Poly-*exo*-methylene Small-Ring Hydrocarbons. IV.[1] Trimethylenecyclopropane[2a–c]

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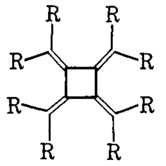
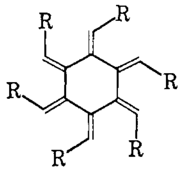
Abstract: Trimethylenecyclopropane (**3a**), a theoretically interesting cross-conjugated hydrocarbon isomeric with benzene and the simplest member of the class of radialenes, has been synthesized by two independent routes. This radialene is stable in the condensed phase in dilute solutions to both acid and base and has been characterized by spectral as well as chemical means. By classical standards **3a** cannot be considered aromatic although it is sufficiently stable to be collected by glpc and is indefinitely stable in dilute solution at −78° in the absence of oxygen and for prolonged periods in the gas phase under reduced pressure in an inert atmosphere. The marked sensitivity of trimethylenecyclopropane to oxygen and its tendency to polymerize may be rationalized in theoretical terms.

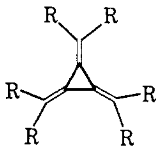
Radialenes,[3a] a class of cyclic hydrocarbons ($C_{2n}H_{2n}$) possessing *n* ring atoms and *n* exocyclic double bonds (symmetry D_{nh}), have been the object of extensive synthetic and theoretical interest in recent years.[3] Only one *parent* member of this class of cross-conjugated hydrocarbons has been prepared previously, namely, tetramethylenecyclobutane (**1a**) which was first reported by Griffin and Peterson[1,4] in 1962. However, two derivatives of hexamethylenecyclohexane, namely, hexaethylidenecyclohexane (**2a**)[5a] and the propylidene analog (**2b**),[5b] and a surprisingly stable derivative of trimethylene cyclopropane, hexamethyltrimethylenecyclopropane (**3b**),[6] also have been synthesized recently. In addition, the photodimer of tetraphenylbutatriene, first reported in 1921,[7a] has been characterized as octaphenyltetramethylenecyclobutane (**1b**).[7b] The related thermal dimer of tetra-*t*-butylhexapentaene (**4**) also may be considered a substituted radialene and as such included in this context[7c] as may the stable triquinocyclopropanes.[7d]



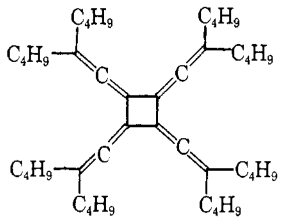
1a, R = H
b, R = C_6H_5



2a, R = CH_2
b, R = C_2H_5



3a, R = H
b, R = CH_3



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At least two previous attempts to prepare the simplest member of the radialene series **3a**, trimethylenecyclopropane, an isomer of benzene, have been recorded and have led, at best, to insufficient quantities of the hydrocarbon to permit complete characterization.[8,9]

Application of simple Hückel molecular orbital theory to trimethylenecyclopropane leads to the prediction that **3a** will possess a singlet ground state and a delocalization energy (DE) of 1.30β.[10a] A free-valence index of 0.90 was calculated for **3a**[10b] and suggests that polymerization in the condensed phase and sensitivity to air oxidation should be anticipated.

Destabilizing factors must be assessed in order to translate DE into the hypothetical resonance energy. Qualitatively it would be expected that the appreciable strain of the cyclopropane ring would be increased by the introduction of three sp^2-hybridized carbon atoms. However, it would be difficult to estimate with any degree of certainty the total σ and π strain which would accumulate on introducing three trigonal centers into an

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(1) For the initial paper in this series, see G. W. Griffin and L. I. Peterson, *J. Am. Chem. Soc.*, **84**, 3398 (1962).

(2) (a) This investigation was supported by the National Science Foundation (Grants G-13759, GP-2543, and GP-6420) to whom the authors wish to express their gratitude. (b) For a preliminary communication on this subject, see P. A. Waitkus, L. I. Peterson, and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 181 (1966). (c) Prior to publication of our initial work in this area, another route to the synthesis of trimethylenecyclopropane employing Feist's acid as a precursor was reported; see E. A. Dorko, *ibid.*, **87**, 5518 (1965). In retrospect we now know that A. T. Blomquist and D. T. Longone (*ibid.*, **81**, 2012 (1959), and subsequent papers) also had been able to generate trace quantities of trimethylenecyclopropane *via* a similar synthetic scheme employing Feist's acid as a precursor. (d) Abstracted in part from the thesis of P. A. Waitkus submitted in partial fulfillment of the Doctor of Philosophy degree at Tulane University, New Orleans, La. (e) Proctor and Gamble Predoctoral Fellow, 1962–1963, Yale University, New Haven, Conn. (f) To whom requests for reprints and other inquiries regarding this paper should be directed.

(3) (a) This name was first proposed by Professor J. R. Platt; see footnote 3 in von R. Weltin, F. Gerson, J. N. Murrell, and E. Heilbronner, *Helv. Chim. Acta*, **44**, 1400 (1961); (b) M. J. S. Dewar and G. S. Gleicher, *J. Am. Chem. Soc.*, **87**, 692 (1965).

(4) G. W. Griffin and L. I. Peterson, *ibid.*, **85**, 2268 (1963).

(5) (a) H. Hopff and A. K. Wick, *Helv. Chim. Acta*, **44**, 380 (1961); (b) H. Hopff and A. Gati, *ibid.*, **48**, 1289 (1965).

(6) (a) G. Köbrich and E. Heinemann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 594 (1965); *Angew. Chem.*, **77**, 590 (1965); (b) von F. Gerson, E. Heilbronner, and G. Köbrich, *Helv. Chim. Acta*, **48**, 1525 (1965); (c) G. Köbrich, H. Heinemann, and W. Zündorf, *Tetrahedron*, **23**, 565 (1967); (d) E. Heilbronner, *Theoret. Chim. Acta*, **4**, 64 (1966).

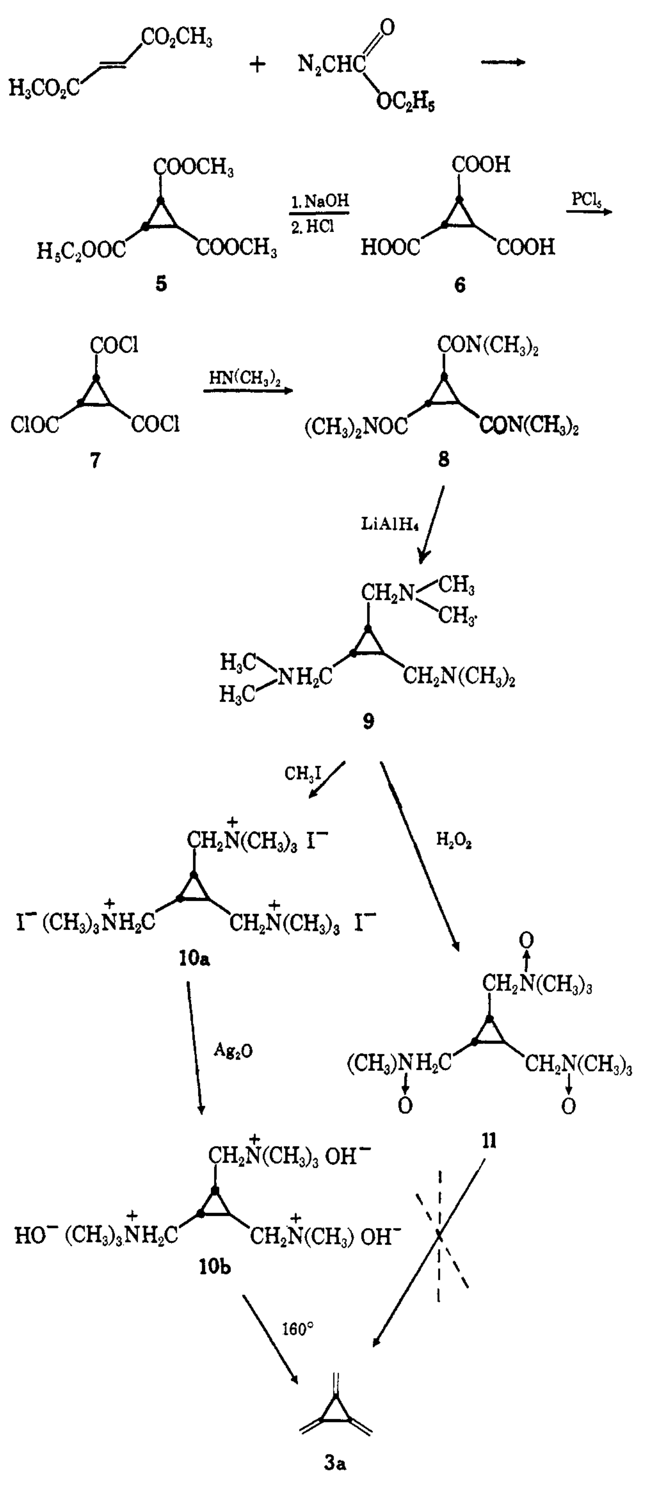
(7) (a) K. Brand, *Ber.*, **54**, 1947 (1921); (b) R. O. Uhler, H. Shechter, and G. V. D. Tiers, *J. Am. Chem. Soc.*, **84**, 3397 (1962); (c) H. O. Hartzler, *ibid.*, **88**, 3155 (1966); (d) R. West and D. C. Zecher, *ibid.*, **89**, 152 (1967).

