column of alumina (activated at 200° for 18 hr.) packed in petroleum ether (b.p. 60–68°). Sulfur (35 mg., 54% yield, m.p. 107–109°, mixed m.p. with authentic (m.p. 115–116°) sulfur, 113–116°) was eluted from the column with petroleum ether. Further elution of the column with 19–20% solutions of methylene chloride in petroleum ether (b.p. 60–68°) gave the principal fractions (466 mg., m.p. 65–139°, 77% recovery) which were shown[7] to contain 21% of VI (18% yield), 29% of V (25% yield) and 43% of starting material (IV, 33% recovery). The ratio VI/V was essentially identical to that found in the previous experiment, and the composition of the mixture was again unchanged by recrystallization from petroleum ether (b.p. 60–68°) (85% recovery, m.p. 134–139°, 23% VI/33% V/44% IV) or methanol (75% recovery, m.p. 135–145°, 23% VI/32% V/46% IV).

Ethyl *p*-Methoxyphenacyl Xanthate.—A stirred solution of *p*-methoxyphenacyl chloride (5.6 g., 0.030 mole) in dry acetone (10 ml.) was added dropwise to a suspension of potassium ethyl xanthate (4.83 g., 0.030 mole) in dry acetone (100 ml.). The precipitated potassium chloride was removed by filtration, the solvent was removed by distillation at reduced pressure and the residue was recrystallized from ethanol. There was obtained 6.08 g. (80% yield) of ethyl *p*-methoxyphenacyl xanthate (m.p. 60–64°). Further recrystallization of this product from ether–petroleum ether (b.p. 30–60°) gave yellow transparent plates melting at 67.5–68.0°.

Anal. Calcd. for $C_{12}H_{14}O_3S_2$: C, 53.31; H, 5.22. Found: C, 53.36; H, 5.58.

Ethyl *p*-nitrophenacyl xanthate was prepared from *p*-nitrophenacyl chloride (6.00 g., 0.030 mole) by a procedure similar to that described above for ethyl *p*-methoxyphenacyl xanthate. The crude product (7.52 g., 93% yield, m.p. 84–87°) was purified by recrystallization from ether–petroleum ether (b.p. 30–60°) and the pure xanthate was obtained as fine white needles melting at 88–89°.

Anal. Calcd. for $C_{11}H_{11}O_4NS_2$: C, 46.30; H, 3.89. Found: C, 46.80; H, 3.79.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

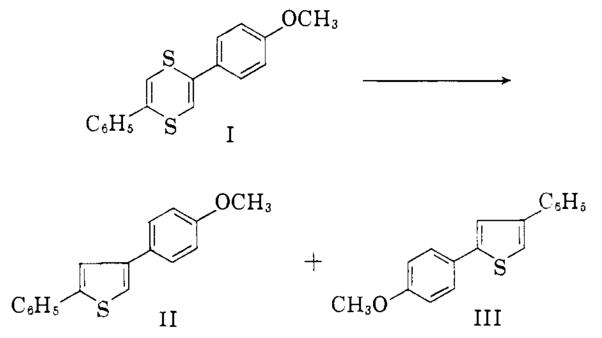
Heterocyclic Vinyl Ethers. XIX. Unsymmetrical 2,4-Diarylthiophenes[1]

BY WILLIAM E. PARHAM AND EDWIN T. HARPER[2]

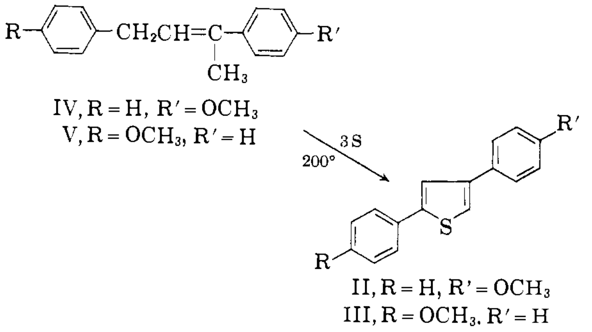
RECEIVED MARCH 5, 1960

The synthesis of 2-phenyl-4-*p*-methoxyphenylthiophene (II) and 2-*p*-methoxyphenyl-4-phenylthiophene (III) is described by procedures which involve the high temperature sulfuration of appropriate olefins. A by-product, believed to be 2-(*p*-methoxyphenyl)-thieno[2,3-b]thianaphthene (X), was isolated from the reaction of 1-phenyl-3-*p*-methoxyphenyl-2-butene (IV) and sulfur. The composition of mixtures of the isomeric thiophenes, either alone or containing 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiadiene (I), can be determined conveniently by infrared spectroscopic analysis.

