were collected in a receiver cooled to −78°. When the pyrolysis was complete, the tube was flushed with an additional 2 ml. of acetic acid. The trapped products were diluted with ether and worked up in the usual way to give 1.7 g. of neutral pyrolysate. Upon distillation at atmospheric pressure, 0.2 g. of a colorless liquid boiling between 100 and 130° was collected. Continued distillation at reduced pressure gave only unchanged starting material. The low-boiling product had an infrared spectrum very similar to that of 2,3-dihydroöxepine, and showed $\lambda_{\max}^{\mathrm{EtOH}}$ 260 mμ, $\epsilon \cong 6500$. This product readily yielded an adduct, m.p. 204–206°, with tetracyanoethylene. A mixture melting point with the authentic adduct derived from 2,3-dihydrooxepine (m.p. 206–209°) gave no depression (204–208°), and infrared spectra of the two samples were superimposable.

ITHACA, N. Y.

[CONTRIBUTION NO. 2492 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

The Peroxidation of Bicyclo[2.2.1]heptadiene

BY JOHN P. SCHAEFER[1,2]

RECEIVED NOVEMBER 21, 1959

The peroxidation of bicyclo[2.2.1]heptadiene has been found to give a mixture of 3-*exo*-hydroxy-5-*exo*-tricyclo[2.2.1.0^{2,6}]-heptyl formate, 3-*exo*-hydroxy-5-*endo*-tricyclo[2.2.1.0^{2,6}]heptyl formate, tricyclo[2.2.1.0^{2,6}]heptanone and 3-hydroxy-3-tricyclo[2.2.1.0^{2,6}]heptyl formate. A procedure for the preparation of tricyclo[2.2.1.0^{2,6}]heptanone from the corresponding alcohol is described.

In connection with other investigations which we are pursuing related to the chemistry of bicyclic systems, it became necessary to prepare a substantial quantity of *exo*-3-hydroxy-*exo*-5-hydroxytricyclo[2.2.1,0^{2,6}]heptane[3] (I). This compound was first reported to have been isolated in low yield by Roberts and his co-workers[5] from the solvolysis of 2,3-*trans*-dichlorobicyclo[2.2.1]-5-heptene.

Alder[6] has subsequently reported the preparation of the corresponding diacetate from the reaction of bicyclo[2.2.1]heptadiene (II) with lead tetraacetate and obtained what presumably is I (*vide infra*) on saponification. Although the yields for these reactions were high, the necessity of working with large quantities of lead tetraacetate presents a distinct disadvantage.

More recently, Wilder[7] has claimed that compound I could be obtained in small amounts from the oxidation of II with performic acid followed by saponification of the resulting formate ester. Due to the availability of these starting materials, we chose to investigate this reaction further in an attempt to develop a practical and convenient synthesis of I.

Reactions which involve the addition of various substances to II have been the subject of numerous papers in recent years.[8] The products which arise can be accounted for on the basis of: (a) simple 1,2-addition, (b) addition followed by skeletal rearrangement and (c) addition followed by homoallylic rearrangement.[9] In the bromination of II, products are formed which can be attributed mechanistically to all three of these reaction paths.

Oxidation of II with performic acid at 40–50° with ethyl acetate as a solvent gave a complex mixture of products from which we were able to isolate 3-*exo*-hydroxy-5-*exo*-tricyclo-[2.2.1.0^{2,6}]heptyl formate (III), 3-*exo*-hydroxy-5-*endo*-tricyclo[2.2.1.-0^{2,6}]heptyl formate (IV), tricyclo[2.2.1.0^{2,6}]heptanone (3-keto-nortricyclene) (V) and 3-hydroxy-3-tricyclo[2.2.1.0^{2,6}]heptyl formate (VI). The formation of 3-keto-nortricyclene as one of the reaction products is of special interest since it represents a new mode of reaction for II; *i.e.*, one in which a 1,3-hydride shift has occurred after homoallylic rearrangement has taken place. The reaction and a mechanistic rationalization of the products is depicted in formula Fig. 1.

The major portion of the reaction products consisted of the hydroxy-formate fraction (III and IV) which was isolated in a total yield of 40%. The ratio of the low boiling to the high boiling isomer was estimated by vapor phase chromatography (v.p.c.) analysis to be about 5:1, a figure which varied slightly with experimental conditions. Due to the similarity of the boiling points of the two isomers, separation by distillation was impractical and purification was deferred until a crystalline mixture of diols was obtained.