(8) D. J. Connolly, Ph.D. Thesis, Cornell University, 1962; *Dissertation Abstr.*, **23**, 66 (1962); see also Blomquist and Longone, ref 2c.

(9) L. I. Peterson, Ph.D. Thesis, Yale University, 1963.

(10) (a) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952). (b) For comparison, the predicted index for *p*-xylylene is 0.92 and while this molecule is stable in the gas phase it undergoes rapid polymerization in solution.

Scheme I



already strained cyclopropane ring. While thermochemical data are available for related systems, they are in some cases inconsistent.[4] As a consequence, the destabilization of 3 due to strain could exceed the calculated delocalization energy. It therefore remained to be established experimentally whether the delocalization energy would be sufficient to compensate for the presumed strain.

The present study was initiated in order to determine whether trimethylenecyclopropane could be prepared and characterized as a discrete chemical species, capable of even precarious independent existence, despite unfavorable predictions with regard to free valency and potential adverse effects of strain. In addition, trimethylenecyclopropane represents an attractive substrate for spectral studies in view of its molecular simplicity and high symmetry.[6a,d]

Aside from theoretical implications, especial interest is attached to the possibility that **3a** could possess potential synthetic utility and provide a convenient precursor for heretofore unknown methylenecyclopropenes and/or dimethylenecyclopropanes depending on its predisposition to assume the role of diene or dienophile in Diels–Alder reactions.

The background developed in our laboratories during the course of the synthesis, isolation, and characterization of tetramethylenecyclobutane (**1a**) was of invaluable aid in achieving the successful preparation of **3a**. In view of earlier experience with **1a**, two routes to **3a** seemed especially promising, namely, the pyrolysis of the trisquaternary ammonium hydroxide **10b** of *trans*-1,2,3-tris(N,N-dimethylaminomethyl)cyclopropane and the dehydrohalogenation of *trans*-1,2,3-triiodomethylcyclopropane (**15**). In both instances a mixture of the isomeric 1-carbethoxy-2,3-dicarbomethoxycyclopropanes (**5**), prepared by the method of Buchner,[11] emerged as the most attractive starting material from a synthetic standpoint since it may be obtained in excellent yield easily, and the carboalkoxy groups are conveniently converted to the desired substituents.

The preparation of **10b** from **5** is outlined in Scheme I. Hydrolysis of **5** in aqueous basic methanol gives *trans*-1,2,3-cyclopropanetricarboxylic acid (**6**) in 90% yield. Attempts to prepare **6** under nonaqueous basic conditions invariably afforded lower yields. Treatment of the tribasic acid **6** with phosphorus pentachloride provides the corresponding tribasic acid chloride **7** in 81% yield.[12] In our initial attempts to prepare *trans*-1,2,3-tris(N,N-dimethyl)cyclopropanetricarboxamide (**8**) by treatment of the acid chloride **7** with dimethylamine a large quantity of polymeric material was obtained. Polymerization can be avoided, however, by carefully controlling the addition of the acid chloride to a stirred ether solution of dimethylamine at −70°, and the desired amide can be obtained in 55% yield. The conversion of **5** to **8** was also achieved, albeit in lower yield (20%), directly by treating **5** with dimethylamine at elevated temperatures and pressures in the presence of traces of water and the amine hydrochloride.[13]

The reduction of **8** with lithium aluminum hydride proceeded satisfactorily to give a 68% yield of *trans*-1,2,3-tris(N,N-dimethylaminomethyl)cyclopropane (**9**). Exhaustive methylation of the triamine **9** gave the trisquaternary ammonium iodide **10a** in 86% yield which was then converted to the Hofmann base **10b** with silver oxide in the conventional manner. The salt **10a** ob-

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[11] E. Buchner, *Ber.*, 21, 2637 (1888). The product obtained by decomposition of the pyrazoline formed by addition of ethyl diazoacetate to dimethyl fumarate is not homogeneous and consists of a mixture of at least two of the stereoisomers of **5**.

[12] The acid chloride **7** also was recently reported by G. Maier, *ibid.*, **95**, 611 (1962). Higher yields in the conversion of **6** to **7** than those reported (30%) are obtained if the reaction time is merely extended.

[13] An alternate route to the triamide **8** has recently been reported and consists of treating 2-chloro-N,N-dimethylacetamide with potassium *t*-butoxide. In our hands this method proved less convenient than that outlined in Scheme I; see A. J. Speziale, L. R. Smith, and J. E. Fedder, *J. Org. Chem.*, **30**, 1199 (1965).

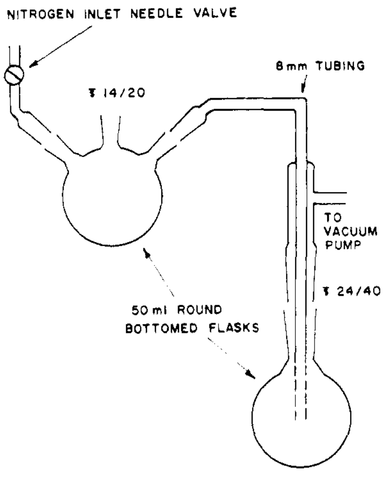
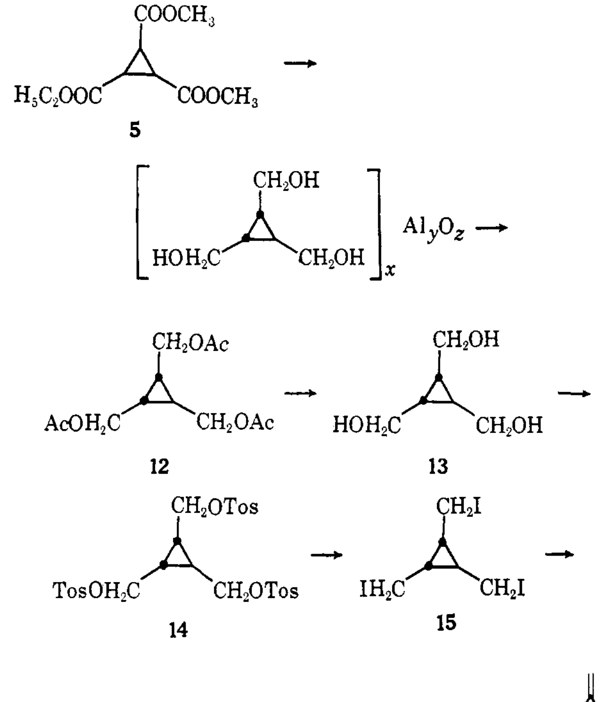


Figure 1. Apparatus for the pyrolysis of the Hofmann base **10b**.

tained by treating the triamine **9** with methyl iodide was also obtained by quaternization of *trans*-1,2,3-triiodomethylcyclopropane (**15**) (*vide infra*) with trimethylamine in ethanol.

The preparation of *trans*-1,2,3-triiodomethylcyclopropane (**15**) is delineated in Scheme II. The mixed *cis–trans* isomeric 1-carbethoxy-2,3-dicarbomethoxycyclopropanes (**5**) may be reduced with lithium aluminum hydride; however, some difficulties were encountered in the isolation of the desired *trans*-1,2,3-tris(hydroxymethyl)cyclopropane (**13**) owing to formation of a complex of the polyol with aluminum salts from which the organic product could not be separated conveniently. However, treatment of the complex with acetic anhydride in methylene chloride gave *trans*-1,2,3-tris(acetoxymethyl)cyclopropane (**12**) in 50% yield.

Scheme II



The triacetate **12** was then converted to the triol **13** by transesterification with ethanol and sodium ethoxide. Several attempts to convert **13** directly to **15** with phosphorus triiodide proved unrewarding. Consequently the crude polyol was converted into the tritosylate **14** (40%) by treating a solution of the triol in acetone with *p*-toluenesulfonyl chloride and aqueous sodium hydroxide. This method of preparing **14** proved far superior to others tried employing nonaqueous solvents and tertiary amines as bases. The conversion of the tosylate **14** to *trans*-1,2,3-triiodomethylcyclopropane (**15**) was accomplished rapidly and efficiently (80%) by treatment with sodium iodide in acetone under conventional Finkelstein conditions. The triiodide **15** is relatively stable at 0° provided an opaque container is used for storage.