As part of our study[3] of the formation of 2,4-diarylthiophenes from 2,5-diaryl-1,4-dithiadienes (such as I), it became necessary to prepare 2-phenyl-4-*p*-methoxyphenylthiophene (II) and 2-*p*-methoxyphenyl-4-phenylthiophene (III) and to devise a method for determining the composition of mixtures of I, II and III.



The synthesis of 2,4-diarylthiophenes has been studied in detail,[4] but these methods have been generally limited to thiophenes in which the aryl substituents are identical. Schmitt[5] and co-workers recently have reported the synthesis of 2-*p*-methoxyphenyl-4-phenylthiophene (III) by the reaction of V with sulfur, and we have employed this procedure (reaction of IV and V, respectively, with sulfur) for the preparation of the isomeric thiophenes II and III. It became evident that the product obtained by Schmitt was not 2-*p*-methoxyphenyl-4-phenylthiophene (III) as described, but more probably the isomeric thiophene II.[5b]



IV, R = H, R′ = OCH$_3$
V, R = OCH$_3$, R′ = H

II, R = H, R′ = OCH$_3$
III, R = OCH$_3$, R′ = H

The olefins, 1-phenyl-3-*p*-methoxyphenyl-2-butene (IV) and 1-*p*-methoxyphenyl-3-phenyl-2-butene (V) were synthesized, in 37% and 56% yields, respectively, by Grignard reactions.

The dehydration of the alcohols VII and IX could logically give olefins with structures corresponding to A, B or C. Structure A (*cis*-2-butene) was assigned to olefin V (Ar = *p*-$CH_3OC_6H_4$-, Ar′ = C_6H_5) in the following way. Structure C was eliminated on the basis of the infrared spectrum of

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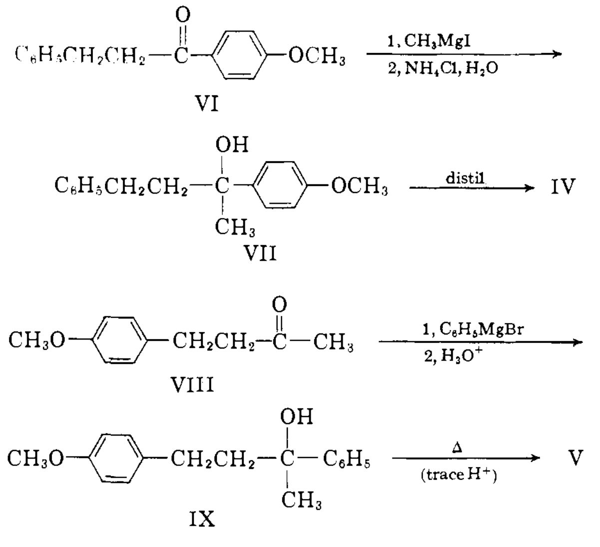
(1) Part of this work was supported by the Office of Ordnance Research, U. S. Army, Contract No. DA-11-022-Ord-2616.

(2) From the Ph.D. Thesis of E. T. Harper, University of Minnesota, 1959.

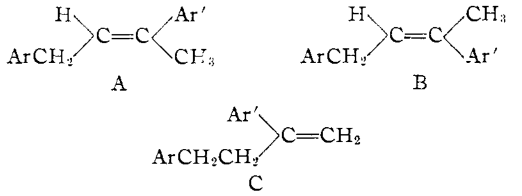
(3) W. E. Parham and E. T. Harper, THIS JOURNAL, **82**, 4932 (1960).