Saponification of the hydroxy-formate mixture with aqueous potassium hydroxide gave a mixture of the two diols in 86% yield. Careful fractional crystallization from acetonitrile yielded two pure diols, m.p. 157.5–158.8° (A) and m.p. 167.8–168.6° (B). Diol A was obtained in much greater quantity than B and therefore must be related to the low boiling hydroxy formate. That the two diols in question were geometrically isomeric nortricyclene diols was supported by elemental analysis and the infrared spectrum which showed characteristic absorption peaks at 3490 (hydroxyl group) and 812 cm.$^{-1}$ (nortricyclene ring system) in carbon tetrachloride. The absence of any unsaturated diols was indicated by a negative reaction of the diols with bromine and by the absence of any olefinic absorption in the infrared region of the spectrum. It

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[2] Department of Chemistry, The University of California, Berkeley 4, Calif.

[3] The system of nomenclature suggested by Cristol and LaLonde (ref. 4) for the naming of nortricyclene derivatives will be used in this paper.

[4] S. J. Cristol and R. T. LaLonde, THIS JOURNAL, **80**, 4355 (1958).

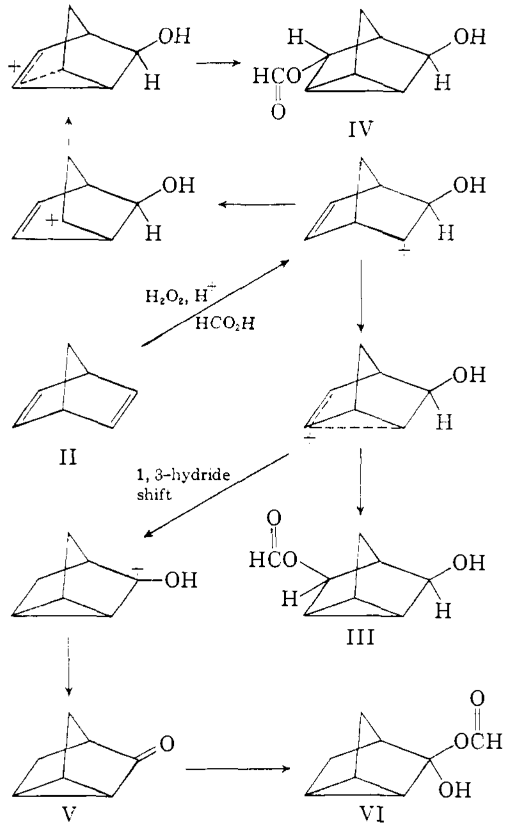
[5] J. D. Roberts, F. O. Johnson and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

[6] K. Alder, F. H. Flock and H. Wirtz, *Ber.*, **91**, 609 (1958).

[7] G. T. Youngblood, C. D. Trivette and P. Wilder, *J. Org. Chem.*, **23**, 684 (1958).

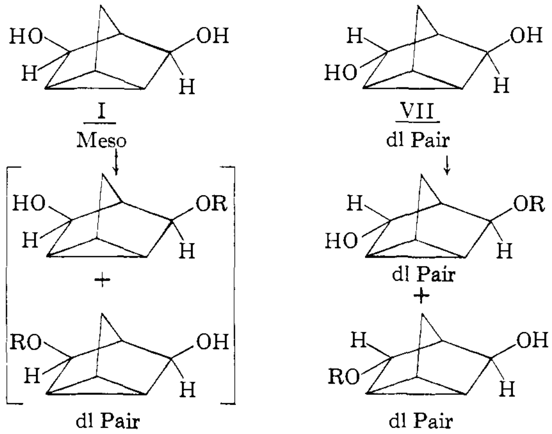
[8] Reference 6 contains a list of the pertinent papers on the chemistry of bicyclo[2.2.1]heptadiene.

[9] S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956).



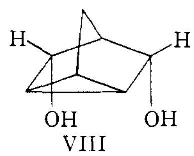
now remained to distinguish the two diols with regard to stereochemistry.

