_4$) gave a viscous oil which crystallized after trituration with hexane. Three recrystallizations (Norit) from methylene chloride–hexane gave the pure thiourea, mp 129–130°.

Anal. Calcd for $C_{15}H_{20}N_2S$: C, 69.19; H, 7.74; N, 10.76; S, 12.31. Found: C, 69.14; H, 7.94; N, 10.66; S, 11.99.

1-Vinylcyclohexanol (XIV) was prepared in 17% yield by the addition of vinylmagnesium chloride to cyclohexanone utilizing the technique of Johnson, Cheer, and Goldsmith[41] for 1-vinylcyclopentanol. The alcohol had bp 71° (14 mm) [lit.[42] bp 67–68° (10 mm)]; ir (film) 3392, 3090, 3010, 1645, 990, 955, 916, and 900 cm⁻¹; nmr (CCl_4), τ 4.08 (q, 1, J_{cis} = 10.0 and J_{trans} = 17.0 cps, —CH=CH₂), 4.92 (three distinct doublets, 2, —CH=CH₂), 7.60 (s, 1, OH), 8.46 (s, 10, C_6H_{10}). A purity of 93% was indicated by vpc (Dowfax). The 3,5-dinitrobenzoate had mp 124–125° from hexane (lit.[42] mp 122–123°).

2-(1-Cyclohexenyl)ethanol.—1-Cyclohexenylacetonitrile[43] was hydrolyzed with aqueous KOH giving a 65% yield of 1-cyclohexenylacetic acid, bp 117–121° (2.5 mm) [lit.[44] bp 137–138° (11 mm)]. A solution of 35.0 g (0.25 mol) of 1-cyclohexenylacetic acid in 200 ml of anhydrous ether was added to a stirred suspension of 9.3 g (0.33 mol) of lithium aluminum hydride in 300 ml of anhydrous ether at such a rate as to maintain gentle reflux. After stirring for 1 hr at room temperature, excess lithium aluminum hydride was decomposed by the dropwise addition of water. Cold dilute sulfuric acid was added until the aluminum salts dissolved. The aqueous phase was extracted with two 150-ml portions of ether. The combined ether solution was washed with water, saturated $NaHCO_3$, and water and dried over $MgSO_4$. Distillation of the residue after removal of the ether gave 22.2 g (71%) of 2-(1-cyclohexenyl)ethanol: bp 83–85° (3.5 mm); $n^{20}D$ 1.4892 [lit.[45] bp 74–75° (2 mm), $n^{20}D$ 1.4878]; homogeneous by vpc (Dowfax). The 3,5-dinitrobenzoate had mp 85–87°, from hexane (lit.[46] mp 85–87°).

1-Vinylcyclohexene (XV).—A mixture of 15.0 g (0.09 mol) of 2-(1-cyclohexenyl)ethanol and 4.0 g of freshly fused $KHSO_4$ was heated at 170–180° for 2 hr in a distillation apparatus under a nitrogen atmosphere. The distillate was washed with cold water (30 ml) and the olefin layer separated. The water was extracted with two 10-ml portions of ether and the combined organic layers were dried ($MgSO_4$). Removal of the ether and distillation of the residue gave 2.9 g (29%) of 1-vinylcyclohexene: bp 66–67° (54 mm); $n^{20}D$ 1.4955 [lit.[47] bp 48° (12 mm), $n^{20}D$ 1.4952]. A purity of 75.3% was indicated by vpc (Dowfax).

Cyclohexylideneethanol (XVI).—Ethyl 1-hydroxycyclohexylacetate[48] was hydrolyzed with ethanolic KOH yielding in 64% 1-hydroxycyclohexylacetic acid [mp 59–61°, from ether–hexane (lit.[49] mp 59–60°)] which in turn was dehydrated in 66% yield to cyclohexylideneacetic acid with acetic anhydride by the method of Schmid and Karrer,[49] mp 89–90° (lit.[49] mp 90–91.5°).

A solution of 4.0 g (0.03 mol) of cyclohexylideneacetic acid in 60 ml of anhydrous ether was added dropwise (1 hr) to a cold (0°) stirred suspension of 1.0 g (0.036 mol) of lithium aluminum hydride in 50 ml of anhydrous ether. After stirring 1 hr at 0°, excess hydride was decomposed by the addition of water followed by the addition of 90 ml of 20% Rochelle salt to complex the alumina.[50] The aqueous layer was extracted with ether and the combined ether extracts were dried over $MgSO_4$. Removal of the ether and fractionation of the colorless residue gave 1.2 g

(36) N. E. Searle, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 424.

(37) W. J. Bailey, J. J. Hewitt, and C. King, *J. Amer. Chem. Soc.*, **77**, 357 (1955).

(38) Material used for elemental and spectral analyses was obtained by trapping from the effluent gases of the vpc.

(39) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 200.

(40) See ref 39, p 226.

(41) C. R. Johnson, C. J. Cheer, and D. J. Goldsmith, *J. Org. Chem.*, **29**, 3320 (1964).

(42) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 58 (1938).

(43) A. C. Cope, A. A. D'Adieco, D. E. Whyte, and S. A. Glickman, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 212.

(44) M. D. Farrow and G. A. R. Kon, *J. Chem. Soc.*, 2128 (1926).

(45) R. A. Benkeser, C. Arnold, R. F. Lambert, and O. H. Thomas, *J. Amer. Chem. Soc.*, **77**, 6042 (1955).

(46) H. B. Henbest and B. B. Millward, *J. Chem. Soc.*, 3575 (1960).

(47) S. F. Birch, *J. Org. Chem.*, **20**, 1178 (1955).

(48) S. Notelson and S. P. Gottfried, *J. Amer. Chem. Soc.*, **61**, 970 (1939).

(49) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **31**, 1068 (1948).

(50) R. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3736 (1948).

(33%) of cyclohexylidenethanol: bp 104° (17 mm); $n^{20}D$ 1.4928 [lit.[51] bp 101–106° (15 mm), $n^{20}D$ 1.4930]. Vpc (Dowfax) indicated a purity of 85%. The 3,5-dinitrobenzoate had mp 90–91°, from hexane (lit.[51] mp 90–91°): nmr ($CDCl_3$), τ 0.77 (s, 3, ArH), 4.49 (t, 1, J = 7.0 cps, —C=CH—), 5.03 (d, 2, —CH_2—O—), 7.75 (m, 4, allylic ring H), 8.39 (s, 6, ring H).