(4) (a) E. Campaigne, *ibid.*, **66**, 684 (1944). (b) P. Demerseman, Ng. Buu-Hoï, R. Royer and A. Cheutin, *J. Chem. Soc.*, 2720 (1954).

(5) (a) J. Schmitt, R. Fallard and M. Suquet, *Bull. soc. chim. France*, **2**, 1147 (1956). (b) These workers reported their starting ketone, β-*p*-methoxyphenylpropiophenone, to melt at 99–100° and the thiophene (III) to melt at 162°. Neither of these melting points are correct. β-*p*-Methoxyphenylpropiophenone melts at 59–60°, and the thiophene III melts at 145°. It is reasonable to assume that Schmitt and co-workers started with the isomeric ketone β-phenyl-*p*-methoxypropiophenone (m.p. 97°) and prepared thiophene II (m.p. 163°).



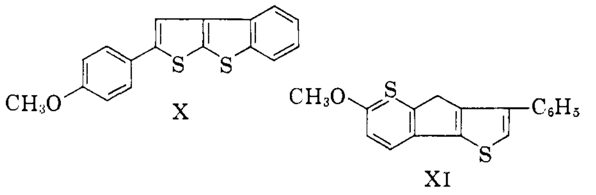
V, which did not show absorption characteristic of the terminal methylene group.[6] Comparison of the ultraviolet spectrum of V with those of model compounds (Table I, Experimental) indicated that the olefin was principally, if not exclusively, *cis*-1-*p*-methoxyphenyl-3-phenyl-2-butene (VA). The main absorption of V coincided in wave length and intensity with that of *cis*-2-phenyl-2-butene,[7] and there was no shoulder at 235 mμ characteristic of *trans*-2-phenyl-2-butene.[7] Since the spectra of *cis*- and *trans*-2-*p*-methoxyphenyl-2-butene were not available, the assignment of structure A to olefin IV was made by analogy. This assignment was supported,[6] however, by the infrared spectrum of IV, which was quite similar to that of V.



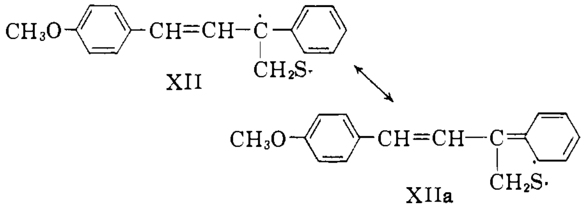
The formation of *cis*-2-butenes by dehydration of VII and IX was not unexpected, since the *trans*-2-butenes (IVB and VB), with the 3-aryl group sandwiched between alkyl groups, should be thermodynamically less stable than the *cis* isomers (IVA and VA). The larger barrier to coplanarity of the 3-aryl group with the olefinic double bond in the *trans* isomers undoubtedly decreases their styrene-like conjugation, reducing their stability. The greater stability of *cis*- compared to *trans*-2-phenyl-2-butene may also be inferred from the spectra shown in Table I. The lessened styrene-like conjugation is reflected by the smaller extinction coefficient and shorter wave length of the ultraviolet maximum of the *trans* isomer.

It may be that the *cis* 2-butene structure of the olefins IV and V, which is sterically similar to the carbon skeleton of thiophene, was partly responsible for the success of the sulfuration reactions. The optimum reaction conditions probably have not yet been realized, although a cursory exploration of the conditions revealed the deleterious effect of excess sulfur. These data are summarized in Table II (Experimental).

An interesting by-product was isolated during the preparation of 2-*p*-methoxyphenyl-4-phenylthiophene (III). The white, crystalline solid, m.p. 177.0–179.0°, was assigned the structure 2-(*p*-methoxyphenyl)-thieno[2,3-b]thianaphthene (X) in view of the data that the composition and molecular weight required the molecular formula $C_{17}H_{12}OS_2$; thus the two most reasonable structural formulas seemed to be X and XI. Assignment of structure X was based on the infrared spectrum of the product which did not show absorption characteristic of a monosubstituted benzene (690 cm.$^{-1}$).[6]



The possibility was considered that the by-product X was formed by further direct sulfuration of 2-*p*-methoxyphenyl-4-phenyl-thiophene (III). However, no crystalline products were isolated when III was heated with sulfur at 200° for 60 hr. The formation of X, instead of its isomer XI, can be rationalized on the basis of a free radical mechanism similar to the one postulated by Horton[8] for the sulfuration of toluene and which involves the intermediate diradical XII.