Inspection of models show that if a derivative of one of the hydroxyl functions was to be made (*e.g.*, a monoacetate), isomer I could give only one product (a *dl*-pair) whereas VII should give two products which, furthermore, *should be formed with equal probability*.

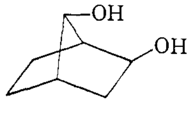


Acetylation of the pure diols with pyridine–acetic anhydride proceeded smoothly in both cases to give a mixture of the mono- and diacetate derivatives. Vapor phase chromatography of the reaction mixture, followed by infrared analysis showed that diol A gave only one monoacetate whereas diol B gave two distinct monoacetates which were formed in equal portions. On the basis of this evidence diol A must have the *meso* structure I and diol B the *dl*-structure VII which are indicated in Fig. 2.

A third nortricyclene diol (VIII) which has a *meso* structure is also theoretically possible. However, the formation of VIII is objectionable on mechanistic grounds since it would have to arise from electrophilic attack by the oxidizing agent from the *endo* side of II followed by a skeletal and a homoallylic rearrangement. This mode of addition would not be expected to be as energetically favorable as one initiated by *exo* attack, since the considerable energy of delocalization of the bicycloheptenyl cation would not be available to stabilize the transition state for the initial peroxidation step. In this respect it is interesting to note that a compound has yet to be isolated which can be ascribed unambiguously as arising from *endo* attack on I.[8]



VIII



IX

To demonstrate that the *meso*-diol had the structure I rather than VIII we attempted to treat the diol with *p*-nitrobenzaldehyde. Walborsky and Loncrini[10] have shown that *syn*-2,7-bicyclo[2.2.1]-heptane diol (IX) readily gives a *p*-nitrobenzylidene derivative with this reagent. Models of VIII and IX indicate that the stereochemistry of the hydroxyl groups are almost identical and therefore a similar facile reaction would be expected for VIII. At the conditions previously stated[10] our *meso*-diol was recovered unchanged from the reaction mixture and on these grounds we feel we are reasonably safe in eliminating VIII as a possible structure for the *meso*-diol.

In an attempt to characterize the two diols further, we prepared the dibenzoates. Unfortunately, both isomers had identical melting points of 110–111°, but it is interesting to note that a mixed melting point of approximately equivalent amounts of the dibenzoates showed a melting point elevation to 118.4–120.8°. This phenomenon was not investigated further.

It should be pointed out that there is a discrepancy between the melting point of the diol obtained by Roberts and his co-workers[5] (m.p. 161–163°) and by Wilder and his co-workers[6] (m.p. 160–161°), for which the structure I was assigned, and the diol of this structure obtained by us. Since five recrystallizations of our diol and chromatography did not change the melting point, it seems probable that the diols previously reported[5,7] were mixtures of the two isomers we have obtained in the present investigation.

3-Keto-nortricyclene was obtained as a reaction product in small yield. It was identified by its 2,4-dinitrophenylhydrazone[11] and by comparison of its retention time during vapor phase chromatography with an authentic sample of the ketone prepared by the oxidation of 3-hydroxy-nortricyclene.

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[10] H. M. Walborsky and D. F. Loncrini, THIS JOURNAL, **76**, 5396 (1954).

[11] J. D. Roberts, E. R. Trumbull W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

Transannular hydride shifts in the opening of epoxides with acid in cyclic systems where the stereochemistry is favorable have been shown to occur by Cope[12] and Prelog[13] and their co-workers. The constrained nature of the nortricyclene ring system produces an extremely favorable stereochemical relationship for a hydride shift between the homoallylic carbonium ion and the transannular hydrogen atoms which bear a 1,3-relationship to it. In view of this, we feel that the postulation of a hydride shift of this nature to account for the formation of 3-ketonortricyclene is not unreasonable.

In order to obtain a sample of 3-keto-nortricyclene for comparison purposes, the oxidation of 3-hydroxy-nortricyclene was carried out and the desired ketone was isolated in 80% yield. However, as soon as the ketone was exposed to the atmosphere it began to soften and finally melted. This "melting" process was accompanied by the formation of strong hydroxyl bands in the infrared region of the spectrum. Therefore we were led to the conclusion that the melting process was actually deliquescence and that the ketone was forming a *gem*-diol. A sample of the ketone was recovered in its pure form by passing this *gem*-diol through a silicone–stearic acid vapor phase chromatographic column heated to 150°.