The procedure utilized for the pyrolysis of **10b** was essentially the same as that employed by Schlatter for the preparation of cyclopropene[14] and by Griffin and Peterson[4] for the synthesis of tetramethylenecyclobutane (**1a**). An aqueous solution (30%) of **10b**, concentrated by lyophilization, was introduced into the pyrolysis apparatus (see Figure 1) maintained at 160–170° under reduced pressure (4.5 mm under nitrogen). The effluent pyrolysate was trapped at −78° and a solvent such as carbon disulfide, Chromatoquality isopentane (Matheson Coleman and Bell), or carbon tetrachloride was added as required. After an initial short-path distillation under conditions designed to prevent codistillation of polymers with solvent and **3a**, the dilute solution of the pyrolysis product in carbon disulfide, for example, was washed in turn with (1) 1.5 *N* hydrochloric acid (three times) to remove the volatile amines which were formed on pyrolysis, (2) water (three times), and (3) dilute aqueous sodium bicarbonate (three times). The washing operation as well as the drying procedure over anhydrous sodium sulfate was conducted at 0°. That **3a** is indeed produced on pyrolysis of **10b** is confirmed by the results of infrared, nmr, ultraviolet, and mass spectral analyses as well as hydrogenation (*vide infra*). The yield of trimethylenecyclopropane, identified from spectral data, was calculated to be approximately 1.5%.[15] Moreover, the trimethylenecyclopropane was contaminated by a second product which was not identified.[16]

We have found that the amine oxide **11** is extremely stable and appears to remain substantially unchanged on heating to 200°. At 250°, however, decomposition does occur to liberate what appear to be volatile amines. Large quantities of polymeric material were obtained. Traces of hydrocarbons also were produced, but none possessed ultraviolet spectra characteristic of a highly conjugated structure such as **3a**.

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(14) M. J. Schlatter, *J. Am. Chem. Soc.*, **63**, 1733 (1941).

(15) In this and subsequent calculations of a similar nature requiring a knowledge of the concentration of **3a** we have assumed that the ultraviolet extinction coefficient of **3a** approximates that of **3b**. The ultraviolet data for the latter, a stable crystalline compound, has been determined accurately (λ_{max}^{hexane} 309.5 mμ (log ε 4.26)).[6a] This assumption appears valid since quantitative hydrogenation data indicate a value of log ε 4.18 for **3a**. The validity of the latter determination, of course, rests on the assumption that hydrogenation is complete and that the extent of hydrogenolysis was determined accurately (*vide infra*). It should be noted that Dorko[2c] reports a value of log ε 3.57 for **3a** which differs significantly from that of ours and of **3b** reported by Köbrich.

(16) This product which possesses a shorter retention time than **3a** exhibits an ultraviolet absorption maximum at 241 mμ; however, an insufficient amount was isolated to permit complete characterization.

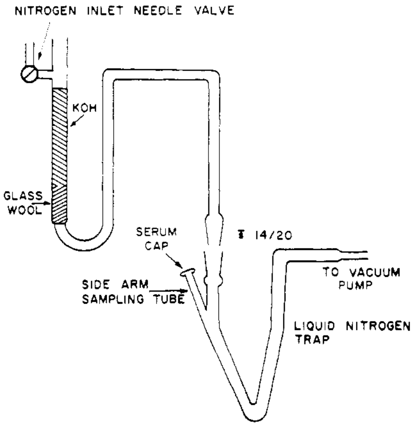
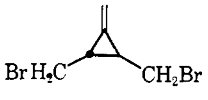


Figure 2. Apparatus for dehydrohalogenation of *trans*-1,2,3-triiodomethylcyclopropane (**15**).

The results obtained from the base-catalyzed dehydrohalogenation of **15** eventually proved to be far superior to those obtained from the pyrolysis of **10b**. In our initial dehydrohalogenation studies reported earlier,[2b] **15** was subjected to treatment with sodium ethoxide in ethanol under nitrogen. Within a few hours the characteristic ultraviolet spectrum of **3a** appears and the hydrocarbon may be collected by codistillation with ethanol. A significant improvement in yield was achieved by using a modification of the dehydrohalogenation method employed by Dorko[2c] on 2,3-dibromomethylmethylenecyclopropane (**16**). An ether solution of **15** was introduced into a tube (see Figure 2) packed with solid potassium hydroxide at 140° under reduced pressure, and the pyrolysate was trapped, as before, at −78°. The yield of **3a** in this case was estimated to be about 20%.[15] Furthermore, the product prepared according to this procedure is obtained free of other hydrocarbons which conceivably might arise from thermal reorganization. This is in sharp contrast to the results obtained with **10b** in which, as noted, an artifact is produced. The spectral data for trimethylenecyclopropane obtained in this manner are identical with those obtained for **3a** generated by pyrolysis of the quaternary ammonium hydroxide **10b**.



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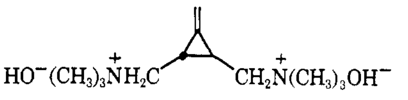

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The following evidence may be cited in favor of the structural assignment for the triene **3a**.[17]

(1) The mass spectrum of **3a** exhibits the expected peak at *m/e* 78 for the molecular ion. Fortunately, **3a** is sufficiently stable in the gas phase, provided precautions are taken to exclude contact with oxygen, that the homogeneous samples of **3a** required for spectra could be collected from a gas chromatograph operated at 50–60° and equipped with a short glass column (5 ft × 0.25 in) packed with Carbowax 20M on base-washed Chromosorb P. The collection vessel was purged with helium and evacuated prior to collection. By means of a needle valve, flow into the vessel was adjusted to equal precisely the flow from the chromatograph at the time of peak emergence. A by-pass bubble flow meter was employed as a sensitive detector to any flow imbalance.[18]

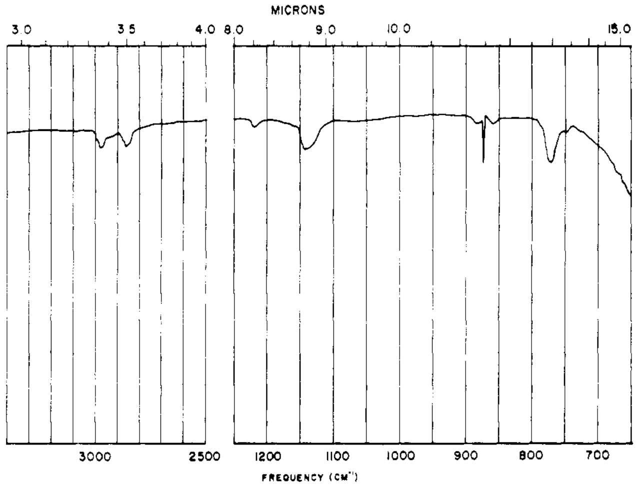

Figure 3. Gas-phase infrared spectrum of trimethylenecyclopropane determined in helium in a 10-cm cell. While exceedingly dilute, the sample is gas chromatographically pure.

(2) The infrared spectrum (Figure 3) of **3a** taken in the gas phase in helium shows a sharp intense peak at 872 cm^{-1} which is near the characteristic region for the hydrogen out-of-plane vibration in terminal disubstituted olefins.[19] Also present in the infrared spectrum of **3a** are six strong bands at 2991, 2924, 2874, 1139, 1130, and 770 cm^{-1} and three weak absorptions at 1217, 885, and 860 cm^{-1}. It is noteworthy that the infrared spectrum of tetramethylenecyclobutane (**1a**) also shows strong absorption at 880 cm^{-1}.

A qualitative normal coordinate analysis of trimethylenecyclopropane was carried out and compared with the observed gas-phase infrared spectrum of **3a**. The results of this analysis indicate that the observed infrared spectrum of trimethylenecyclopropane is in good agreement with that anticipated on the basis of D_{3h} symmetry. Experimental confirmation of the symmetric-top nature of the molecule was obtained by the observation of the hydrogen out-of-plane vibration as a parallel band in the infrared spectrum.[2d]

(3) The nmr spectrum of **3a** in carbon disulfide consists of a sharp singlet signal at τ 4.86 (in deuteriochloroform, τ 4.76) which is consistent with the value of τ 4.81 observed for the higher homolog **1a** in carbon tetrachloride. The nmr signal for **1** gradually decreases and disappears after 45 min when precautions such as cooling the sample and excluding oxygen are not exercised.

(4) The gas-phase ultraviolet spectrum of **3a** (Figure 4), which perhaps reflects the most strikingly interesting property of **3a**, consists of an intense band at 288 $m\mu$

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(17) It is clear that Blomquist and his group at Cornell University deserve credit for having observed trimethylenecyclopropane for the first time.[2c] Connolly, under the direction of Professor Blomquist, found that 1-methylene-*trans*-2,3-bis(trimethylammoniummethyl)cyclopropane dihydroxide (**17**) and the related amine oxide upon pyrolysis gave a product, possessing an ultraviolet spectrum with two maxima at 295 and 305 $m\mu$, which is remarkably similar to ours. It was also established that this product, a C_6 hydrocarbon, exhibited infrared absorption characteristic of unsubstituted *exo*-methylene groups.

(18) A commercial total collection system (Model TCS-3) of the type described is available from the F & M Scientific Division of Hewlett-Packard, Avondale, Pa. 19311.

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 51.