The analysis of mixtures of the thiophenes II and III was carried out by an infrared spectroscopic technique after it was found that the melting points of mixtures of the thiophenes were poor criteria of composition (Fig. 1, Experimental). Mixtures containing 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiadiene (I), as well as the thiophenes II and III, also were analyzed successfully by this method. The application of this analysis is discussed in the preceding paper,[3] and details of the method appear in the Experimental section of this report.

Experimental

1-Phenyl-3-*p*-methoxyphenyl-2-butene (IV).—(a) A solution containing benzene (100 ml.) and β-phenyl-*p*-methoxypropiophenone[9] (VI, 13.12 g., 0.0546 mole, m.p. 97–98°) was added to a solution containing ether (30 ml.) and methyl magnesium iodide (0.17 mole) over a 2-hr. period. The mixture was heated at the reflux temperature overnight, saturated aqueous ammonium chloride (50 ml.) was added and the organic layer was distilled.[10] The product (8.43 g.,

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[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

[7] D. J. Cram, THIS JOURNAL, **71**, 3883 (1949).

[8] A. W. Horton, *J. Org. Chem.*, **14**, 761 (1949).

[9] E. Rothstein, *J. Chem. Soc.*, 1459 (1951).

[10] *Cf.* the synthesis of 1,3-diphenyl-3-butanol: R. Stoermer and H. Kootz, *Ber.*, **61**, 2333 (1928).

TABLE I

ULTRAVIOLET ABSORPTIONS OF V AND MODEL COMPOUNDS

Compound	Wave lengths (ϵ) of maxima						
V	225 (14600)[a]	243 (13900)	248 (13700)[b]	254 (12100)[b]	260 (9100)[c]	274 (3920)[c]	284 (2250)[b]
α-Methylstyrene[e]		242 (13000)					285 (280)
β-Methylstyrene[e]		244 (13000)					280 (710)
cis-2-Phenyl-2-butene[f]		242 (13000)					
trans-2-Phenyl-2-butene[f]		235 (8000)					
p-Methoxytoluene[g]		244 (5)[d]				278(1600)	

[a] Plateau. [b] Shoulder. [c] Inflection. [d] Minimum. [e] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951. [f] Ref. 7. [g] P. Ramart–Lucas, *Bull. soc. chim. France*, [5] **9**, 934 (1942).

65% yield) was collected at 125–150° (0.25 mm.). The infrared spectrum of the product was essentially identical to that of the undistilled polymeric residue (3.54 g., 27% yield) and neither contained absorption characteristic[6] of the hydroxyl group. The olefin was redistilled (b.p. 118–121° (0.03 mm.), $n^{25}\text{D}$ 1.5860–1.5893) and a fraction with $n^{25}\text{D}$ 1.5893 was analyzed.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.48; H, 7.70.

The infrared spectrum of IV (b.p. 130–133° (0.18 mm.)) was consistent with the absence of appreciable terminal olefin.[6] The principal ultraviolet absorption of IV occurred at 254 mμ (ϵ 17,200).

(b) **1-Phenyl-3-*p*-methoxyphenyl-2-butene** (IV) was obtained by a procedure similar to that described in (a), above, from the Grignard reagent of β-phenylethyl bromide (19.1 g., 0.103 mole) and *p*-methoxyacetophone (12.6 g., 0.084 mole). The principal fraction of the product (5.65 g., b.p. 140° (0.19 mm.), 28% yield) was redistilled at 0.18 mm. and collected at 120–125° ($n^{25}\text{D}$ 1.5819), 125–130° ($n^{25}\text{D}$ 1.5850) and 130–133° ($n^{25}\text{D}$ 1.5882). The infrared and ultraviolet spectra of the fraction $n^{25}\text{D}$ 1.5882 were essentially identical to those reported under (a), above; however, qualitative vapor-phase chromatography indicated that this fraction was only about 90% pure. This fraction of the product could be used successfully for the next synthetic step.