Similarly, when the ketone was dissolved in pure formic acid and a sample of it chromatographed in the vapor phase, a new peak appeared which was not ascribable to either formic acid or 3-keto-nortricyclene. Since a complete separation of this new compound from 3-keto-nortricyclene could not be effected, a mixture of known composition was isolated and purified by vapor phase chromatography. Elemental analysis of the mixture enabled us to calculate the carbon–hydrogen percentages for the unknown and this agreed well with the formula $C_8H_{10}O_2$. A tetranitromethane test for unsaturation was negative. The infrared spectrum and low boiling point were most consistent with the formulation of a *gem*-hydroxyformate and the compound has been assigned structure VI. This was also isolated as one of the products of oxidation of II.

Formation of *geminal* derivatives from ketones appears to be characteristic of highly strained carbonyl compounds since Hatchard and Schneider[14] have recently reported similar carbonyl activity in the case of a substituted bicyclo[2.2.1]heptan-7-one. The driving force for this type of reaction probably results from the relief of considerable angular strain which is obtained in a rehybridization at C-7 from sp^2 to sp^3 bonding. The strained nature of the carbonyl group is further reflected in the unusually high position of its infrared absorption maxima (ν_{CHCl_3} 1753 cm.$^{-1}$).

Acknowledgment.—The author wishes to thank the National Science Foundation for a fellowship and the California Institute of Technology for making its facilities available to him. He also wishes to express his gratitude to Professor George S. Hammond for a very stimulating year.

Experimental

Oxidation of Bicyclo[2.2.1]heptadiene.—To 250 ml. of ethyl acetate was added 92 g. (1.0 mole) of bicyclo [2.2.1]-heptadiene and 230 g. (5.0 moles) of 98–100% formic acid. The solution was heated to reflux and 100 ml. of 30% hydrogen peroxide was added slowly and cautiously with stirring so that refluxing continued without external heating. After the addition was completed the solution was allowed to cool and stirred at room temperature for 12 hours, after which it was poured into 1 liter of ice-water, and cautiously neutralized with concentrated sodium hydroxide at 0–10°. The aqueous solution was then saturated with salt, extracted five times with 1:1 ether–methylene chloride and discarded. The combined organic extracts were then washed repeatedly with saturated ferrous sulfate solution to remove any peroxides, after which they were dried over anhydrous magnesium sulfate, concentrated and distilled. The fraction boiling from 50–60° at 6 mm. weighed 6.0 g. and was found to consist of 2 g. of 3-keto-nortricyclene and 4 g. of the corresponding *gem*-diformate as indicated by quantitative v.p.c. analysis (silicone–stearic acid column, 150°). These materials were identified by comparisons of their retention times during v.p.c., by their infrared spectra, and, in the case of 3-keto-nortricyclene, by its 2,4-dinitrophenylhydrazone, m.p. 188–189.5° (reported[11] 188.2–189.6°).

Continued distillation resulted in the isolation of an additional 63 g. of material, b.p. 93–98° (0.5 mm.), which consisted mainly of two isomeric hydroxyformates. Small portions of these were purified by vapor phase chromatography for identification purposes. Infrared analysis indicated that they were structurally isomeric hydroxynortricycloformates (ν_{CHCl_3} 3490, 1724, 1175, 812 cm.$^{-1}$).

About 50 g. of undistillable tar remained after distillation ceased.

Saponification of the Formate Mixture and Purification of the Diols A and B.—To 95 g. (0.77 mole) of the crude hydroxyformate mixture was added 56 g. (1.0 mole) of potassium hydroxide in 100 ml. of water. The solution turned dark brown and refluxed. An additional 100 ml. of water was added and after 2 hours the solution was filtered free of a small amount of tar which had formed and continuously extracted with methylene chloride. After 3 days there was obtained 62 g. of crude diol, m.p. 141–148°. Further extraction for one week gave an additional 3 g. The total yield of diol was 86%.

To 33 g. of the crude diol was added 200 ml. of acetonitrile. The solution was boiled with 1 g. of charcoal, filtered, and cooled slowly to give 20 g. of diol A, m.p. 156.8–158°. A second crystallization raised the melting point of this isomer to 157.5–158.8°. This remained unchanged after three more recrystallizations and chromatography (Woelm Alumina, Activity No. 3).