2-Methylenecycloheptanol and 1-Cycloheptenylmethanol.—2-Hydroxymethylenecycloheptanone was obtained in 72% yield from cycloheptanone and ethyl formate as described by Prelog, *et al.*:[52] bp 85–88° (9 mm); $n^{20}D$ 1.5058 [lit.[53] bp 86–88 (11 mm), $n^{20}D$ 1.5106].

The method described by Dreiding and Hartman[54] for the preparation of 2-methylenecyclohexanol and 1-cyclohexenylmethanol by the lithium aluminum hydride reduction of 2-hydroxymethylenecyclohexanone was employed. The reduction of 21.8 g (0.155 mol) of 2-hydroxymethylenecycloheptanone by 6.7 g (0.174 mol) of lithium aluminum hydride gave 18.0 g of a crude oil which was fractionated through a 60-cm silver-lined vacuum-jacketed Vigreaux column at 47 mm. The fractions of bp 111–118° were rich in 2-methylenecycloheptanol and the fractions of bp 124–126° were rich in 1-cycloheptenylmethanol [lit.[55] bp 93.5–95.0° (10 mm)]. Pure 2-methylenecycloheptanol[38] had $n^{20}D$ 1.4884; ir (film), 3350, 3063, 1800, 1641, 1009, and 894 cm^{-1}.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.08; H, 11.09.

The *p*-nitrobenzoate had mp 59–60° after repeated crystallization from hexane.

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.31; H, 6.22; N, 5.27.

The phenylurethan of 2-methylenecycloheptanol had mp 77–78° (hexane).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.36; H, 7.62; N, 5.73.

The 3,5-dinitrobenzoate of 1-cycloheptenylmethanol had mp 85–86° (hexane).

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.04; N, 8.75. Found: C, 56.45; H, 5.17; N, 8.64.

Deamination of 1-Aminospiro[2.5]octane.—A solution of 1.62 g (0.0244 mol) of sodium nitrite in 6 ml of water was added dropwise to a cold (ice bath) stirred solution of 0.7300 g (0.00584 mol) of VII in 5 ml of water and 9 ml of 1 *N* perchloric acid. After stirring at room temperature for 18 hr (two phases now present) the mixture was extracted with four 25-ml portions of ether. The dried ($MgSO_4$) ether solution was carefully concentrated by atmospheric distillation yielding 0.7070 g of a pale orange liquid residue:[56] ir (film), 3390, 3090, 3040, 1670, 1643, 985, 915, and 885 cm^{-1}. Vpc (Dowfax) indicated four components.

The first component had a retention time of 8.8 min and its relative abundance was 0.9%. This component was identified as 1-vinylcyclohexene by virtue of its matching retention time (peak enhancement) to that of an authentic sample.

The second component had a retention time of 11.9 min and its relative abundance was 5.6%. The vpc retention time (peak enhancement) and ir and the nmr spectra of this component were identical with those of cyclohexanone.

The third component had a retention time of 15.8 min and its relative abundance was 91.2%. This component was identified as 1-vinylcyclohexanol (XIV) from its matching retention time and its ir and nmr spectra were superimposable with those of an authentic sample of XIV.

The fourth component had a retention time of 27.0 min and its relative abundance was 2.3%. Cyclohexylidenethanol and 1-cycloheptenylmethanol had retention times of 27.2 and 28.3 min, respectively, and both enhanced this component's peak area on a 6-ft Dowfax column. However, when an 11-ft Dowfax column was used, only cyclohexylideneethanol gave peak enhancement. The ir spectrum was identical with that of cyclohexylideneethanol.

(51) R. N. Lacey, *J. Chem. Soc.*, 827 (1954).

(52) V. Prelog, L. Ruzicka, and O. Metzler, *Helv. Chim. Acta*, **30**, 1883 (1947).

(53) W. Trebs and H. J. Neupert, *Ann.*, **595**, 219 (1955).

(54) A. S. Dreiding and J. A. Hartman, *J. Amer. Chem. Soc.*, **75**, 939 (1953).

(55) E. Buchta and J. Kranz, *Ann.*, **601**, 170 (1956).

(56) Assuming the products have an empirical formula of $C_8H_{14}O$ and neglecting the small amount of ether present, this represents a 95% material balance.

Methylenecyclopentane (VIIIb).—1-Cyclopentenylacetonitrile [bp 66–68° (7 mm); $n^{25}D$ 1.4660 (lit.[57] bp 72–73° (10 mm); $n^{25}D$ 1.4672)] was obtained in 92% yield by the technique of Cope, *et al.*,[43] for the synthesis of 1-cyclohexenylacetonitrile. Hydrolysis (KOH) to a mixture of 1-cyclopentenylacetic and cyclopentylideneacetic acids (84%) and their decarboxylation to methylenecyclopentane in 89% yield was carried out according to the procedure described by Arnold, *et al.*:[58] bp 74–75°; $n^{20}D$ 1.4360 (lit.[58] bp 74.1–74.3°; $n^{20}D$ 1.4354).

Ethyl 1-Spiro[2.4]heptanecarboxylate (IXb).—This ester was prepared from methylenecyclopentane [98.5 g (1.17 mol) in 70 ml of methylcyclopentane], ethyl diazoacetate[36] (157 g, 1.37 mol), and copper-bronze[30b] (10.0 g) in exactly the same manner as for IXa except that the diazo ester was added over a 16-hr period giving a 75% yield of 1-carboethoxyspiro[2.4]heptane: bp 85–87° (8 mm); $n^{25}D$ 1.4561 [lit.[12a] bp 110–112° (33 mm); $n^{25}D$ 1.4548]. A purity of 95.5% was indicated by vpc (Apiezon).

1-Spiro[2.4]heptanecarboxylic Acid (Xb).—The procedure employed for the synthesis of Xc was used. From 296.5 g (1.76 mol) of IXb and 154 g (3.85 mol) of sodium hydroxide there was obtained 226.0 g (92%) of 1-spiro[2.4]heptanecarboxylic acid: bp 105–106° (2 mm); $n^{20}D$ 1.4812, which was homogeneous by vpc (silicone rubber).

Anal.[38] Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.40; H, 8.78.

The amide had mp 190–191° after three recrystallizations from aqueous methanol.

Anal. Calcd for $C_8H_{13}NO$: C, 69.02; H, 9.41; N, 10.06. Found: C, 69.30; H, 9.55; N, 10.00.

The anilide obtained in the usual manner[39] had mp 117–118° (aqueous methanol).

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.02; H, 7.95; N, 6.47.