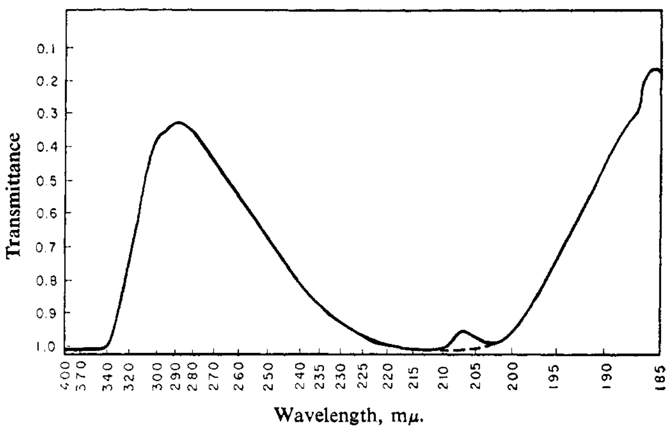


Figure 4. Gas-phase ultraviolet spectrum of trimethylenecyclopropane (**3a**) in helium.

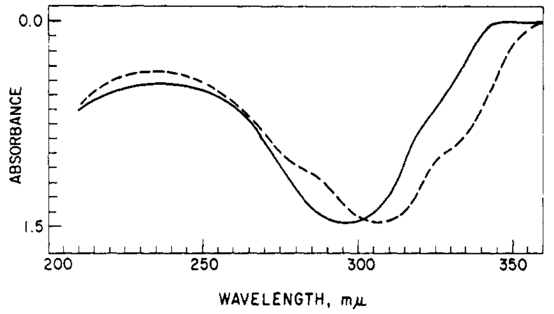


Figure 5. Comparison of the ultraviolet spectra of trisisopropylidenecyclopropane (- - - -) (**3b**) and trimethylenecyclopropane (———) (**3a**) in cyclohexane and isopentane, respectively.

with shoulders visible at 278, 298, and 317 mμ. In solution the ultraviolet spectrum of **3a** exhibits bands at $\lambda_{\max}^{\text{isopentane}}$ 295 and 305 mμ with a shoulder at 322 mμ. Precise extinction coefficients cannot be reported at this time in view of the problems associated with establishing accurately the concentration of **3a** in dilute solution. The long-wavelength absorption band reported for **3b** is at $\lambda_{\max}^{\text{hexane}}$ 309.5 mμ (log ϵ 4.26),[15] and for that matter the entire spectrum is reassuringly similar to that of **3a**. It is not unexpected that the introduction of six methyl groups would result in a bathochromic shift of about 30 mμ.[20,21] A comparison of the spectral characteristics of **3a** and **b** is presented in Figure 5 and in our mind represents convincing evidence for the assignment of structure. Furthermore, Dorko and Blomquist[2c,17] independently report identical spectral characteristics for materials obtained in quantities insufficient for further characterization, derived from **16** and **17**, by entirely different routes.

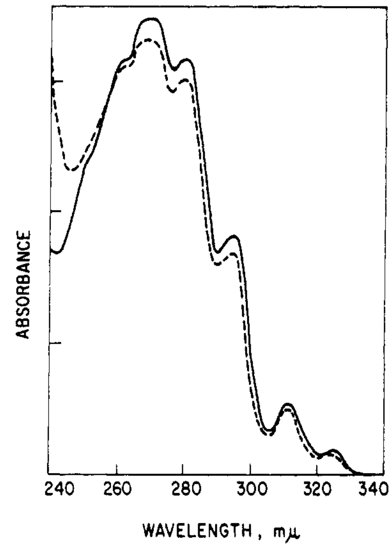
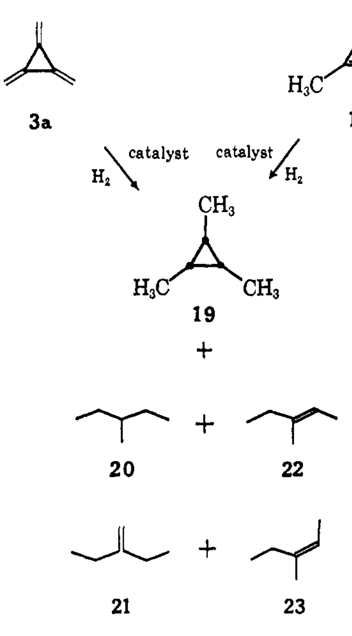


Figure 6. Ultraviolet spectra of tetramethylenecyclobutane (**1a**) generated from the amine oxide (———, hexane) and the tetraiodide (- - - -, ethanol). The scale on the ordinate has been omitted since exact concentrations are unknown.

It has been predicted that the long-wavelength maximum in the ultraviolet spectrum of **3b** is due to a transition which is allowed in **3b** but forbidden in radialenes of higher order such as **1a**.[6a,d] This prediction is in qualitative agreement with the experimental observation that an intense long-wavelength band is absent in the ultraviolet spectrum of the next higher homolog of **3a**, namely, tetramethylenecyclobutane (**1a**) (Figure 6).[4]

Despite the accumulation of convincing spectral data we still desired chemical confirmation that we had indeed succeeded in synthesizing trimethylenecyclopropane (**3a**). It was felt that successful catalytic reduction of **3a** to *cis*-1,2,3-trimethylcyclopropane (**19**) would provide sufficient corroborative chemical evidence. Hydrogenation of **1a**, a homolog of **3a**, exclusively to *cis,cis,cis*-tetramethylcyclobutane had been achieved earlier, using platinum on charcoal as a catalyst.[4] Unfortunately, catalytic hydrogenation of



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(20) H. E. Simmons (personal communication) has calculated the ultraviolet spectrum for trimethylenecyclopropane assuming D_{3h} symmetry. These calculations suggest an intense band should appear in the vicinity of 260 mμ accompanied by only weak absorption bands outside the vacuum ultraviolet region where the next strongest absorption should occur at about 175 mμ. It is clear that the absorption band at 213 mμ interpreted by Dorko[2c] as a maximum is undoubtedly a false peak resulting from instrumental limitations or impurities. "False energy" maxima arising from scattered light are known to appear in the region 200–215 mμ when spectra of simple monoolefins are determined on standard photoelectric spectrophotometers; see O. H. Wheeler and J. L. Mateos, *J. Org. Chem.*, **21**, 1110 (1956).

(21) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Richard Clay and Co., Ltd., Bungay, Suffolk, 1954, p 83.

the hydrocarbon **3a** to **19** proved to be somewhat more challenging and we were forewarned of impending difficulties by our experience in the preparation of an authentic sample of *cis*-1,2,3-trimethylcyclopropane (**19**) for comparison.[22]

The synthesis of **19** was eventually achieved by catalytic hydrogenation of 1,2,3-trimethylcyclopropene (**18**) prepared according to the method of Closs and coworkers.[23] Catalytic hydrogenation of **18** proceeded to completion with either palladium on charcoal (10%) or rhodium on alumina[24] and gave as the major product a hydrocarbon showing a parent peak in the mass spectrum at *m/e* 84. The nmr spectrum determined in carbon tetrachloride of a sample of this hydrocarbon collected by glpc[25a] and shown to be homogeneous[25b] exhibited a signal at τ 9.15 which is consistent with the structural assignment for **19**. While this peak is broad and appears to exhibit structure (Figure 7), the limited sample size and lack of resolution prevented further refinement of the data. Inconclusive results were obtained with **18** when Raney nickel was employed as a hydrogenation catalyst.

In addition to **19** at least four hydrogenolysis products were obtained upon reduction of trimethylcyclopropene (**18**).[26] These products included 3-methylpentane (**20**), 2-ethyl-1-butene (**21**), and *cis*- and *trans*-3-methyl-2-pentene (**22** and **23**, respectively). These hydrocarbons were prepared independently, and, with the exception of **20**, homogeneous samples were collected by glpc.[25a] The structures of **21–23** were confirmed by comparison of infrared spectra with API data.[27] The reduction products of **18** obtained in limited quantities were then compared with trimethylcyclopropene reduction products on two different capillary columns and shown to be identical using peak enhancement techniques.

The relative quantities of **19–23** obtained from **18** varied with the catalyst employed and are tabulated in Table I, which also includes data obtained upon catalytic reduction of trimethylenecyclopropane (**3a**).

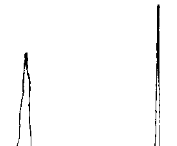

Figure 7. Nmr spectrum (CCl_4) of *cis*-1,2,3-trimethylcyclopropane (**19**) using TMS as a standard.

Table I. Reduction Products of 1,2,3-Trimethylcyclopropene (**18**) and Trimethylenecyclopropane (**3a**)[a]

Substrate	Catalyst	Approx rel amounts of products 19	20	21	22	23
18	Pd–C	26	4.5	1	23.5	10
	Rh–Al_2O_3	52	14	1	3	1
3a	Pd–$CaCO_3$				1	
	Pd–C		3		1	
	Rh–Al_2O_3	2	6	1	7	3

[a] The absence of data indicates insufficient quantities were produced to be detected by glpc.