2-Phenyl-4-*p*-methoxyphenylthiophene (II).—A mixture of IV (1.87 g., 7.85 mmoles) and sulfur flowers (0.75 g., 23 mg. atoms) was heated at 175–185° for 41 hr. The cooled mixture was dissolved in methylene chloride (40–50 ml.) and chromatographed on a 35 × 420 mm. column of alumina (activated at 170° (15 mm.) for 3 days) packed in petroleum ether (b.p. 60–68°). Recovered sulfur (0.37 g., 49%) was eluted with petroleum ether (b.p. 60–68°). 2-Phenyl-4-*p*-methoxyphenylthiophene (II, 0.47 g., 22% yield, m.p. 145–161°) was eluted with a solution of 35% methylene chloride in petroleum ether (b.p. 60–68°). Fractions eluted subsequently may have contained more II but were not processed. The product was recrystallized from carbon tetrachloride (25 ml.), which afforded 0.45 g. (21% yield) of II, m.p. 162–163°. The melting point was raised to 161.5–163.5° by further recrystallization of this product from 2-propanol.

Anal. Calcd. for $C_{17}H_{14}OS$: C, 76.65; H, 5.30. Found: C, 76.37; H, 5.35.

1-*p*-Methoxyphenyl-3-phenyl-2-butene (V).—An ether solution (25 ml.) containing 1-*p*-methoxyphenyl-3-butanone[11] (VIII, 9.16 g., 0.0515 mole) was added dropwise (20 minutes) to a solution (50 ml.) of phenyl Grignard reagent (prepared from bromobenzene, 18 g., 0.11 mole). The resulting solution was stirred and heated at the reflux temperature overnight. The crude 1-*p*-methoxyphenyl-3-phenyl-3-butanol (IX), obtained from the ether solution after the action of aqueous ammonium chloride, was treated with boiling 5% sulfuric acid (5 ml.) for 12 hr. The resulting oil was washed with water, dried and distilled. The crude 1-*p*-methoxyphenyl-3-phenyl-2-butene (V, 9.26 g., 75% yield, b.p. 124–149° (0.2 mm.), $n^{25}\text{D}$ 1.5795–1.5827) thus obtained was refractionated (b.p. 121° (0.03 mm.), $n^{25}\text{D}$ 1.5842).

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.61; H, 7.90.

The infrared spectrum of V (b.p. 135–138° (0.13 mm.)) was consistent[6] with the absence of appreciable terminal olefin. The ultraviolet spectrum of V was essentially identical to the spectra of model compounds (Table I) and was consistent with the proposed *cis*-2-butene structure (VA).

2-*p*-Methoxyphenyl-4-phenylthiophene (III).—A mixture of V (3.09 g., 13.0 mmoles) and sulfur (1.26 g., 39.3 mg. atoms) was heated at 190–205° for 50 hr. The mixture was chromatographed on a 35 × 440 mm. column of alumina (activated at 250° for 18 hr.) packed in petroleum ether (b.p. 60–68°). Recovered sulfur (0.15 g., 12%, recrystallized from petroleum ether, m.p. and mixed m.p. 114–116°) was eluted with petroleum ether (b.p. 60–68°). The thiophene (III, 1.84 g., 53% yield), eluted with a solution of 40% methylene chloride in petroleum ether (b.p. 60–68°), was recrystallized twice from petroleum ether (b.p. 60–68°), which afforded 1.43 g. (41%) of III, m.p. 141–144°. The melting point was raised to 144.5–145.5° by further recrystallization from petroleum ether.

Anal. Calcd. for $C_{17}H_{14}OS$: C, 76.65; H, 5.30. Found: C, 76.80; H, 5.23.

This sulfuration reaction was carried out a number of times, but the results did not point to an optimum set of conditions. The data are summarized in Table II.