1-Aminospiro[2.4]heptane (VI).—The technique employed for the preparation of VII[16a] was used. From 28.3 g (0.20 mol) of Xb, 23.8 g (0.24 mol) of triethylamine, 28.3 g (0.22 mol) of ethyl chloroformate, and 19.8 g (0.30 mol) of sodium azide, 23.8 g (80%) of crude, hygroscopic 1-aminospiro[2.4]heptane hydrochloride was isolated. The free amine obtained by treatment of the hydrochloride with alkali had bp 100–101° (153 mm), $n^{24}D$ 1.4743. Vpc (Dowfax) indicated one component.

Anal.[38] Calcd for $C_7H_{13}N$: C, 75.62; H, 11.78; N, 12.60. Found: C, 75.40; H, 11.52; N, 12.50.

Pure 1-aminospiro[2.4]heptane hydrochloride was obtained after repeated crystallization of the crude salt from methanol–ethyl acetate and had mp 146–147°.

Anal. Calcd for $C_7H_{14}ClN$: C, 56.95; H, 9.56; Cl, 24.01; N, 9.49. Found: C, 56.64; H, 9.63; Cl, 24.00; N, 9.55.

The benzamide, after several recrystallizations from methylene chloride–hexane, melted at 114–115°.

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.25; H, 8.01; N, 6.48.

The phenylthiourea obtained in the manner described for that of VII had mp 116–118° (methylene chloride–pentane).

Anal. Calcd for $C_{14}H_{18}N_2S$: C, 68.25; H, 7.36; N, 11.37; S, 13.01. Found: C, 68.50; H, 7.60; N, 11.44; S, 13.00.

1-Vinylcyclopentanol (XVIII).—The procedure of Johnson, Cheer, and Goldsmith[41] was followed. From 16.8 g (0.20 mol) of cyclopentanone and vinylmagnesium chloride from 6.8 g (0.28 g-atom) of magnesium turnings, there was obtained 13.9 g of XVIII (62%): bp 68° (27 mm); $n^{23}D$ 1.4701 [lit.[41] 68–70° (26 mm), $n^{25}D$ 1.4697]; nmr (CCl_4), τ 4.07 (q, 1, J_{cis} = 10.0 and J_{trans} = 17.0 cps, -CH=CH_2), 4.93 (two doublets flanking a triplet, 2, CH=CH_2), 7.50 (s, 1, -OH), 8.32 (m, 8, -C_5H_8). Vpc (Dowfax) indicated the presence of 2% of 1-vinylcyclopentene in addition to the 1-vinylcyclopentanol.

The *p*-nitrobenzoate had mp 100–101° after being recrystallized several times from hexane.

Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.79; N, 5.36. Found: C, 64.47; H, 5.88; N, 5.53.

The 3,5-dinitrobenzoate had mp 96–97° (hexane).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.61; N, 9.15. Found: C, 55.07; H, 4.73; N, 9.21.

2-(1-Cyclopentenyl)ethanol (XX).—The mixture of acids (mainly 1-cyclopentenylacetic acid) used for the synthesis of

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(58) R. T. Arnold, R. W. Amidon, and R. M. Dobson, *J. Amer. Chem. Soc.*, **72**, 2871 (1950).

methylenecyclopentane was converted into 1-cyclopentenylacetic acid by the procedure employed by Kon and Linstead[59] for the isomerization of cyclopentylideneacetic acid. After two crystallizations from petroleum ether (30–60°), the 1-cyclopentenylacetic acid had mp 50–51° (lit.[59] mp 52°).

Reduction of the acid with lithium aluminum hydride by the procedure previously described for the synthesis of 2-(1-cyclohexenyl)ethanol gave XX (70%): bp 74–75° (8 mm); $n^{23}D$ 1.4788 [lit.[58] bp 76.5–76.8° (8.5 mm), n^{25} 1.4765]. The 3,5-dinitrobenzoate had mp 85–86° (hexane) (lit.[58] mp 84.5–85.5°).

1-Vinylcyclopentene (XVII).—The procedure employed for the preparation of 1-vinylcyclohexene was used. From 12.0 g (0.12 mol) of 2-(1-cyclopentenyl)ethanol and 3.0 g of $KHSO_4$, 2.6 g (25%) of 1-vinylcyclopentene was obtained: bp 109–110°; $n^{20}D$ 1.4865 (lit.[47] bp 109–112°; $n^{20}D$ 1.4863). The olefin contained less than 3% impurities by vpc (Dowfax).

Cyclopentylideneethanol (XIX).—A Reformatsky reaction between cyclopentanone and ethyl bromoacetate gave ethyl 1-hydroxycyclopentylacetate in 34% yield, bp 105–110° (11 mm) [lit.[60] bp 108° (18 mm)], which upon hydrolysis (KOH–ethanol) readily afforded a 78% yield of 1-hydroxycyclopentaneacetic acid, mp 76–77°, from ether–hexane (lit.[59] mp 77°). Dehydration of the hydroxy acid with acetic anhydride by the literature method failed to give a clean product. Instead, from 20.0 g (0.14 mol) of this hydroxy acid, 5.2 g of an oil was obtained (lit.[59] mp 63–64°) whose ir spectrum indicated it was most likely a mixture of 1-acetoxycyclopentylacetic acid and the desired cyclopentylideneacetic acid (1736, 1693, 1642, and 860 cm^{-1}). This mixture (5.1 g) was reduced with lithium aluminum hydride in the same manner as described for the preparation of XVI. The fraction boiling at 81–82° (6 mm) was collected (3.0 g) and found to contain 62% of cyclopentylideneethanol and 32% of 2-(1-cyclopentenyl)ethanol (vpc, Dowfax).

Pure XIX[38] had $n^{20}D$ 1.4871; ir (film) bands at 3320, 1678, 1428, 1068, and 990 cm^{-1}.

Anal.[38] Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.84; H, 10.59.

The 3,5-dinitrobenzoate had mp 97–98° (hexane); nmr ($CDCl_3$), τ 0.85 (s, 3, ArH), 4.46 (m, 1, =CH—), 5.08 (d, 2, J = 7.2 cps, —CH_2O—), 7.65 and 8.27 (m, 8, C_5H_8, 7.65 = allylic H).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.98; H, 4.70; N, 9.17.

2-(2-Cyclopentenyl)ethanol was obtained by the reduction of 2-cyclopentenylacetic acid with lithium aluminum hydride by the procedure described for the synthesis of 2-(1-cyclohexenyl)-ethanol. From 5.0 g of the acid and 2.0 g of lithium aluminum hydride, 3.7 g (71%) of product alcohol was obtained: bp 93–95° (24 mm); $n^{20}D$ 1.4713 [lit.[61] bp 98° (30 mm), $n^{20}D$ 1.4722]; homogeneous by vpc (Dowfax).