Catalytic reduction of **3a** over rhodium on alumina gives **19** in addition to the same hydrogenolysis products obtained from **18**, namely, **20–23**, albeit in different relative amounts (see Table I).[28] The hydrogenation of **3a** is conveniently followed by the disappearance of its characteristic ultraviolet absorption spectrum. The differences in reduction product ratios observed in the case of **3a** and **18** suggest that hydrogenation of **3a** to **19** cannot proceed, at least entirely, through **18**. Thus two consecutive 1,4 additions are excluded and a 1,2-hydrogenation step is implicated.

In view of the minute quantities of **3a** conveniently generated in single experiments (~10 mg), it was necessary to make direct comparisons of 1,2,3-trimethylcyclopropane obtained from the two sources (**3a** and **18**) by gas chromatography using capillary columns. The presence of **19** among the reduction products of **3a** was confirmed by enriching the reduction mixture obtained from **3a** with samples of pure **19** obtained from **18**. Comparisons were made on two different capillary columns to reduce the possibility that an erroneous assignment might be made because of fortuitous coincidence of retention times.[25b,c]

The similarity of reduction products obtained from **3a** and **18** and in particular the identification of the *cis*-1,2,3-trimethylcyclopropane among these products in conjunction with the infrared, ultraviolet, nmr, and

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(22) Treatment of a dibromide thought to be 3-methyl-2,4-dibromopentane with zinc is reported to give *cis*- and *trans*-1,2,3-trimethylcyclopropane; see J. D. Bartleson, R. E. Burk, and H. P. Lankelma, *J. Am. Chem. Soc.*, **68**, 2513 (1946); R. G. Kelso, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **77**, 1751 (1955). In our hands the dibromide prepared in the prescribed fashion afforded only *cis*- and *trans*-3-methyl-2-pentene. Glpc analyses on several different columns failed to reveal the presence of additional hydrocarbons in the product mixture. The nmr spectrum of the dibromide precursor exhibited the two-proton quartet (τ 8.08) and three-proton triplet (τ 8.90) typical of a carbon-bound ethyl group which is inconsistent with the assigned structure. The inconsistency was resolved by demonstrating that the presumed 1,3-dibromide must in fact be a 1,2-dibromide and identical with a sample of 2,3-dibromo-3-methylpentane obtained independently by addition of bromine to 3-methyl-2-pentene.

(23) G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963).

(24) A. I. Meyers, W. Beverung, and G. Garcia-Munoz, *J. Org. Chem.*, **29**, 3427 (1964). We wish to thank Professor Meyers for his suggestion that this catalyst should minimize hydrogenolysis of the cyclopropane ring which indeed proved to be correct; see also J. H. Stocker, *ibid.*, **27**, 2289 (1962).

(25) (a) SE-30 (20%) glass column (20 ft × 0.4 in.) at 55°; (b) AP-L support coated ("fuzzy walled") capillary column (50 ft × 0.02 in.) at 50°; (c) same as b with didecyl phthalate.

(26) Precedent for hydrogenolysis of cyclopropenes such as **18** to acyclic alkanes may be found in the literature; see F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964). However, to our knowledge the isolation of olefinic cleavage products such as **21–23** is without precedent in such reductions and suggests that initial cleavage of the σ cyclopropene bond of **18** may compete with reduction of the olefinic bond.

(27) American Petroleum Institute (Research Project 44) Spectra No. 709 (**21**), 720 (**22**), and 721 (**23**). The index of refraction of **20** prepared independently and its infrared spectrum were also consistent with available literature data.

(28) No reduction products were isolated when Raney nickel was employed as a catalyst in attempts to reduce **3a**. With palladium on calcium carbonate as a catalyst only **22** could be detected while both **20** and **22** are produced when palladium on charcoal was employed.

mass spectral data confirms that trimethylenecyclopropane has been generated from **10b** and **15**.

Perhaps the most characteristic chemical property of **3a** like that of **1a** is its marked sensitivity to oxygen. On brief exposure to air, **3a** forms intractable products. This behavior is qualitatively in agreement with the theoretical predictions (*vide supra*) of high free valency anticipated at the termini of the exocyclic double bonds. All reactions and physical measurements on **3a** were conducted under an inert atmosphere blanket in order to avoid oxidation and polymer formation. Trimethylenecyclopropane (**3a**) was found to be remarkably stable to dilute mineral acids and strong bases and to the gas-chromatographic conditions employed in the isolation of gas-phase samples.

Unfortunately no definitive conclusions can be drawn regarding π-electron delocalization in **3a** from nmr data. A comparison of the proton chemical shifts of the methylene protons of **3a** and dimethylenecyclopropane might provide information on possible ring currents in the cyclic cross-conjugated system **3a**. Unfortunately, only substituted dimethylenecyclopropanes lacking the requisite methylenic hydrogens are known,[29] and in the absence of data for the parent system the importance of diamagnetic anisotropy in **3a** cannot be assessed with any degree of certainty.

Pyrolysis of esters has been employed to prepare very sensitive and unstable polyenes including 5-methylene-1,3-cyclohexadiene (isotoluene).[30] In view of the availability of the triacetate **12** a pyrolysis study was initiated despite our prior unsuccessful experience with 1,2,3,4-tetraacetoxymethylcyclobutanes as precursors for **1a**.[31] Acetic acid was produced upon introducing **12** into a column 15 cm long packed with glass helices and heated to 570°. A stream of nitrogen carrier gas (10 ml/min) was employed to sweep the volatile products from the reaction zone into a trap maintained at −78°. The major product (20%) was benzene, and studies are in progress to establish if trimethylenecyclopropane (**3a**) is an intermediate in this reaction.

Trimethylenecyclopropane was found to react rapidly with bis(benzonitrile)-μ-dichloro-palladium (II) in xylene or benzene to yield a red-brown complex with an empirical formula $C_6H_6Cl_2Pd$.[32] The structure of this extremely insoluble 1:1 complex is still under study as are reactions with other metallic complexing agents. The tendency of **3a** to form palladium complexes may explain why atypical results are obtained if catalysts of this heavy metal are employed in reductions (see Table I). If it is assumed that qualitative precipitation of **3a** occurs, then the weight of the complex obtained further corroborates the extinction coefficient reported above for **3a**.[15]

Other studies on the physical and chemical properties of **3a** including its reactions with dienes and dienophiles will be the subject of a future communication.

Experimental Section[33]

1-Carbethoxy-2,3-dicarbomethoxycyclopropane (5).[11] To a fused mass of 61.0 g (0.42 mole) of dimethyl fumarate was added 61.0 g (0.54 mole) of ethyl diazoacetate over a period of 40 min. The resulting mixture subsequently was heated on a water bath for 1 hr to ensure complete formation of the intermediate pyrazoline. Decomposition of the pyrazoline was accomplished by heating the crude reaction mixture for an additional 16 hr at 195°. Fractional distillation of the reaction mixture at 115° (0.35 mm) through a 6-cm column packed with glass helices gave 75 g (77%) of the triester **5**.

The infrared spectrum of **5** determined in CCl_4 exhibits bands at 1750, 3010, and 1034 cm^{-1}. An nmr spectrum (CCl_4) possesses quartets at τ 5.82 (J = 7 cps) and 5.86 (J = 7 cps), singlets at 6.20, 6.28, and 6.33, a multiplet at 7.42, and triplets at 8.68 (J = 7 cps) and 8.72 (J = 7 cps).

***trans*-1,2,3-Cyclopropanetricarboxylic Acid (6).** A solution containing 34 g (0.84 mole) of sodium hydroxide dissolved in 240 ml of distilled water and 100 ml of methanol was prepared. To this solution was added immediately 30 g (0.13 mole) of the triester **5**. The resulting mixture was boiled for 17 min, and the volume of the reaction mixture was maintained by continuous addition of water. The acidity of the mixture was then adjusted to pH 1 with concentrated hydrochloric acid. The resulting solution was then treated with Norit and evaporated to near dryness on a rotary evaporator, and the residue was dried further overnight in a vacuum desiccator over phosphorus pentoxide. The tribasic acid was separated from the residual sodium chloride by pulverizing the dry cake and boiling the mixture with eight successive 125-ml portions of ether. The combined ether extracts were filtered, the filtrate was evaporated to dryness on a rotary evaporator, and the resulting solid was finally dried overnight in a vacuum desiccator to yield 19.7 g (90%) of the tribasic acid **6**, mp 207–211° (lit.[12] 220°).

The infrared spectrum of **6** (KBr) exhibits bands at 3460, 1730, and 1700 cm^{-1}. The nmr spectrum (CD_3COCD_3) shows a singlet at τ 0.52 and multiplets at 7.34–7.44.

***trans*-1,2,3-Cyclopropanetricarbonyl Chloride (7).** To a round-bottomed flask equipped with a reflux condenser protected in turn by a calcium chloride drying tube was added 17.1 g (0.10 mole) of the tribasic acid **6** and 83 g (0.40 mole) of phosphorus pentachloride. The ensuing exothermic reaction was controlled by cooling. After the initial reaction had subsided, the mixture was heated under reflux for 5 hr and then cooled in an ice bath. The acid chloride and phosphorus oxychloride were separated from the residual phosphorus pentachloride by extraction with two 15-ml portions of anhydrous ether. The washings were filtered through a glass plug into a pear-shaped flask and fractionally distilled through a 15-cm Vigreux column to yield 17.4 g (81%) of the desired colorless acid chloride **7**, bp 92–95° (1.0 mm) [lit.[12] 90° (0.3 mm)].