TABLE II

SYNTHESIS OF THIOPHENES BY SULFURATION OF OLEFINS

Olefin	Thiophene	*S*[a]	Temp., °C.	Time[b]	H_2S[c]	% S[d]	Thiophene[e]
IV	II	3.4	175–185	41	No	49	22
V	III	3.0	190–205	50	Yes	12	53
V	III	3.0	180–185	18	?	42	46
V	III	3.0	190–200	60	Yes	38	36
V	III	18	240–250	4	No	17	<5[f]

[a] Mole ratio, sulfur/olefin. [b] Reaction time in hours. [c] Hydrogen sulfide evolution had ceased. [d] Recovered by chromatography. [e] Crude thiophene from chromatogram. [f] A black, insoluble residue accounted for 47% of total starting material.

In one of the experiments, on twice as large a scale as described above, a white, crystalline by-product, believed to be 2-(*p*-methoxyphenyl)-thieno[2,3-b]thianaphthene (X), was eluted along with the last fractions of III. This by-product was not completely separated but was estimated to be present in less than 5% yield. Recrystallization of this material from petroleum ether (b.p. 60–68°) afforded the pure by-product, m.p. 177.0–179.0°.

Anal. Calcd. for $C_{17}H_{12}OS_2$: C, 68.88; H, 4.08; S, 21.64; mol. wt., 296.40. Found: C, 68.49; H, 4.15; S, 22.10; mol. wt. (cryoscopic in benzene), 290.

The infrared spectrum of the by-product contained no absorption maximum near 690 cm.$^{-1}$, indicating that the compound contained no monosubstituted benzene ring.[6]

Attempted Sulfuration of 2-*p*-Methoxyphenyl-4-phenylthiophene (III).—A mixture of III (134 mg., 0.504 mmole, m.p. 141–144°) and sulfur flowers (34 mg., 1.1 mg. atoms) was heated at 200–210° for 60 hr. Hydrogen sulfide was evolved. The cooled reaction mixture was dissolved in methylene chloride and chromatographed on a 15 × 380 mm. column of alumina packed in petroleum ether (b.p.

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[11] Aldrich Chemical Co.; fractionated before use (b.p. 86–88° (0.20 mm.), $n^{25}\text{D}$ 1.5178).

60–68°). Recovered sulfur (19 mg., 56%)[12] was eluted with petroleum ether (b.p. 60–68°). Recovered III (0.09 g., 67%, m.p. 127–145°) was eluted with a 30% solution of methylene chloride in petroleum ether (b.p. 60–68°). The purest fraction of III, m.p. 142–145°, gave a mixed m.p. of 140–143° with authentic III (m.p. 144.5–145.5°). Subsequent fractions were eluted with solutions containing up to 100% methylene chloride, but the yellow oils and semi-solids obtained bore no resemblance to the by-product X.

Infrared Analysis of Mixtures of I, II and III.—The infrared spectra were recorded on the Perkin–Elmer Model 21 double beam spectrophotometer equipped with sodium chloride optics. The analysis was based on the following characteristic maxima: 2-*p*-methoxyphenyl-4-phenylthiophene (III), 731 cm.$^{-1}$; 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiadiene (I), 746 cm.$^{-1}$; 2-phenyl-4-*p*-methoxyphenylthiophene (II), 762 cm.$^{-1}$. All three maxima were strong sharp peaks and, in mixtures, were neatly resolved. The intensities of the maxima were measured relative to an absorbance minimum which appeared in all the spectra at 677 cm.$^{-1}$. Three other minima, and three lines drawn among the four minima, were also examined as prospective base lines.[13] But absorptivity, tabulated as a function of base line in a series of reference spectra, varied much less among different base lines in a single spectrum than among different spectra at the same base line, indicating that any of the seven base lines considered was suitable within the experimental error. It was convenient to use the absorption minimum at 677 cm.$^{-1}$.[14]

Reference spectra for the analysis were prepared from samples of the pure compounds (I, II, III) and from mixtures of I, II and III. Calibration curves constructed from these spectra showed that the intensities measured at the three wave lengths varied linearly with concentration.

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[12] Sulfur was determined by the ultraviolet spectroscopic method of J. K. Bartlett and D. A. Skoog, *Anal. Chem.*, **26**, 1008 (1954).