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.67; H, 7.94. Found: C, 66.72; H, 8.01.

Concentration of the mother liquors gave an additional 5 g. of diol A. This was removed by filtration and the filtrate concentrated to *ca.* 20 ml. and cooled to give 3 g. of diol B, m.p. 162–167°. Recrystallization from acetonitrile followed by sublimation raised the melting point to 167.8–168.6°. Infrared spectra showed hydroxyl absorption at 3490 cm.$^{-1}$ and nortricyclene absorption at 812 cm.$^{-1}$ for both diols.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.67; H, 7.94. Found: C, 66.31; H, 7.86.

The dibenzoate of diol A was prepared by treatment of the diol with benzoyl chloride and pyridine, followed by recrystallization from ethanol; m.p. 110–111°.

Anal. Calcd. for $C_{21}H_{18}O_4$: C, 75.44; H, 5.39. Found: C, 75.38; H, 5.34.

The dibenzoate of diol B, prepared in analogous fashion to the procedure used for A, melted at 110–111°. A mixed melting point of approximately equal amounts of the two dibenzoates melted at 118.4–120.8°.

Anal. Calcd. for $C_{21}H_{18}O_4$: C, 75.44; H, 5.39. Found: C, 75.37; H, 5.39.

Attempted Reaction of Diol A with *p*-Nitrobenzaldehyde.—To 1.26 g. (0.01 mole) of diol A was added 1.51 g. (0.01

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[12] A. C. Cope, A. Fournier and H. C. Simmons, This Journal, **79**, 3906 (1957), and other papers in this series.

[13] V. Prelog and V. Boarland, *Helv. Chim. Acta*, **38**, 1775 (1955), and other papers in this series.

[14] W. R. Hatchard and A. K. Schneider, This Journal, **79**, 6261 (1957).

mole) of *p*-nitrobenzaldehyde, 75 ml. of anhydrous benzene and a catalytic amount of *p*-toluenesulfonic acid. The solution was refluxed for 2 hours and then 30 ml. of benzene was distilled off. Cooling and crystallization gave 1.0 g. of the starting diol.

Preparation of the Monoacetates of Diols A and B.—To 1.26 g. (0.01 mole) of diol was added 2 ml. of anhydrous pyridine and 1.02 g. (0.01 mole) of acetic anhydride. The solution was heated on a steam bath for 5 minutes and cooled. Vapor phase chromatography (Silicone column, 180°) of the crude reaction mixture was then carried out and the fractions were collected and infrared spectra were taken.

Diol A gave two peaks on v.p.c. analysis which were shown to be due to the diacetate and monoacetate of the diol by their infrared spectra.

Diol B gave an almost identical v.p.c. pattern with the important exception that the monoacetate fraction was split into a distinct doublet. From these data it follows that A must be 3-*exo*-5-*exo*-tricyclo[2.2.1^{2,6}]heptane diol, and that B must be 3-*exo*-5-*endo*-tricyclo[2.2.1^{2,6}]heptane diol.

3-Keto-nortricyclene.—To 100 ml. of glacial acetic acid was added 55.0 g. (0.5 mole) of 3-hydroxynortricyclene and the solution was heated to 50°. To this was added 40.0 g. (0.4 mole) of chromium trioxide in 15 ml. of water at such a rate that the temperature did not exceed 55°. After the addition was completed, the solution was kept at 50° for 18 hours and then poured into 1 liter of water. The aqueous solution was then extracted five times with 100-ml. portions of ether and discarded. The ether extracts were neutralized with aqueous potassium carbonate, dried, and concentrated. Distillation gave 44 g. of the desired ketone, b.p. 50–55° (6 mm.). The material immediately solidified on cooling to a hard white solid. Upon exposure to the air the crystals soon became soggy and melted. A pure sample of the ketone was prepared by vapor phase chromatography (silicone–stearic acid column, 150°). The carbonyl maximum of a pure sample of the ketone was at 1753 cm.$^{-1}$ ($CHCl_3$).