2-Methyl-2-cyclohexen-1-ol was synthesized by the reduction of 2-methylcyclohexane-1,3-dione:[62] bp 83–84° (24 mm); $n^{22}D$ 1.4830 [lit.[62] bp 73–75° (18 mm); $n^{25}D$ 1.4838]. The phenylurethan had mp 93–94° from hexane [lit.[62] bp 91.5–92.8°].

2-Methylenecyclohexanol (XXII) and 1-Cyclohexenylmethanol.—The lithium aluminum hydride reduction of 2-carboethoxycyclohexanone by the literature procedure[54] readily afforded the two allylic alcohols: 2-methylenecyclohexanol [bp 82–85° (28 mm); $n^{25}D$ 1.4854 (lit.[54] bp 81–85° (27 mm), $n^{25}D$ 1.4883)] and 1-cyclohexenylmethanol[38] isolated from a fraction boiling at 98–99° (28 mm) which contained 87% of this alcohol, $n^{25}D$ 1.4879 (lit.[54] $n^{25}D$ 1.4905). The 3,5-dinitrobenzoates of 2-methylenecyclohexanol and 1-cyclohexenylmethanol had mp 86–87° and 98–99°, respectively (lit.[54] mp 86.5–87.5° and 100–100.5°).

Deamination of 1-Aminospiro[2.4]heptane (VI).—This deamination was carried out in exactly the same manner as that described for amine VII. From 1.030 g (0.0092 mol) of VI in 10 ml of water and 13.8 ml (0.014 mol) of 1 N perchloric acid, and 2.54 g (0.039 mol) of sodium nitrite in 10 ml of water, 0.9714 g of an orange liquid mixture was obtained. Assuming an empirical formula of $C_7H_{12}O$ for the products, this accounts for 94% of the starting amine. Vpc (Dowfax) indicated nine components: ir (film), 3375, 3085, 1644, 1062, 990, and 915 in addition to a band at 1730 cm^{-1}.

The first component had a retention time of 4.1 min and its relative abundance was 0.6%. Although this component was not identified (retention time different from all comparison compounds), it had the same retention time as a minor component in the vpc of synthetic 1-vinylcyclopentene and is possibly a double bond isomer of XVII, *viz.*, 2- or 3-vinylcyclopentene.

The second and third components had retention times of 4.6 and 8.7 min, and their relative abundances were 1.1 and 1.0%, respectively. These were identified as 1-vinylcyclopentene (XVII) and cyclopentanone XXI by comparison of their retention times (peak enhancement) with authentic samples.

The fourth component had a retention time of 12.7 min and its relative abundance was 79.0%. The ir and nmr spectra of this component were superimposable upon that of authentic XVIII. The *p*-nitrobenzoate (mp 98–100°) and 3,5-dinitrobenzoate (mp 96–97°) gave no depression upon admixture with the same derivatives of XVIII. Likewise, the ir spectra of the two *p*-nitro- and 3,5-dinitrobenzoates were identical.

The fifth and seventh components had retention times of 17.2 and 19.8 min and their relative abundances were 1.2 and 3.1%, respectively; these were shown by vpc to be 2-methylenecyclohexanol (XXII) and 2-(1-cyclopentenyl)ethanol (XX).

The sixth and eighth components, with retention times of 18.0 and 22.0 min, and present to the extent of 1.8 and 0.7%, respectively, were unknown, their retention times being dissimilar to any of the compounds synthesized for structural comparison.

The ninth component had a retention time of 23.3 min and its relative abundance was 11.5%. This component was identified as cyclopentylideneethanol (XIX) by comparison of its ir spectrum and vpc retention time with those of an authentic sample. The 3,5-dinitrobenzoate (mp 97–98°) gave no melting point depression on admixture with the authentic material and had identical ir and nmr spectra.

Ethyl 1-Spirohexanecarboxylate (IXa).—Ethyl diazoacetate[36] (75.0 g) was added to a stirred refluxing mixture of 12.0 g of methylenecyclobutane (0.17 mol), obtained by the amine oxide route,[63] 30 ml of pentane, and 2.0 g of freshly prepared copper-bronze[30b] over a 6-hr period. The mixture was stirred at reflux for 7 hr, then at room temperature for 15 hr. Unreacted methylenecyclobutane and pentane were distilled at atmospheric pressure giving 18.9 g of distillate which analyzed for 13.8% (2.6 g) recovered methylenecyclobutane (vpc on a Dowfax column at room temperature). Filtration of the copper catalyst and fractionation of the residue gave 12.4 g of crude 1-carboethoxyspirohexane, bp 95–102° (36 mm) [lit.[12a] bp 104–106° (33 mm)]. Analysis by vpc (silicone rubber) indicated a purity of 62.5%; the contaminants were diethyl maleate and diethyl fumarate. Pure IXa[38] had $n^{20}D$ 1.4532 (lit.[12a] $n^{20}D$ 1.4510).

1-Spirohexanecarboxylic Acid (Xa).—Crude IXa (12.3 g, 62.5%), was added to a solution of 11.2 g of sodium hydroxide in 100 ml of water. After stirring at reflux for 5 hr the solution was stirred at room temperature for 16 hr. The solution was extracted with two 20-ml portions of ether, acidified with concentrated hydrochloric acid and reextracted with four 50-ml portions of ether. After drying ($MgSO_4$), the ether was removed leaving a mixture of an oil and white solid (probably a mixture of maleic and fumaric acids). The solids were removed by partitioning the mixture with 80 ml of hexane in which they were insoluble. Removal of the hexane gave 6.0 g (95%) of crude 1-spirohexanecarboxylic acid. Vpc (silicone rubber) revealed the presence of one unsymmetrical peak.

Anal.[38] Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.55; H, 8.12.

The amide obtained in the usual way had mp 160–161° after several crystallizations from water.

Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.10; H, 8.85; N, 10.87.

The anilide had mp 145–146° (ether).

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.79; H, 7.63; N, 7.01.

1-Aminospirohexane (V).—This spiroamine was obtained by a modification of the technique described by Weinstock.[16a] From 6.40 g (0.050 mol) of crude Xa, 5.9 g (0.059 mol) of triethylamine, 7.0 g (0.064 mol) of ethyl chloroformate, and 5.0 g (0.076 mol) of sodium azide, there was obtained 5.0 g (74%) of crude, hygroscopic, crystalline 1-aminospirohexane hydrochloride. The azide (2120 cm^{-1}) was extracted into and rearranged in benzene, yielding the isocyanate (2260 cm^{-1}) which was hydrolyzed by

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the addition of 20% hydrochloric acid (70 ml) to the benzene solution of the isocyanate (distillation of the benzene resulted in a sizable loss of isocyanate by codistillation). Recrystallization of the hydrochloride from methanol–ethyl acetate gave 3.2 g, mp 151–153°. The analytical sample had mp 154–155° after two additional recrystallizations.