[13] For a discussion of the base line technique see R. P. Bauman in "Advanced Analytical Chemistry," by L. Meites and H. C. Thomas, McGraw–Hill Book Co., Inc., New York, N. Y., 1958, Chap. 9.

[14] Good results were also obtained with a single minimum for a base line by G. S. Hammond and K. J. Douglas, THIS JOURNAL, **81**, 1184 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

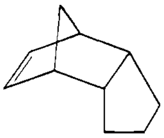
Some Reactions of 2-Aza-1,2-dihydrodicyclopentadiene[1,2]

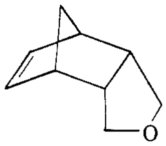
BY CHICITA F. CULBERSON AND PELHAM WILDER, JR.

RECEIVED MARCH 10, 1960

Both the *exo* and the *endo* isomers of 2-aza-1,2-dihydrodicyclopentadiene react with halogen acids to give unrearranged 9-halo derivatives and in the *endo* compound the stereochemical configuration of the halogen substituent permits facile intramolecular cyclization. The lack of rearrangement in the 2-oxa- and 2-aza-1,2-dihydrodicyclopentadiene systems is discussed briefly.

While 1,2-dihydro-*endo*-dicyclopentadiene (I), *endo*-dicyclopentadiene and similar systems are known to rearrange to their less hindered *exo* forms by addition of acids to the norbornylene double bond,[3-5] 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene (II) undergoes many of the same reactions with little or no rearrangement.[6] The synthesis of the *endo* and *exo* isomers of 2-aza-1,2-dihydrodicyclopentadiene (III and IV)[7] now leads to a study of the reactions of these amines with acids. Neither isomer undergoes rearrangement, but the stereochemistry of the addition of halogen acids to the *endo* compound allows intramolecular cyclization leading to a novel tertiary amine.[8]


I



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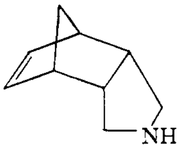
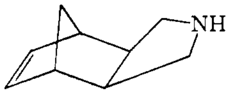
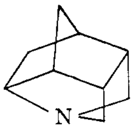


III



IV



V

The tertiary amine V was originally isolated upon addition of hydrobromic acid to 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (III). After the publication of a brief statement of these results, it was found that the tertiary amine V can be more easily obtained in pure form by the reaction of hydrochloric acid with the secondary amine III. The present paper concerns the addition of hydrobromic and hydrochloric acids to 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (III), the addition of hydrobromic acid to 2-aza-1,2-dihydro-*exo*-dicyclopentadiene (IV) and the proof of the structure of the tertiary amine V.

The *endo*-amine III, cooled in an ice-bath and treated with concentrated hydrobromic acid, yields the hydrobromide VI. After heating the amine III for five hours in excess hydrobromic acid, it is converted to a bromoamine hydrobromide VIII. This salt, difficult to isolate and purify, was removed in one run to determine the nature of the product before neutralization. Addition of base to the reaction mixture precipitates the tertiary amine V contaminated with starting material. Both these amines are subliming solids. Although a pure sample of the tertiary amine V can be obtained by repeated vacuum sublimations of the mixture, such purification is both tedious and

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[1] Presented in part before the Division of Organic Chemistry, 135th National Meeting, American Chemical Society, Boston, Mass., April 5–10, 1959.

[2] Taken in part from a dissertation submitted by Chicita F. Culberson to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree, 1959.

[3] P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946).

[4] H. A. Bruson and T. W. Riener, *ibid.*, **67**, 723, 1178 (1945); **68**, 8 (1946).

[5] P. Wilder, Jr., Chicita F. Culberson and G. T. Youngblood, *ibid.*, **81**, 655 (1959).

[6] Chicita F. Culberson, J. H. Seward and P. Wilder, Jr., *ibid.*, **82**, 2541 (1960).

[7] Chicita F. Culberson and P. Wilder, Jr., *J. Org. Chem.*, **25**, 1358 (1960).

[8] P. Wilder, Jr., and Chicita F. Culberson, THIS JOURNAL, **81**, 2027 (1959).