The infrared spectrum of **7** determined in CCl_4 shows bands at 1807 and 1002 cm^{-1} while the nmr spectrum (CCl_4) exhibits a multiplet at τ 6.55.

***trans*-1,2,3-Tris(N,N-dimethyl)cyclopropanetricarboxamide (8).** A solution of 8.70 g (0.038 mole) of the triacid chloride **7** in 100 ml of anhydrous ether was added over a period of 0.5 hr to 20.5 g (0.46 mole) of anhydrous dimethylamine in 250 ml of anhydrous ether. An 18-gauge hypodermic needle was employed for introduction of the acid chloride in order to control carefully the addition and ensure that the reaction occurred below the surface of the amine solution. This technique was found to be a critical factor in minimizing polymer formation. Throughout the course of the

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(29) J. K. Crandall and D. R. Paulson, *J. Am. Chem. Soc.*, **88**, 4302 (1966).

(30) W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, **27**, 3476 (1962).

(31) A variety of aromatic compounds including benzene, toluene, ethylbenzene, styrene, *o*-xylene, and anthracene were obtained upon pyrolysis of the tetraacetate, and no tetramethylenecyclobutane (**1a**) could be detected; see A. F. Vellturo, Ph.D. Thesis, Yale University, 1962.

(32) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938); P. E. Slade, Jr., and H. B. Jonassen, *ibid.*, **79**, 1277 (1957).

(33) Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected while boiling points are uncorrected. Infrared spectra were determined, in the solvents indicated, on a Perkin-Elmer 337 spectrophotometer and calibrated against polystyrene film at 1944 and/or 906 cm^{-1}. Ultraviolet spectra were recorded on Cary Model 14 and Perkin-Elmer 202 spectrophotometers with the exception of that shown in Figure 4 which was obtained on a Perkin-Elmer Model 450 instrument purged with nitrogen. Mass spectra were taken on a CEC Model 6201 and an Atlas CH4 spectrometer (University of Illinois, Urbana, Ill.). Capillary gas chromatographic analyses were performed on a Perkin-Elmer 810 gas chromatograph equipped with the columns indicated,[25] while separations were achieved on an Aerograph A-90P instrument. Nmr spectra were recorded on a Varian A-60A instrument with TMS as an internal reference and reported in τ units. Elemental analyses were performed by Galbraith Microanalytical Labs., Knoxville, Tenn. All microhydrogenations were conducted at atmospheric pressure using an Arthur H. Thomas Co. Model 5938-N microhydrogenation apparatus.

addition the temperature was maintained at −70°, and the solution was stirred continuously. After the acid chloride addition was completed, the mixture was stirred for an additional hour at −70° and then permitted to warm slowly to 30° over a period of 0.5 hr whereupon vigorous evolution of the excess dimethylamine occurred. After the dimethylamine evolution subsided, the remaining mixture was cooled to 20° and rapidly filtered under vacuum. The solid residue was then collected on a filter and extracted in a Soxhlet thimble with the filtrate (diluted to 500 ml with ether) for a period of 18 hr. The ether extract was concentrated to a volume of 125 ml on a rotary evaporator. Crystallization was allowed to proceed for 0.5 hr at room temperature and then for 2 hr at −20°. The crystals were collected on a filter and dried overnight in a vacuum desiccator. A total of 5.3 g (54%) of crude triamide **8**, mp 110–117°, was obtained. Recrystallization from ether–methanol yielded pure white, hygroscopic needles, mp 117.5–118° (lit.[13] 116–118°).

The infrared spectrum of **8** (KBr) shows bands at 1630 and 3020 cm^{-1}. The nmr spectrum ($CDCl_3$) possesses six-proton singlets at τ 6.88, 7.01, and 7.05, a two-proton singlet at 7.38, and a one-proton singlet at 7.46.

Anal. Calcd for $C_{12}H_{21}O_3N_3$: C, 56.45; H, 8.29; N, 16.46; mol wt, 255. Found: C, 56.55; H, 8.11; N, 16.41; mol wt, 252 (ebullioscopic in benzene).

***trans*-1,2,3-Tris(N,N-dimethylaminomethyl)cyclopropane (9).** A solution of 2.0 g (0.05 mole) of lithium aluminum hydride in 50 ml of ether was prepared. To this solution was added 3.0 g (0.012 mole) of the triamide **8** which previously had been dried in a vacuum desiccator over sodium hydroxide. The mixture was then stirred under reflux for 24 hr and then cooled to 0°. The excess lithium aluminum hydride was destroyed by cautiously adding 8 ml of water. The resulting mixture was stirred for 1 hr, and the white crystalline material which precipitated was collected on a filter and treated with two successive 50-ml portions of boiling ether. The combined ether solutions were then dried over anhydrous magnesium sulfate and distilled to yield 1.70 g (68%) of the colorless triamine **9**, bp 59.5–60.0° (0.20 mm).

The infrared spectrum of **9** determined in CS_2 has major bands at 1050 and 1040 cm^{-1}, and the nmr spectrum (CS_2) shows multiplets at τ 7.75, 7.87, and 9.37.

Anal. Calcd for $C_{12}H_{27}N_3$: C, 67.55; H, 12.75; N, 19.69. Found: C, 65.10; H, 13.11; N, 19.72.

The elemental analysis which is less than satisfactory was not repeated since quaternization of **9** gave an iodide with a consistent combustion analysis (*vide infra*).

Trisquaternary Ammonium Iodide 10a. Over a 15-min period, 11.2 g (0.05 mole) of the triamine **9** was added dropwise to a solution of 25.5 g (0.18 mole) of methyl iodide in 160 ml of absolute ethanol and 40 ml of 95% ethanol. After the ensuing mildly exothermic reaction had subsided, the mixture was stirred overnight. The resulting mixture finally was heated under reflux for 0.5 hr and then cooled. The crystals which had deposited were collected on a filter, washed with 20 ml of ether, and dried *in vacuo* overnight to give 28.7 g (86%) of the colorless trisquaternary iodide (**10a**), mp >360°.

The infrared spectrum of the iodide (KBr) exhibits absorption bands at 3010 and 1011 cm^{-1}, and the nmr spectrum determined in D_2O shows a six-proton multiplet at τ 6.27, a 27-proton singlet at 6.71, and a three-proton multiplet at 8.05.

Anal. Calcd for $C_{15}H_{36}N_3I_3$: C, 28.20; H, 5.64; N, 6.56; I, 59.60. Found: C, 27.91; H, 5.86; N, 6.75; I, 59.40.

Trisquaternary Ammonium Hydroxide 10b. A solution of 10 g (0.01 mole) of the trisquaternary ammonium iodide **10a** in 126 ml of distilled, deionized water and 16 ml of methanol was prepared. Silver oxide, freshly prepared from the reaction of 21.3 g (0.13 mole) of silver nitrate and 4.9 g (0.12 mole) of sodium hydroxide, was added to this solution in small portions with rapid magnetic stirring. After the initial exothermic reaction had subsided, the mixture was stirred for 3 hr at room temperature, and the black silver iodide which deposited was removed by filtration. The resulting aqueous solution was lyophilized until the concentration of **10b** reached approximately 30%.

The nmr spectrum of the aqueous solution displays two poorly resolved doublets at τ 6.33 and 6.39 (six protons), a 27-proton singlet at 6.77, and a three-proton multiplet at 8.13.

***trans*-1,2,3-Tris(acetoxymethyl)cyclopropane (12).** A solution of 23.0 g (0.10 mole) of 1-carbethoxy-2,3-dicarbomethoxycyclopropane (**5**) in 140 ml of ether was added dropwise with rapid stirring to a cooled solution of 15.6 g (0.41 mole) of lithium aluminum hydride in 500 ml of anhydrous diethyl ether. The mixture was stirred for 1 hr and then cooled to 0°. The excess lithium aluminum hydride was destroyed by adding 60 ml of water dropwise, after which the reaction mixture was stirred for 1 hr. The ether was then removed on a rotary evaporator, and 16.4 g (0.20 mole) of anhydrous sodium acetate and 300 ml of methylene chloride was added. The methylene chloride mixture was brought to reflux while stirring, and 122.4 g (1.20 moles) of acetic anhydride was added dropwise. This reaction mixture was then heated under reflux for 36 hr. The hot solution was then poured into 2 l. of cold 10% potassium carbonate solution and allowed to stand for 2 hr. The aqueous mixture was filtered, and the filtrate was extracted with four 200-ml portions of methylene chloride. The filter cake was boiled with an additional 200 ml of methylene chloride and the residual solid was removed by filtration. The resulting filtrate was combined with the methylene chloride extracts which were then washed twice in turn with 200 ml of 5% hydrochloric acid and twice with 200 ml of water. After drying over magnesium sulfate, the methylene chloride was removed on a rotary evaporator. The pure triacetate **12** was obtained by distillation through a 6-in. Vigreux column, bp 150–155° (2.0 mm). The yield was 11.7 g (49%).

