concerted reaction with the concurrent elimination of CO (and orbital symmetry governed the mode of this reaction), butadiene should behave in a manner similar to other trapping agents. Since III, VIa, and VIb were the products with maleic anhydride, maleate, and fumarate, respectively, IX should react with butadiene at C-1 and C-2 rather than at C-1 and C-4, the product being VIII (which is not what we observed). In sharp contrast with species such as A, B, and IX, all the experimental results are entirely consistent with the mechanism that 1,3-dimethylcyclobutadiene is an intermediate which reacts with the trapping agents, as shown by model experiments generating cyclobutadiene in the presence of these reagents. The rather inadequate reproducibility of CO measurement does not permit one to decide whether or not CO is extruded at the rate-determining step, although the two rates (CO evolution and disappearance of Ia) are of the same magnitude. Therefore we are unable at the present moment to determine whether IIa is formed directly from Ia or there exists another intermediate such as IX as a percursor of IIa.[12] Further discussions on this point are deferred until the definite result is obtained.[13]

When Ia (0.7 mm, 1100 ml) was irradiated by a Hanovia mercury lamp through a Corex filter at room temperature for 4 hr, 94% of Ia reacted and the products, condensable at −190° but noncondensable at −80°, consisted of acetylene (2%), propyne (6%), and butyne (2%). This result suggests that dimethyltetrahedrane might be involved during the photolysis. Irradiation of carbon suboxide in the presence of cyclopropene afforded acetylene and the intermediacy of teterahedrane was proposed.[14] The C-2,4 distance in Ia is as short as 2 Å[2] and a photochemically induced, linear cheletropic reaction might proceed to close the ring during the removal of CO. However, obviously this interpretation is highly speculative at the present time and further investigation is demanded to attest it.

Acknowledgment. We thank the National Research Council of Canada and the Defense Board for financial support.

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[12] The reaction of Ia leading to IIa can be viewed as a symmetry-allowed linear cheletropic reaction [R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 842 (1969)] with respect to CO and the C-1,5 bond of Ia. Also symmetry allowed is the conversion of Ia into IX ($\sigma 2s + \sigma 2a$).

[13] Flash-vacuum pyrolysis experiments are now being performed in the Laboratory of Dr. Hedaya.

[14] P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, **92**, 406 (1970).

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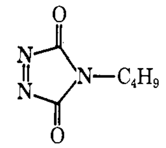
Nitrogen-Backboned Polymers. I

Sir:

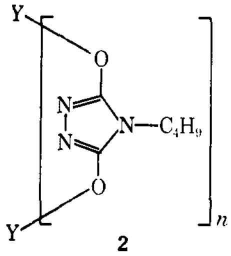
We herein report the synthesis of the first nitrogen-backboned polymer, a heretofore unknown type of compound which is expected to be of great fundamental and practical interest.

Visible irradiation of a 0.3 *M* carbon tetrachloride solution of the red 4-*n*-butyl-1,2,4-triazoline-3,5-dione[1] (**1**) with a 150-W quartz–iodine tungsten lamp for 8 min affords a colorless solution of a polymer having an observed (vapor pressure osmometry) average molecular weight of 4200. The average polymer molecule contains at least 20 monomer units, a value which may be rather low owing to the sensitivity of the osmometric technique toward nonpolymeric impurities. In solution, the polymer is unstable; 4% of the red monomer is regenerated at 27° within 30 min after the completion of the photopolymerization of the 0.3 *M* solution of **1**. Ultimately, about 80% of the monomer is regenerated. Low-temperature evaporation of the solvent affords the polymer as a colorless glass which may be kept at least a year at 14° without appreciable monomer reappearance. However, when the stored polymer is redissolved, monomer begins to be regenerated.



1

A priori, only three types of repeating units, **2**, **3**, and **4**, would seem plausible for this labile colorless polymer. Of the three, only **4** is consistent with infrared spectral data.[2] Infrared study of model compounds **5** and **6**, obtained[4] through diazomethane treatment of urazole **7**, shows that intense absorption bands (1513 and 1605 cm^{-1}) are associated with the imidate-like functionality of **5** but not with the urazole functionality of **6**. Since the infrared spectrum of the polymer shows carbonyl absorption (1768 cm^{-1}) but no absorption near 1513 and 1605 cm^{-1} which might be attributed to the imidate-



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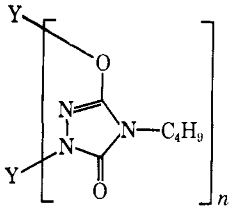

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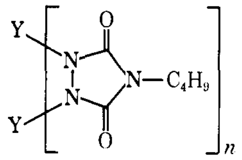

4

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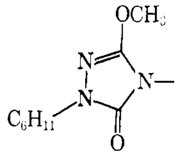
[1] J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, **31**, 3444 (1966).