Anal. Calcd for $C_6H_{12}ClN$: C, 53.92; H, 9.05; N, 10.48. Found: C, 54.06; H, 8.92; N, 10.31.

The free amine, obtained by alkali treatment of the hydrochloride and extraction with methylene chloride, had bp 85–87° (150 mm) and $n^{20}D$ 1.4680. When the amine was subjected to vpc (Dowfax column at an injection block temperature of 305°), the presence of five components was evident, the major to the extent of 83.6%. This major component had an nmr drastically changed from a distilled sample of V, several new peaks being present, particularly in the olefinic region (τ 5.08). Apparently decomposition was taking place during the vpc analysis.

The benzamide had mp 128–130° after several crystallizations from ether–hexane.

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.43; H, 7.43; N, 7.08.

The phenylthiourea after several crystallizations from methylene chloride–hexane had mp 107–108°.

Anal. Calcd for $C_{13}H_{16}N_2S$: C, 67.21; H, 6.94; N, 12.06. Found: C, 67.10; H, 6.87; N, 12.01.

1-Vinylcyclobutanol (XXIII) was obtained in exactly the same manner as that described for 1-vinylcyclopentanol (XVIII). From 2.0 g of cyclobutanone and vinylmagnesium chloride (from 1.4 g of Mg), 0.70 g of XXIII was isolated, bp 71–72° (65 mm) [lit.[25] bp 49–50° (15 mm)]. The distillate analyzed for two components by vpc (Dowfax), the major being present to the extent of 77.0%. Pure 1-vinylcyclobutanol[38] had $n^{20}D$ 1.4618; ir (film), 3340, 3085, 1840, 1644, 1140, 987, 955, and 910 cm^{-1}; nmr (CCl_4), τ 3.97 (q, 1, J_{cis} = 10.0 and J_{trans} = 17.0 cps, —CH=CH_2), 4.91 (two doublets flanking a triplet, 2, —CH=CH_2), 6.23 (s, 1, OH), 8.05 (m, 6, C_4H_6).

The *p*-nitrobenzoate of XXIII had mp 91–92° (hexane).

Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.66. Found: C, 63.05; H, 5.66; N, 5.86.

Cyclobutylideneethanol (XXIV).—The reduction of crude cyclobutylideneacetic acid[64] (2.1 g) with lithium aluminum hydride (1.0 g) was carried out by the technique employed for XVI giving 0.16 g of a crude mixture of alcohols: bp 84–89° (23 mm); $n^{18}D$ 1.4741 [lit.[25] bp 74–75° (19 mm); $n^{19}D$ 1.4860]. Vpc (Dowfax) indicated the presence of three components in 55.0, 33.5, and 11.5% in order of increasing retention time. The 33.5% component was shown to be cyclobutylideneethanol by analogy with the corresponding five- and six-membered ring systems and by isolation[38] to give pure XXIV: $n^{20}D$ 1.4818; ir (film), 3320, 3020, 1692, 1410, 1059, and 987 cm^{-1}; nmr (CCl_4), τ 4.81 (m, 1, =$CHCH_2OH$), 6.14 (2d, 2, =$CHCH_2OH$), 7.30 (m, 4, allylic ring **H**), 7.90 (m, 2, ring **H**), 8.06 (s, 1, OH). The 55.0% component was assumed to be 2-(1-cyclobutenyl)-ethanol, and the 11.5% component 2-cyclobutylethanol.

The *p*-nitrobenzoate of XXIV had mp 67–67.5° (hexane).

Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.66. Found: C, 63.04; H, 5.28; N, 5.61.

2-Methylenecyclopentanol and 1-cyclopentenylmethanol were obtained by the lithium aluminum hydride reduction of 2-carboethoxycyclopentanone, as described by Dreiding and Hartman,[54] giving 2-methylenecyclopentanol [bp 94–98° (78 mm); $n^{25}D$ 1.4738 (lit.[54] bp 85–86° (68 mm); $n^{25}D$ 1.4750)] and 1-cyclopentenylmethanol, isolated[38] (Carbowax) from a fraction boiling at 107–108° (78 mm) which contained 83% of this alcohol, $n^{25}D$ 1.4771 (lit.[54] $n^{25}D$ 1.4851). The *p*-nitrobenzoate of 2-methylenecyclopentanol had mp 85–86° (lit.[54] mp 84.8–85.8°) whereas that of 1-cyclopentenylmethanol had mp 75–76° (lit.[54] mp 75.0–75.6°) after both were recrystallized from hexane.

Deamination of 1-Aminospirohexane (V).—A solution of 1.75 g (0.025 mol) of sodium nitrite in 7 ml of water was slowly added to a cold (ice bath), stirred solution of 0.8501 g (0.0063 mol) of 1-aminospirohexane hydrochloride in 10 ml of water and 3.2 ml of 1 *N* perchloric acid. After the initial vigorous reaction, the mixture was stirred at room temperature for 18 hr and worked up as in the deamination of amines VI and VII giving 0.6001 g of a brown oil (96% material balance assuming an empirical formula of $C_6H_{10}O$ for the products and neglecting the small amount of ether present). Vpc (Dowfax) indicated the presence of four components.

The first component had a retention time of 4.6 min and its relative abundance was 2.4%. This component was identified as cyclobutanone from its matching retention time (peak enhancement).

The second component had a retention time of 6.2 min and its relative abundance was 3.2%. This component was unidentified, its retention time being different from all of the compounds prepared for structural comparison: 1-vinylcyclobutanol, cyclobutylideneethanol, 1-cyclopentenylmethanol, 2-methylenecyclobutanol, and cyclobutanone.

The third component had a retention time of 10.4 min and its relative abundance was 84.6%. This component and authentic 1-vinylcyclobutanol had identical ir and nmr spectra. Its *p*-nitrobenzoate had mp 90–92° and gave no melting point depression upon admixture with the *p*-nitrobenzoate of authentic XXIII (mp 91–92°) and had matching ir spectra.