The infrared spectrum of a neat sample of **12** displays bands at 1740, 3010, and 1032 cm^{-1}, and the nmr spectrum (CCl_4) shows two poorly resolved doublets at τ 5.88 and 6.00 (six protons), a nine-proton singlet at 7.98, and a three-proton multiplet at 8.71.

***trans*-1,2,3-Tris(*p*-toluenesulfonylmethyl)cyclopropane (14).** To a solution of sodium ethoxide, freshly prepared from 4.6 g (0.2 g-atom) of sodium metal in 100 ml of absolute ethanol, was added 12.8 g (0.05 mole) of the triacetate **12**. The resulting solution was heated under reflux for 10 min and then cooled to room temperature. Solid phenolphthalein was added, and the reaction mixture was titrated to the disappearance of the red color with a 50% solution of sulfuric acid in absolute ethanol. The solvent was removed on a rotary evaporator and the mixture of crude triol **13** and sodium sulfate was dried over calcium chloride *in vacuo* overnight. To the dry triol **13** was added 100 ml of acetone and 38 g (0.2 mole) of *p*-toluenesulfonyl chloride, recrystallized from 20:1 petroleum ether (bp 60–75°)–benzene. To the resulting solution was added 120 ml of a 25% sodium hydroxide solution at 0° over a period of 30 min. The reaction mixture was stirred for an additional 4.5 hr, after which it was added to 1000 ml of water. The aqueous mixture was extracted with four 200-ml portions of chloroform. The chloroform extracts were combined, washed with two 100-ml portions of water, and dried over magnesium sulfate. Removal of the solvent on a rotary evaporator yielded an oil which crystallized upon trituration with a small quantity of ethanol. Recrystallization from 95% ethanol gave 10.1 g (34%) of the tritosylate **14**, mp 101–102.5°.

The infrared spectrum taken in $CHCl_3$ shows bands at 1600, 1350, 1178, and 1035 cm^{-1}. An nmr spectrum ($CDCl_3$) exhibits an AB quartet at τ 2.46, a multiplet at 6.08, a singlet at 7.57, and a multiplet at 8.74.

Anal. Calcd for $C_{27}H_{30}O_9S_3$: C, 54.53; H, 5.08. Found: C, 55.03; H, 5.18.

***trans*-1,2,3-Triiodomethylcyclopropane (15).** A solution of 3.0 g (0.005 mole) of tritosylate **14** in 20 ml of anhydrous acetone was added at room temperature to a solution of 2.85 g (0.019 mole) of anhydrous sodium iodide in 100 ml of acetone. Sodium *p*-toluenesulfonate began to precipitate in about 1 min, but stirring was continued for 7 hr. The mixture was then heated under gentle reflux for 1 hr and cooled, and the precipitated salt separated by filtration. Upon removal of the solvent under reduced pressure 2.1 g of crude triiodide was deposited which was recrystallized from methylcyclohexane (temperature maintained below 68°) and dried in a vacuum desiccator to yield 1.94 g (83%) of white needles, mp 82.5–83.5°.

The infrared spectrum taken in $CHCl_3$ shows bands at 1440, 1040, and 601 cm^{-1}. The nmr spectrum ($CDCl_3$) displays two doublets at τ 6.71 and 6.83 (J = 5.5 cps) and multiplets at 8.31 and 8.91.

Anal. Calcd for $C_6H_9I_3$: C, 15.71; H, 1.32; I, 82.97. Found: C, 15.51; H, 1.32; I, 82.80.

Trimethylenecyclopropane (3a). Method A. Pyrolysis of the Trisquaternary Ammonium Hydroxide 10b. The pyrolysis apparatus (see Figure 1) consisted of a 50-ml, three-necked flask equipped with a nitrogen inlet tube, a rubber septum, and an exit tube. The exit tube was connected in turn to a 50-ml 24/40 standard taper flask, as shown, which served as a pyrolysate collection vessel and was maintained at −78° during the pyrolysis.

The desired quantity of the trisquaternary ammonium hydroxide **10b** was introduced by means of a syringe into the pyrolysis flask, which was preheated to 160°. An attempt was made to control the addition rate of the **10b** solution at 0.2 ml/min. During the pyrolysis, the pressure of nitrogen in the system was maintained at 4.5 mm. When the addition was complete, the conditions were maintained for an additional 15 min to ensure complete reaction. Following equalization of the pressure with nitrogen, 10 ml of solvent/g of Hofmann base was added to the thawing pyrolysate. After thorough stirring of the pyrolysate–solvent mixture, the hydrocarbon-containing layer was separated and washed with three portions of 0.5 *M* hydrochloric acid and three portions of water prior to drying over sodium sulfate. By quantitative dilution of the dry solvent extracts and subsequent ultraviolet analysis[15] it was established that the yield of trimethylenecyclopropane (**3a**) obtained was 1.5%. The nmr spectrum in carbon disulfide displays a resonance signal at τ 4.86 (singlet). The expected molecular ion peak at *m/e* 78 was observed in the mass spectrum of **3a**.

Under these reaction conditions a by-product was obtained. This product emerged shortly before (30 sec) trimethylenecyclopropane on a 5 ft × 0.25 in. Carbowax 20M column operated at 65°. Under these conditions, the retention time of trimethylenecyclopropane was approximately 9 min. This by-product has an ultraviolet spectrum with a single absorption maximum at 241 mμ. An insufficient quantity of this material was obtained in order to permit further characterization.

Trimethylenecyclopropane (3a). Method B. Base-Catalyzed Dehydrohalogenation of *trans*-1,2,3-Triiodomethylcyclopropane (15). The reaction vessel was constructed from 8-mm Pyrex tubing and a standard 150 × 10 mm side-arm test tube (see Figure 2). The Pyrex tubing was fashioned into a U-shaped trap which was connected directly to a vacuum pump and was maintained at −78° during the course of the reaction.

The test-tube portion of the apparatus was packed with a tuft of glass wool and filled to a depth of 80 mm with finely ground potassium hydroxide, which had been freshly fused in a Pyrex flask under reduced pressure (0.5 mm) to remove the water. The tube was then stoppered with a rubber septum, and a nitrogen supply was attached to the side arm.

In a typical experiment, 100 mg of *trans*-1,2,3-triiodomethylcyclopropane (**15**) dissolved in 2 ml of diethyl ether, was added in 100-μl increments by means of a syringe through the septum. Care was exercised to introduce the iodide solution below the level of the potassium hydroxide. During the course of the addition the temperature of the base and the nitrogen pressure were constantly monitored and kept at 140° (6 mm), respectively. The total addition time was 10 min, but the conditions were maintained for an additional 15 min before nitrogen was admitted to equalize the pressure.

After thawing the pyrolysate and quantitative dilution of the product, the ultraviolet spectrum was measured. The yield of trimethylenecyclopropane (**3a**) was 20%.[15]

None of the isomeric material found when method A was employed was observed in these experiments.[16] In deuteriochloroform, trimethylenecyclopropane exhibits a single nmr signal at τ 4.76 (singlet). Infrared analysis in the gas phase discloses absorption at 2991, 2874, 1217, 1139, 872, and 770 cm^{-1}.

3-Methyl-3-pentanol. Ethylmagnesium bromide, prepared from 60 g (0.55 mole) of ethyl bromide and 12 g (0.5 g-atom) of magnesium, was treated with 26 g (0.5 mole) of 2-butanone. Distillation of the crude alcohol, bp 42–43.5° (15 mm), gave 26.2 g (51%) of 3-methyl-3-pentanol, n^{20}D 1.4178 (lit.[34] n^{20}D 1.4183).

Dehydration of 3-Methyl-3-pentanol. Acid-catalyzed dehydration of 3-methyl-3-pentanol was accomplished by heating a mixture of 26 g (0.33 mole) of the alcohol and 75 g of oxalic acid at 100° for 8 hr. The resulting mixture of olefins was distilled rapidly from the reaction flask, washed with five 20-ml portions of water, and dried over magnesium sulfate. The dry distillate was then redistilled, bp 67–69° (1 atm), to give 12.5 g (45%) of product. Analysis of this product mixture by glpc[25b] at 50° showed that three components are present in the ratio 1:6.5:13. A homogeneous sample of each component was obtained for purposes of identification by preparative glpc.[25a] The three components were identified as 2-ethyl-1-butene (**21**), *trans*-3-methyl-2-pentene (**23**), and *cis*-3-methyl-2-pentene (**22**), respectively, from comparison of infrared spectra with spectra of authentic samples.[27]

3-Methylpentane (20). 3-Methylpentane was prepared by catalytic hydrogenation (3 atm) of 6.0 g (0.07 mole) of the 2-ethyl-1-butene and *cis*- and *trans*-3-methyl-2-pentene mixture over 50 mg of prereduced platinum oxide in 25 ml of ethanol. After hydrogenation was complete, 150 ml of water was added to the hydrogenation mixture. The organic phase was separated, washed with five 10-ml portions of water, and dried over magnesium sulfate. Distillation gave 2.1 g (34%) of 3-methylpentane, bp 62–63° (1 atm), n^{20}D 1.3772 (lit.[35] n^{15}D 1.3792).