[2] An alternate structure involving dione ring opening has been eliminated from serious consideration owing to the fact that the polymer is colorless. The n–π^* absorption of the azodicarbonyl chromophore present in a polymer of structure $Y[C(=O)N=NC(=O)N(C_4H_9)]_nY$ would be expected to cause the polymer to be yellow. Typical azodicarbonyl n–π^* bands occur at 410–475 nm (ϵ 37–56).[3] Using these values, it can be estimated that there is less than 4% of this type of chromophore in the polymer.

[3] E. Fahr and H. Lind, *Angew. Chem., Int. Ed. Engl.*, **5**, 372 (1966).

[4] Diazomethane treatment of **7** affords a 1 :3 mixture of the chromatographically separable *O*-methyl and *N*-methyl derivatives, **5** and **6**, which have elemental compositions and spectral properties in accordance with the assigned structures. For other examples of the action of diazomethane upon urazoles, see F. Arndt, L. Loewe, and A. Tarlan-Akön, *Istanbul Univ. Fen. Fak. Mecm., Ser. A*, **13**, 127 (1948); *Chem. Abstr.*, **42**, 8190*d* (1948).



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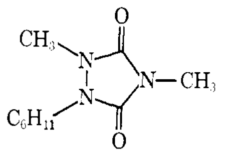

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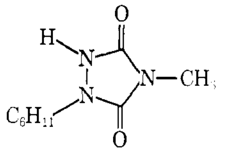


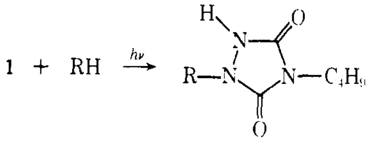
7

like groups in repeating units **2** and **3**, it is clear these two units occur seldom, if ever, in the polymer. Accordingly, **4** is the only remaining plausible repeating unit and the labile polymer hence appears to have a nitrogen backbone. Consistent with this view is the observation that the integrated intensity of the polymer's carbonyl absorption band (relative area 1.81) indicates, when compared to similar measurements on model compounds **5**, **6**, and **7** (relative areas 1.01, 2.00, and 2.29, respectively), that essentially all carbonyl groups are retained upon polymerization.

Additional chemical and spectral data bear upon the structure of the polymer. It has been previously noted that a carbon tetrachloride solution of the polymer slowly regenerates the bulk (60–80% after several days) of the red monomer. A comparable amount of regeneration occurs within minutes after addition of a trace of pyridine, a mild base, to a carbon tetrachloride solution of the polymer. This base-catalyzed depolymerization strongly suggests that the polymer chain terminates with hydrogen (**4**, Y = H). Removal of an acidic terminal hydrogen by base could afford an anion which subsequently (or concomitantly) eliminates monomer.[5] Infrared and nmr spectroscopy support the terminal hydrogen hypothesis. Weak broad absorption observed at 3220 cm^{-1} and δ 7.35 (220 MHz) is attributable to terminal N–H. Additionally, the 220-MHz nmr spectrum of the polymer shows intense broad featureless bands (δ 1.02, 1.46, 1.71, and 3.66) arising from the four types of protons in the *n*-butyl substituents.