The fourth component had a retention time 17.6 min and its relative abundance was 9.8%. This component was shown to be cyclobutylideneethanol (XXIV) by comparison of its ir and nmr spectra as well as the ir spectrum of its *p*-nitrobenzoate (mp 66–67°) which were superimposable upon those of authentic XXIV.

Ethyl methylenecyclopropanecarboxylate (XI) was obtained by the sodium hydride induced dehydrohalogenation of ethyl 2-bromo-2-methylcyclopropanecarboxylate[20,65] in 72% yield: bp 153–156°; $n^{22}D$ 1.4425 (lit.[20] bp 150–153°, $n^{25}D$ 1.4447); nmr ($CDCl_3$), τ 4.49 (q, 2, J = 2.5 and 4.5 cps, =CH_2), 5.85 (q, 2, J = 7.2 cps, $CO_2CH_2CH_3$), 7.75 (m, 1, $CHCO_2$–), 8.25 (m, 2, ring CH_2), 8.75 (t, 3, –CH_3). Vpc (Apiezon) indicated a purity of >97%.

Ethyl Spiropentanecarboxylate (XII).—The reaction of XI with methylene iodide–zinc copper couple was carried out by the procedure of Ullman and Fanshawe[20] with the exception that the reaction mixture was refluxed 60 hr instead of 24 hr. From 34.0 g (0.28 mol) of XI, 230 g (0.86 mol) of methylene iodide, and 82.0 g (1.25 mol) of freshly prepared zinc–copper couple,[66,67] 39.5 g of a yellowish oil was obtained which consisted of 73% XI and 27% XII (vpc, Apiezon). This product, 39.5 g, was recycled with the same quantities of methylene iodide and zinc–copper couple yielding 35.8 g of a mixture of 44% XI and 56% XII. An additional recycling with 230 g of methylene iodide and 82.0 g of zinc–copper couple gave 39.7 g of a mixture which analyzed for 7% XI and 76% XII. Fractionation gave three cuts: (1) 3.1 g, bp 79–83° (43 mm), $n^{22}D$ 1.4385 (80% XII); (2) 9.9 g, bp 83–84° (43 mm), $n^{22}D$ 1.4406 (84% XII); (3) 3.1 g, bp 84–90° (43 mm), $n^{22}D$ 1.4375 (70% XII). The ir spectrum (Table III) agreed well with the literature.[13a] Fraction 2 was used as is without further purification. Use of less methylene iodide and zinc–copper couple in the initial reaction or recycling gave a lower proportion of XII in the product mixture.

Spiropentanecarboxylic Acid (XIII).—Hydrolysis of XII was effected by refluxing a stirred mixture of 9.7 g of XII (84% pure) in a solution of 9.0 g of sodium hydroxide in 100 ml of water for 2 hr (complete solution), then stirring at room temperature for 16 hr. Work-up of this solution as described for spiro acids Xb and Xc gave 8.0 g of crude acid after removal of the ether. Vpc (silicone rubber) indicated one peak with a small amount of a high boiling impurity (<5%).

Anal.[38] Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.18; H, 7.34.

The amide, prepared by treatment of the acid chloride with concentrated ammonia, had mp 124–125° after several crystallizations from ether.

Anal. Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.73; H, 8.12; N, 12.49.

The anilide after multiple recrystallizations from ether had mp 161–162°.

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.72; H, 6.81; N, 7.27.

The acid hydrazide prepared from the acid chloride and hydrazine had mp 114–115° (lit.[11] 115–117.5°) after crystallization from methylene chloride–hexane.

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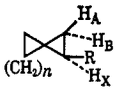
TABLE III