3-Hydroxy-3-tricyclo[2.2.1.0^{2,6}]heptyl Formate (V).—To 1.0 g. of 3-keto-nortricyclene was added 2.0 ml. of 98–100% formic acid. Vapor phase chromatography (silicone–stearic acid column, 158°) indicated a new compound had been formed. This fraction was collected and exhibited infrared maxima at 3500 (broad), 1724 and 812 cm.$^{-1}$ in carbon tetrachloride. Since this material could not be obtained completely free from the starting ketone, a mixture of it and 3-keto-nortricyclene was collected and purified by several distillations on the silicone–stearic acid column. The composition of the mixture was calculated to be 64.2% 3-ketonortricyclene and 35.8% VI using a planimeter to measure the areas of the two peaks.

Anal. Calcd. for 64.2% C_7H_8O and 35.8% $C_8H_{10}O_3$: C, 72.24; H, 7.07. Found: C, 71.94; H, 7.24.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Reaction of Propargyl Alcohols with Thionyl Chloride[1]

BY THOMAS L. JACOBS, WALTER L. PETTY AND EUGENE G. TEACH

RECEIVED DECEMBER 22, 1959

The reaction of secondary propargyl alcohols, $RCHOHC\equiv CH$, with thionyl chloride in the presence of ethers yields larger proportions of the related chloroallenes, $RCH=C=CHCl$, than does the reaction in the presence of pyridine. Both the chloroallene and the propargyl chloride were usually formed. 2-Methyl-3-butyn-2-ol and 2-propyn-1-ol were also studied.

The specificity of the SNi′ mechanism which permits clean conversion of a number of allylic alcohols to rearranged allylic chlorides by formation with thionyl chloride and decomposition of chlorosulfinates in ether[2-5] suggested that chloroallenes might be formed similarly from propargyl alcohols. A preliminary report of the application of this method to 1-hexyn-3-ol has appeared.[6]

Thionyl chloride has been used by a number of workers to convert propargyl alcohols to chloride, but in most instances pyridine was present which favors production of the propargyl chloride rather than the chloroallene. Recently several *t*-propargyl alcohols, $RR'COHC\equiv CH$, were treated with thionyl chloride under a variety of conditions and unrearranged propargyl chlorides were never isolated.[7] Chloroallenes were the major products from highly hindered *t*-propargyl alcohols incapable of elimination to form enynes, but in other instances enynes were produced (especially in the presence of pyridine) and the yields of chloroallenes were reduced. Other products were also found but not identified. Two secondary propargyl alcohols were also examined.

In the conversion of allylic chlorosulfinates to rearranged allylic chlorides, the solvent diethyl ether is believed[2-5,8] to minimize competition from SN2 processes which yield unrearranged chlorides because it forms a hydrogen-bonded, non-ionic complex with hydrogen chloride.[9-11] This solvent was not convenient to use for propargyl chlorosulfinates because higher temperatures are required for their decomposition. We have therefore used higher boiling ethers as solvents and have succeeded in increasing considerably the yield of chloroallenes relative to propargyl chlorides. The results are presented in Table I. This work is incomplete, but is presented at this time in view of work in another laboratory.[7]

Diisopropyl ether was used first, but the chlorosulfinate from 1-hexyn-3-ol decomposed only slowly at the boiling point of this solvent (68°). In bis-(2-ethoxyethyl) ether (diethyl Carbitol) at 100–120° this chlorosulfinate gave about the same pro-

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[1] Most of this work was carried out under a contract with the office of Ordnance Research, U. S. Army. Reproduction in whole or in part is permitted for any purpose of the United States Government. Much of the material is taken from the Ph.D. thesis of Walter L. Petty, May, 1958.

[2] W. G. Young, F. F. Caserio, Jr., and D. Brandon, Jr., *Science*, **117**, 473 (1953).

[3] F. F. Caserio, Jr., G. E. Dennis, R. H. De Wolfe and W. G. Young, THIS JOURNAL, **77**, 4182 (1955).

[4] R. H. De Wolfe and W. G. Young, *Chem. Revs.*, **56**, 813 (1956).

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[6] T. L. Jacobs, E. G. Teach and D. Weiss, THIS JOURNAL, **77**, 6254 (1955).

[7] Y. R. Bhatia, P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 24 (1959).

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[9] A. M. Buswell, W. H. Rodebush and M. F. Roy, *ibid.*, **60**, 2528 (1938).

[10] D. R. Chesterman, *J. Chem. Soc.*, 906 (1935).

[11] T. Mounajed, *Compt. rend.*, **197**, 44 (1933).