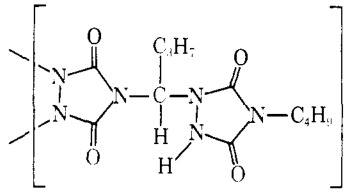
Since diazomethane methylates urazole **7**, it was expected that it would similarly react with the ends of the polymer chain to afford a methyl-capped polymer showing improved stability. Diazomethane treatment of the fresh polymer (with subsequent removal of excess reagent) affords a material which is not only stable toward pyridine, but is also significantly more stable toward thermal depolymerization. For example, after 2 days at 27°, a carbon tetrachloride solution of the methylated polymer has regenerated only 8.2% of the original monomer. The methylated polymer has a 220-MHz nmr spectrum showing small broad similarly sized resonances (δ 3.07 and 3.92) attributable to *N*-methyl and *O*-methyl end groups in addition to the four larger broad resonances of the *n*-butyl group. The infrared spectrum of the methyl-capped polymer lacks N–H absorption, but contains two weak broad bands at 1610 and 1495 cm^{-1}, which are not present in the infrared spectrum of the unmethylated polymer. Since strong bands appear at 1605 and 1513 cm^{-1} in the infrared spectrum of the O-methylated model compound **5**, it seems clear that partial O-methylation of the ends of the polymer chain has given rise to these new bands. By assuming that the imidate-like group which arises on O-methylation of the polymer has infrared absorption of comparable intensity to that which would be shown by the same functionality in a polymer unit such as **2** or **3**, one can roughly estimate a maximum frequency of occurance of units **2** or **3** in the polymer. The average polymer contains at least 20 monomer units and, on diazomethane treatment, undergoes about equal amounts of N- and O-methylation at the two ends. Since O-methylation is readily detectable by infrared, it may be seen that one imidate-like group per 40 units would be detected. Hence, the estimate is that the frequency of occurrence of units **2** and **3** is less than 2.5%.

Since 4-*n*-butyl-1,2,4-triazoline-3,5-dione undergoes ready photoreaction with hydrogen donors (cyclohexane, cumene, etc.), eq 1, it may be that excited **1**



(1)

occasionally reacts with an *n*-butyl group to afford a repeating unit such as **8**. This type of reaction may



8

explain the incomplete regeneration of the monomer from the polymer.

Whereas both 4-alkyl- and 4-aryl-1,2,4-triazoline-3,5-diones undergo photoreaction with hydrogen donors, we have observed that only the former undergoes ready photopolymerization and then only in certain solvents. Typically, if a 4-alkyl-1,2,4-triazoline-3,5-dione will fluoresce in a solvent, it will undergo photopolymerization in that solvent. Polymerization solvents include carbon tetrachloride, chloroform, methylene chloride, fluorotrichloromethane, dimethyl carbonate, and ethyl acetate. Benzene and most other aromatic solvents quench the fluorescence (presumably by reducing the lifetime of the excited singlet) and inhibit photopolymerization of the 4-alkyl substituted diones. Possibly, the 4-aryl substituted diones, which do not fluoresce well, undergo "self-quenching."

Further work on the polymerization of 4-substituted 1,2,4-triazoline-3,5-diones and related systems is under way. This along with the properties of nitrogen-backbone polymers will be the subject of future accounts.

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(5) Analogy for this reaction is found in the report by G. O. Schenck and H. Formanek [*Angew. Chem.*, 70, 505 (1958)] that the irradiation of diethyl azodicarboxylate in isopropyl alcohol produces a tetracarbethoxytetrazine having terminal hydrogens which, on treatment with ammonia, affords azodicarbonamide and diethyl hydrazodicarboxylate.

Acknowledgments. This investigation was supported by grants-in-aid from the Rohm and Haas and E. I. du Pont Corporations. Funds for the 220-MHz nmr spectrometer were provided in part by the National Science Foundation.

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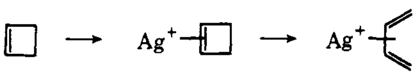
Received June 22, 1970

On the Mechanism of Metal-Catalyzed Rearrangement of Strained Cyclobutane and Cyclobutene Derivatives

Sir:

We have previously reported that silver ions can effect the disrotatory ring opening of certain cyclobutene systems to yield derivatives of butadiene, and it was suggested that the mechanism of this reaction involves insertion of the silver ion into the double bond to form the silver–olefin π complex followed by a concerted disrotatory ring opening process to form the corresponding silver complex of butadiene (eq 1).[1] In the absence of silver ions such a concerted reaction is of course forbidden and arguments attempting to describe how such metal-catalyzed reactions may occur, within the framework of the Woodward–Hoffmann concepts of orbital symmetry conservation, have been given.[1]



(1)

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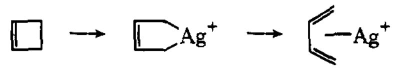
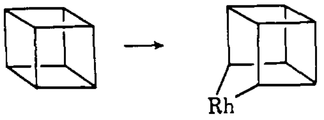


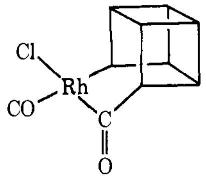
(3)

Recently this interpretation has been brought into question on the basis of the seemingly related ring-opening reactions of certain strained cyclobutane derivatives with various rhodium catalysts to yield diolefin systems.[2,3] In essence it has been suggested that for these latter reactions the overall process is not concerted[4] but involves initial insertion of the metal atom into a σ bond to yield a dialkylmetal derivative followed by conversion to the diolefin (eq 2).[5] It is implied that similar insertion into the carbon–carbon σ bond, rather than the π bond, is involved in the cyclobutene–butadiene conversions mentioned above (eq 3).