IR AND NMR SPECTRA OF SPIRO ACIDS, SPIROAMINES, AND THEIR DERIVATIVES



No.	n	R	Registry no.	Ir bands C=O	Ir bands C–H[b]	Ir bands Ring[b]	Chemical shift,[a] τ, and coupling constants, cps: Cycloalkyl protons	H_A	H_B	H_X	J_{AX}	J_{BX}	J_{AB}
1	4	$-CO_2H$	17202-86-7	1688[c(1)]		1040, 1018							
2	4	$-CO_2C_2H_5$	17202-87-8	1737[c(1)]	3075, 3005	1050, 1030, 1012							
3	4	$-CONH_2$	17202-88-9	1645[c(2)]	3065, 2985	1021							
4	4	-CONHPh	17202-89-0	1650[c(2)]	3050, 2980	1020	8.58 m	9.07 q[d]	9.31 q[d]	8.58 m[e]	8.1[d]	7.9[d]	4.0
5	4	$-NH_2$	17202-90-3	c(1)	3055, 2980	1023, 1013	8.53 m[f]	9.98 t	9.60 q	7.92 q	4.0	7.0	4.2
6	4	$-NH_2 \cdot HCl$	17202-91-4	c(3)		1033, 1021	8.50 m[g]	9.19 t[h]	9.19 t[h]	7.65 q	5.0	7.0	
7	4	-NHCOPh	17202-92-5	1642[c(2)]	3060, 2995	1025	8.50 m	9.59 q	9.21 q	7.22 m	4.6	7.7	5.5
8	4	-NHCSNHPh	17202-93-6	c(3)		1035, 1020, 1015	8.50 s	9.59 q	9.19 q	7.30 m	4.5	7.5	5.6
9	3	$-CO_2H$	17202-94-7	1692[c(1)]		1040	8.30 m	8.82 m[h]	8.82 m[h]	8.30 m[e]			
10	3	$-CO_2C_2H_5$	17202-95-8	1727[c(1)]	3070, 3040	1045, 1020							
11	3	$-CONH_2$	17202-96-9	1685[c(2)]	i	1053, 1030, 1000	8.31 s	9.05 q[d]	8.72 q[d]	8.05 m	8.0	8.7	4.5
12	3	-CONHPh	17202-51-6	1645[c(2)]	3055, 2990	1020, 998, 990	8.36 m	8.71 q	9.10 q	8.36 m[e]	4.5	8.0	4.0
13	3	$-NH_2$	17202-52-7	c(1)	3060, 2980	1040, 1011	8.38 m[j]	9.80 t	9.38 q	7.89 q	4.0	7.3	4.5
14	3	$-NH_2 \cdot HCl$	17202-53-8	c(3)		1030, 1010	8.20 m[k]	9.00 m[h]	9.00 m[h]	7.40 q	4.2	7.5	
15	3	-NHCOPh	17202-54-9	1661[c(4),i]		1030, 1009	8.30 m	9.42 q	8.97 q	7.14 m	4.5	7.8	5.5
16	3	-NHCSNHPh	17202-55-0	c(4),i		1030, 1007	8.29 m	9.39 q	8.97 q	7.17 m	4.6	7.7	5.5
17	2	$-CO_2H$	17202-56-1	1690[c(1)]		1035, 1005	7.81 m	8.86 m[h]	8.86 m[h]	8.41 q	4.8	8.2	
18	2	$-CO_2C_2H_5$	17202-57-2	1725[c(1)]	3070, 3040	1042, 996	7.82 m[l]	8.97 m[h]	8.97 m[h]	8.42 q	5.0	8.5	
19	2	$-CONH_2$	17202-58-3	1647[c(2)]	3060	1040, 1006	7.81 m	8.78 m[h]	8.78 m[h]	8.78 m[h]	4.3 or 5.0[m]	8.0	4.3 or 5.0[m]
20	2	-CONHPh	17202-59-4	1651[c(2)]	3079, 2980	1033, 1015	7.85 d	8.52 m	9.06 m[h]	9.06 m[h]	4.5	7.8	4.0
21	2	$-NH_2$	17202-60-7	c(1)	3057	1040, 1005	7.99 m[n]	9.85 q	9.49 q	7.99 m[e]	4.2	7.2	5.0
22	2	$-NH_2 \cdot HCl$	17202-61-8	c(3)		1056, 1016	7.73 m[o]	9.04 m[h]	9.04 m[h]	7.73 m[e]			
23	2	-NHCOPh	17202-62-9	1630[c(2)]	3055, 3010	1036, 1021	7.89 s	9.50 q	9.04 q	7.21 m	4.5	7.7	6.0
24	2	-NHCSNHPh	17202-63-0	c(2)	3055	1020	7.85 s	9.45 m	9.00 q	7.20 m		7.3	6.0
25	1	$-CO_2H$	17202-64-1	1690[c(1)]		1040, 1005	9.05 s	8.63 t[h]	8.63 t[h]	7.96 q	4.0	7.6	
26	1	$-CO_2C_2H_5$	6142-68-3	1726[c(1),p]	3070, 2990	1049, 1020, 1010	p						
27	1	$-CONH_2$	17202-66-3	1650[c(2)]	3065, 2993	1040, 1005	9.08 s	8.62 t[h]	8.62 t[h]	8.12 q	4.5	7.5	
28	1	$-CONHNH_2$	6142-70-7	1625[c(2),q]	3070, 2995	1062, 1055, 1009, 992	9.10 s[q]	8.61 m[h]	8.61 m[h]	8.22 q	4.0	7.5	
29	1	-CONHPh	17202-68-5	1656[c(2)]	3060, 2989	1040	9.03 t	8.53 m[h]	8.53 m[h]	8.01 q	4.0	7.5	
30	1	$-NH_2$	17202-69-6	c(1)	3060, 2990	1042, 1010							
31	1	$-NH_2 \cdot HCl$	17202-70-9	c(1),r		1040, 1003							
32	1	-NHCOPh	17202-71-0	1643[c(2)]	3055, 2981	1042, 1020	9.04 q	8.64 q[h]	8.64 q[h]	6.68 m	4.5	7.8	
33	1	-NHCSNHPh	6142-72-9	c(2),q	3055, 2990	1020, 992	9.03 m[q]	8.65 q[h]	8.65 q[h]	6.74 m	4.1	7.8	

[a] Spectra were determined in $CDCl_3$. Abbreviations are s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] Cyclopropyl C–H stretching and ring deformation bands. [c] Spectrum determined as (1) film, (2) KBr wafer, (3) Nujol mull, (4) $CHCl_3$ solution. [d] Because of the small difference between J_{AX} and J_{BX} it is uncertain whether H_A or H_B is *cis* to R. [e] Hidden in cycloalkyl multiplet. [f] τ 8.70 (s, $-NH_2$). [g] τ 1.44 (m, $-NH_3$). [h] These protons were not separable. [i] Spectrum determined on a Beckman IR-5A. [j] τ 8.60 (s, $-NH_2$). [k] τ 0.93 (m, $-NH_3$). [l] The 40-Mc spectrum has been reported: D. E. Applequist and D. E. McGreer, *J. Amer. Chem. Soc.*, **82**, 1965 (1960). [m] The complexity of H_A, H_B, and H_X made it impossible to distinguish between these two values. [n] τ 8.13 (s, $-NH_2$). [o] τ 1.52 (m, $-NH_3$). [p] The ir spectrum[11,13a] and the 40[11] and 60[20] Mc nmr spectra have been reported. [q] The ir spectrum[11,13a] and 40-Mc nmr spectrum[11] have been reported. [r] Spectrum determined from the crude hygroscopic salt.

Spiropentylamine (II).—The modified Curtius technique[16a] as described for the synthesis of spiroamine V was employed. From 8.0 g (0.071 mol) of XIII, 8.8 g (0.087 mol) of triethylamine, 10.0 g (0.092 mol) of ethyl chloroformate, and 7.3 g (0.112 mol) of sodium azide, 5.9 g (70%) of crude spiropentylamine hydrochloride was obtained as a viscous hygroscopic oil. Repeated attempts at crystallization failed. Vpc (Dowfax) of a freshly generated ether solution of the free amine indicted one major component present ≈95%. Careful distillation of the ether and vpc of the rapidly darkening amine now indicated a mixture of nine components, the component previously present in 95% (ether solution) now representing only about 30% of the mixture. The ir spectrum of a freshly generated sample (Table III) was consistent with II. The phenylthiourea of II was prepared as described for the same derivative of amine VII and had mp 104–105° (lit.[11] mp 105.5–107.5°) after two crystallizations from hexane.

The benzamide had mp 97–98° (hexane).

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.94; H, 6.99; N, 7.45.

Deamination of Spiropentylamine (II).—Crude spiropentylamine hydrochloride was assayed by titration with standard methanolic sodium methoxide using a phenolphthalein indicator. A solution of 0.3221 g of crude spiropentylamine hydrochloride in 30.0 ml of anhydrous, spectroquality methanol required 40.00 ml of a 0.0968 *N* sodium methoxide solution for neutralization corresponding to an amine content of 88.6%.[68] This titrimetric technique[32] gave less than 2% error when checked with analytically pure samples of the hydrochlorides of amines V, VI, and VII.