1,2,3-Trimethylcyclopropene (18). 1,2,3-Trimethylcyclopropene (**18**) was prepared by the method of Closs and co-workers[23] from 24 g (0.44 mole) of 2-butyne, 8.5 g (0.1 mole) of methylene chloride, and 120 ml of 1.75 *M* methyllithium. Isolation of pure trimethylcyclopropene was accomplished by preparative glpc.[25a] Yields of the pure olefin collected in this manner range from 110 to 170 mg (1–2%). The nmr spectrum (CCl_4) shows a singlet at τ 8.07, a multiplet at 8.73, and a doublet at 9.05 (J = 4 cps) in agreement with the previously reported data.[23]

Hydrogenation of 1,2,3-Trimethylcyclopropene (18). A. Over 10% Palladium on Charcoal. A sample of 1,2,3-trimethylcyclopropene (**18**) (20 mg) collected by glpc in 1 ml of methylcyclohexane (prereduced to ensure complete saturation) was subjected to microhydrogenation over a 10-mg sample of prereduced 10% palladium-on-charcoal catalyst. A total of 5.10 ml of hydrogen (0.95 molar equiv) was absorbed over a period of 2.25 hr. Glpc analysis[25b] at 50° showed the presence of five products with retention times (min) of 4.8, 5.4, 5.6, 6.1, and 6.6, with relative areas of 4.5:1:10:23.5:26, respectively. The products with retention times of 4.8, 5.4, 5.6, and 6.1 min were identified as 3-methylpentane (**20**), 2-ethyl-1-butene (**21**), *trans*-3-methyl-2-pentene (**23**), and *cis*-3-methyl-2-pentene (**22**), respectively, by peak enhancement techniques. The fifth product (retention time 6.6 min) was collected by glpc[25a] at 55°. The infrared spectrum (CCl_4) shows major peaks at 3005, 2950, 2925, 2875, 1450, 1385, 1160, 1095, 1070, 910, and 510 cm^{-1}.

B. Over Rhodium on Alumina. A sample of 1,2,3-trimethylcyclopropene (0.10 g) collected by glpc in 1 ml of methylcyclohexane was subjected to hydrogenation over a 25-mg sample of a prereduced rhodium-on-alumina catalyst at atmospheric pressure. After 5 hr, 25.85 ml of hydrogen (0.95 molar equiv) had been absorbed. Glpc analysis[25b] at 50° showed the presence of five products with retention times of 3.0, 3.3, 3.5, 3.6, and 3.9 min, with relative areas of 14:1:1:3:52. The first four products were identified as 3-methylpentane (**20**), 2-ethyl-1-butene (**21**), *trans*-3-methyl-2-pentene (**23**), and *cis*-3-methyl-2-pentene (**22**), respectively, by enrichment with synthetic samples. The fifth product (retention time, 3.9 min) was collected by glpc[25a] at 55°. The following spectral data were observed for this product. The infrared spectrum (CCl_4) shows major peaks at 3005, 2950, 2925, 2875, 1450, 1385, 1160, 1095, 1070, 910, and 510 cm^{-1}; the nmr spectrum (CCl_4) displays a broad singlet at τ 9.15; the mass spectrum has a molecular ion peak at *m/e* 84. These data are consistent with the assignment of structure **19** (*cis*-1,2,3-trimethylcyclopropane) to this product.

Hydrogenation of Trimethylenecyclopropane (3a). A. Over Palladium on Calcium Carbonate. A sample of trimethylenecyclopropane prepared from 0.51 g of *trans*-1,2,3-triiodomethylcyclopropane (**15**) in 2 ml of tetrahydrofuran was subjected to microhydrogenation over a 10-mg sample of prereduced palladium on calcium carbonate catalyst at atmospheric pressure.[36] After 18 hr, 10.20 ml of hydrogen had been absorbed. Glpc analysis[25b] at 50° showed the presence of only one product, with a retention time of 4.5 min. This product was identified as *cis*-3-methyl-2-pentene (**22**) by peak enhancement with a synthetic sample.

B. Over Palladium on Charcoal. A sample of trimethylenecyclopropane prepared from 0.50 g of *trans*-1,2,3-triiodomethylcyclopropane (**15**) in 2 ml of tetrahydrofuran was subjected to microhydrogenation over a 15-mg sample of prereduced 10% palladium on charcoal at atmospheric pressure. After 5.5 hr, 5.85 ml of hydrogen had been absorbed. Glpc analysis[25b] of the product showed the presence of two compounds with retention times (min) of 3.8 and 4.5 with relative areas of 3:1. The two products were identified as 3-methylpentane (**20**) and *cis*-3-methyl-2-pentene (**22**), respectively, by enrichment with synthetic samples.

C. Over Rhodium on Alumina. A sample of trimethylenecyclopropane prepared from 0.50 g of *trans*-1,2,3-triiodomethyl-

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cyclopropane in 1.5 ml of tetrahydrofuran was subjected to microhydrogenation over a 15-mg sample of prereduced rhodium on alumina. After 3.5 hr, 6.10 ml of hydrogen had been absorbed. Glpc analysis[25b] at 50° showed the presence of five products with retention times of 3.5, 3.8, 4.0, 4.2, and 4.6 min, with relative areas of 6:1:3:7:2, respectively. The four products with retention times of 3.5, 3.8, 4.0, and 4.2 min, were identified as 3-methylpentane (**20**), 2-ethyl-1-butene (**21**), *trans*-3-methyl-2-pentene (**23**), and *cis*-3-methyl-2-pentene (**22**), respectively, by enrichment with authentic synthetic samples. Glpc analysis on two different capillary columns[25b,c] confirmed that the product with a retention time of 4.6 min was identical with *cis*-1,2,3-trimethylcyclopropane (**19**) obtained from the reduction of 1,2,3-trimethylcyclopropene (**18**).

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Buxus Alkaloids. XIII.[1] A Synthetic Approach to the 9(10→19)*abeo*-Pregnane System[2,3]

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Abstract: When 9β,19-cyclo-5α-pregnane-3,11,20-trione 3,20-diethylene ketal (V) was subjected to the Huang–Minlon modification of the Wolff–Kishner reduction, the expected 11-deoxo compound was not obtained. Instead, two crystalline C-10 epimers, 9(10→19)*abeo*-$\Delta^{9(11)}$-5α,10β-pregnene-3,20-dione 3,20-diethylene ketal (IX) and 9(10→19)*abeo*-$\Delta^{9(11)}$-5α,10α-pregnene-3,20-dione 3,20-diethylene ketal (X), were isolated and characterized. Selective ketal hydrolysis of the diketals with boron trifluoride etherate yielded the respective C-20 ketones, XI and XII. Catalytic hydrogenation of the diketals yielded the dihydro derivatives, XIII and XIV, and hydrolysis afforded the respective dihydro monoketones, XV and XVI, and dihydro diketones, XVII and XVIII. The configurations of IX and X were determined by optical rotatory dispersion measurements of XV–XVIII. The potential significance of the ring B enlargement reaction for the chemical interrelation of the two principal structural types of the *Buxus* alkaloids and for the biogenesis of alkaloids of the 9(10→19)*abeo*-pregnane series are discussed.

In 1962, we reported the elucidation of the structure[4] and configuration[5] of cyclobuxine-D (I), an alkaloid isolated from *Buxus sempervirens* L.[6] Cyclobuxine-D was shown to be the prototype of a new class of steroidal alkaloids which contains the 9β,19-cyclo-5α-pregnane system (II) and has a substitution pattern at C-4 and C-14 which is intermediate in the biogenetic scheme between lanosterol and cholesterol-type steroids. Subsequent studies have characterized many structurally related alkaloids.[7] In 1964, the isolation and characterization of buxenine G[8a] ("norbuxamine"[9]) was reported and this alkaloid was later proven to possess the novel structure and configuration III.[8b] Several additional alkaloids which possess the unusual 9(10→19)*abeo*-5α-pregnane[10] system (IV) have been found.[1,9,11,12]

In the course of studies on the synthesis of analogs of *Buxus* alkaloids which contain the 9β,19-cyclo-5α-pregnane system (II), an unusual Kishner reduction which involves cleavage of a carbocyclic ring has been observed. The reaction constitutes a synthetic approach to derivatives of the 9(10→19)*abeo*-5α-pregnane system (IV).

Examination of a Dreiding model of 9β,19-cyclo-5α-pregnane-3,11,20-trione 3,20-diethylene ketal (V)[13] indicated that the 11-carbonyl group in this molecule is not as hindered as that of a normal steroid nucleus, owing to the absence of a 1,3-interaction with the C-19 methyl group. When the compound was subjected to the Huang–Minlon modification of the Wolff–Kishner reduction, however, the expected 11-deoxo compound was not obtained. The infrared spectrum

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[2] This investigation was first described, in part, in a preliminary communication: S. M. Kupchan and E. Abushanab, *Tetrahedron Letters*, 3075 (1965).

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