In the reaction of cubane with norbornadienerhodium chloride $[Rh(NOR)Cl]_2$, leading to the formation of tricyclooctadiene, it has been suggested that the σ-bonded rhodium complex I is involved as an intermediate; taken as support of this scheme is the fact that when $[Rh(CO)_2Cl]_2$ is used as the metal source, the acylmetal complex II can actually be isolated.[2]

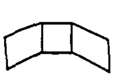


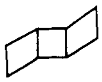
I



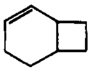
II

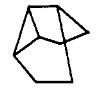
In the present study we have investigated the behavior of *syn*- and *anti*-tricyclooctane (III and IV, respectively), with $AgBF_4$, $[Rh(NOR)Cl]_2$, and $[Rh(CO)_2Cl]_2$. The systems III and IV bear obvious interesting steric relationships to the cubane molecule, and the results have a bearing both on the cyclobutene–butadiene conversion and the reactions of fully saturated hydrocarbons with these metal systems.


III


IV

No reaction of *anti*-tricyclooctane (IV) is observed after 5 days of heating with equimolar amounts of $AgBF_4$ in acetone (0.25 *M* solutions) at 56°.[6] Under identical conditions the syn isomer III is completely converted in approximately 1 min to a mixture of bicyclooctene (V), tetrahydrosemibullvalene (VI), and 1,5-cyclooctadiene (VII) in the ratio of 18:80:2, respectively.[7]


V


VI


VII

Similar behavior is seen in the reactions of the isomeric tricyclooctanes with $[Rh(NOR)Cl]_2$, whereas the syn isomer III reacts completely within 3 hr in benzene at 63° to produce a mixture of the hydrocarbons V, VI, and VII in a ratio of 70:2:28, respectively;[8] the anti isomer IV under similar conditions is completely unaffected after 20 hr.

On the other hand, $[Rh(CO)_2Cl]_2$ reacts with both the *syn*- and *anti*-tricyclooctanes under similar conditions to yield acylrhodium complexes presumably of the type II observed in the reaction with cubane.[9]

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[1] W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788 (1967); R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969).

[2] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970).

[3] T. J. Katz and S. A. Cerefice, *ibid.*, **91**, 2405 (1969).

[4] The catalyzed conversion of quadricyclane to norbornadiene by rhodium complexes had been considered to be a concerted process [F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2184 (1967)].

[5] The interesting question as to whether the second step of eq 2 involves a concerted process or not has not been discussed.

[6] It is significant that *anti*-tricyclo[4.2.0.$0^{2,5}$]oct-3-ene on the other hand reacts readily with $AgBF_4$ at room temperature to yield bicyclo[4.2.0]octa-2,4-diene.

[7] According to the nmr spectrum and vpc analysis of the total reaction product there were no other materials produced in the reaction. The three components can be separated by preparative vpc. We thank Professor H. E. Zimmerman for providing us with the nmr and ir spectra of authentic samples of tetrahydrosemibullvalene. The reaction leading to tetrahydrosemibullvalene is analogous to that observed by W. G. Dauben and coworkers (*Tetrahedron Lett.*, 787 (1970)) and by L. A. Paquette and J. C. Stowell (*J. Amer. Chem. Soc.*, **92**, 2584 (1970)). The cagelike nature of the starting materials used by these workers, however, precluded reactions leading to products analogous to V.

[8] In this experiment the concentrations of syn isomer and the rhodium complex were 1.0 and 0.1 *M*, respectively. Similarly, the reaction of the syn isomer proceeds completely in the presence of only catalytic amounts of Ag^+.

[9] The reactions were run in $CHCl_3$ containing equimolar amounts of hydrocarbon and $[Rh(CO)_2Cl]_2$. The syn isomer reacted faster by approximately one order of magnitude in rate and yielded a red crystalline acyl–rhodium complex displaying a strong carbonyl absorption at