A solution of 6.70 g (0.097 mol) of sodium nitrite in 22 ml of water was added dropwise to a cold (ice bath) stirred solution of 3.278 g of crude spiropentylamine hydrochloride [equivalent to 2.904 g (0.024 mol) of spiropentylamine] in 15 ml of water and 12.2 ml of 1 *N* perchloric acid. After stirring at room temperature for 18 hr, the reaction mixture was worked up by extraction with ether as described previously for amines V–VII giving 1.530 g of a residue (75% material balance assuming an empirical formula of C_5H_8O and neglecting the small amount of ether present). Vpc (Ucon column programmed 5°/min from 100 to 180°) of the residue indicated the presence of ten components; the first, second, and sixth through ninth eluted amounted to less than 1% each and were not investigated.

The third component had a retention time of 10.5 min: relative abundance 5.1%; ir (film), 3360, 3075, 3000, 1840, 1642, 987 and 915 cm^{-1}; nmr (CCl_4), τ 4.97 (J = 10.0 and 15.5 cps, $-CH{=}CH_2$), 6.13 (q, $-CH{=}CH_2$), 8.88 (m, major portion centered at 9.10,[18] cyclopropyl H).[69]

Based upon these data, this component was tentatively identified as 1-vinylcyclopropanol.[70]

The fourth component had a retention time of 14.8 min and its relative abundance was 16.9%. This component was identified as 2-methylenecyclobutanol by comparison of its ir and nmr spectra with those published by Applequist and Fanta.[11,70]

The fifth component had a retention time of 16.4 min and its relative abundance was 69.9%. This component was similarly identified as 3-methylenecyclobutanol by spectral comparison.[11]

(68) This value of 88.6% is probably a minimum value. Because of the hygroscopic nature of the salt, the weight taken may very well be more than the true weight of hydrochloride titrated.

(69) The OH proton was not clearly visible.

(70) An attempt to prepare the *p*-nitrobenzoate ester failed.

The *p*-nitrobenzoate had mp 103–104° (hexane); nmr ($CDCl_3$), τ 1.90 (s, 4, ArH), 4.80 (m, 1, J = 6.8 cps, —CHOCO—), 5.12 (m, 2, =CH_2), 6.97 (m, 4, ring H).

Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.78; H, 4.66; N, 6.10.

The tenth component had a retention time of 28.6 min and its relative abundance was 4.7%: ir (film), 3350, 2960, 2930, 2875, 1455, 1378, 1045, and 1018 cm^{-1} (no bands attributable to an olefinic group were present); nmr (CCl_4), τ 6.19 (m), 8.14 (m), 8.57 (m). From these data this component was assumed to be a polymeric alcohol.

Registry No.—2-Methylenecycloheptanol, 16240-38-3; *p*-nitrobenzoate of 2-methylenecycloheptanol, 17202-74-3; phenylurethan of 2-methylenecycloheptanol, 17202-75-4; 3,5-dinitrobenzoate of 1-cycloheptenylmethanol, 17202-84-5; XVIII, 3859-35-6; *p*-nitrobenzoate of XVIII, 17202-85-6; 3,5-dinitrobenzoate of XVIII, 17206-76-7; XIX, 931-43-1; 3,5-dinitrobenzoate of XIX, 7498-75-1; XXIII, 17202-79-8; *p*-nitrobenzoate of XXIII, 17202-80-1; XXIV, 4415-76-3; *p*-nitrobenzoate of XXIV, 17202-82-3; *p*-nitrobenzoate of 3-methylenecyclobutanol, 17202-83-4.

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Chemistry of Allene. III. Cyclooligomerization. Synthesis of 1,4,7-Trimethylenespiro[4.4]nonane and a New Pentamer

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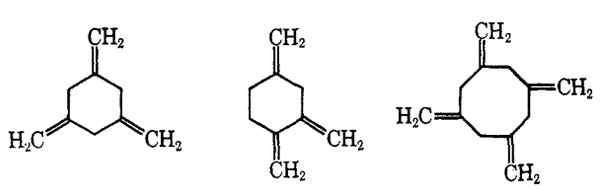
$[(C_6H_5)_3P]_3RhCl$ catalyzes the liquid phase cyclooligomerization of allene to a single tetramer, 1,4,7-trimethylenespiro[4.4]nonane (5), and a single pentamer of unknown structure.

Thermal oligomerization of liquid allene at 140° affords a mixture of cyclic products including two dimers, three trimers, two tetramers, and higher oligomers.[1] The structures of these oligomers have been the subject of recent papers.[2] The chemistry of allene is discussed more broadly in recent reviews.[3]

In earlier work[4] in these laboratories, it was found that allene cyclizes at 110° in solutions containing certain phosphorus-modified nickel catalysts, for example $[(C_6H_5)_3P]_2Ni[CO]_2$, to give products largely different from those obtained in the uncatalyzed reaction. The principal products were two trimers, **1** and **2**, and a tetramer, for which structure **3** was proposed.



1 **2** **3**

This paper describes the synthesis and characterization of some new cyclooligomers obtained with phosphine-modified rhodium catalysts.

Cyclooligomerization Reactions.—A variety of Rh(I) compound such as $(CO)_4Rh_2Cl_2$ and $(AcAc)Rh(C_2H_4)_2$ catalyzed oligomerization of allene in solution at 50–100° to oily or semisolid mixtures. These mixtures contained small amounts of unidentified trimers and tetramers. When triphenylphosphine was added to these catalysts or, better, when a preformed phosphine complex was employed, the principal products were a single tetramer and a single pentamer produced in 42–60% and 5–16% yields, respectively. The reaction was conveniently effected using 0.5 to 2% $[(C_6H_5)_3P]_3RhCl$[5] or $[(C_6H_5)_3P]_2Rh[CO]Cl$[6] in chloroform. These two catalysts gave similar product compositions; however, because a large run using $[(C_6H_5)_3P]_2Rh[CO]Cl$ as catalyst detonated with great violence, the less active $[(C_6H_5)_3P]_3RhCl$ was used in most experiments.[7]

In a typical run, a solution of 150 g of allene, 1 g of $[(C_6H_5)_3P]_3RhCl$, and 0.1 g of hydroquinone in 75 g of chloroform was agitated in a 400-ml, silver-lined pressure tube at 80° for 16 hr; the pressure fell steadily to less than 1 atm. Gas chromatographic analysis of the resulting oil showed that the product contained traces of presumed dimers and trimers, a single tetramer (59% of the total product by weight), and a single pentamer (6%). The remainder was less volatile material probably containing at least two hexamers. Fractionation of the mixture gave tetramer, bp 80° (10 mm), and pentamer, bp 81–81.5° (1.2 mm). These fractions were established by gas chromatography (glpc) to be single compounds of >99.5% purity.

A reaction temperature of 80° appeared to be optimum for tetramer formation. At lower temperatures, the tetramer/pentamer ratio decreased and the re-

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