A simple electron-hopping model for the electrical conductivity is consistent with the observations that the conductivity is relatively insensitive to the anion structure, or to conjugation, but is very sensitive to the fraction of the ferrocene units oxidized.

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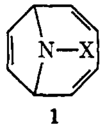
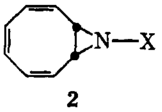
New Routes to 9-Azabicyclo[4.2.1]nona-2,4,7-trienes. On the Rearrangement of 9-Azabicyclo[6.1.0]nona-2,4,6-trienes

Sir:

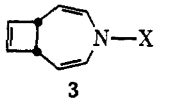
Carbanions are known to react with alkyl nitrites to afford oximes which are convertible to carbonyl compounds.[1] The reaction between dipotassium cyclooctatetraenide (COT^{2-})[2] and isoamyl nitrite in THF could give the bisoxime of cyclooctatetraenequinone, but instead the reaction leads by formal 1,4 bridging[3] to **1a** (74%, mp 112.0–112.5°). This result is most useful anyway because the bridged hydroxylamine (**1a**) represents an efficient, new entry into the 9-azabicyclo[4.2.1]nona-2,4,7-triene ring system **1**.[4] The ready availability of **1a** has allowed an examination of its chemistry and the results have proven to be both synthetically useful and interesting. We report on these results and on still another approach to ring system **1** through valence isomerization of a bicyclo[6.1.0]nonatriene (**2**).



1

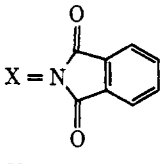


2



3

a, X = OH
b, X = H
c, X = $COOCH_3$
d, X = CN
e, X = NH_2
f, X =



g, X = $CH_2C_6H_5$
h, X = CH_3
i, X = +

Zinc–acetic acid reduction of **1a** affords the parent amine **1b** (95% crude, 61% after flash distillation); reaction of **1b** with methyl chloroformate affords **1c** (75%, mp 51.0–52.5°) and with cyanogen bromide gives **1d** (47%, mp 96.0–97.5°). The latter, the only previously known derivative of **1**, was prepared earlier by Anastassiou in 3.4% yield by reacting cyanogen azide with cyclooctatetraene.[4]

It is interesting that the reaction between COT^{2-} and isoamyl nitrite produces **1a** but not **2a** or **3a**. In earlier work, the urethane **2c** (ethyl ester) was observed to rearrange quantitatively to **3c** (80°, 30 min)[5] and not to **1c**. The previously reported cyanamide **2d** appeared not to rearrange thermally to either **1d** or **3d**.[4] Thus, at first glance it would appear that **1a** results from the direct (presumably in several steps) 1,4 addition of the alkyl nitrite to COT^{2-} and not by initial 1,2 addition followed by rearrangement.[2b,3] Additionally, we have been unable to detect the presence of any skeletal isomer which rearranges to **1a** in the reaction. However, we now report an example of just such a **2** → **1** transformation and this example provides yet another synthetic entry into ring system **1**.[6]

Lead tetraacetate oxidation of *N*-aminophthalimide in the presence of a tenfold excess of cyclooctatetraene in dichloromethane[7] affords a substance identified as **2f** (42%, mp 180.5–182.0°) [nmr ($CDCl_3$) τ 2.1–2.4 (4 H, m, aromatic), 3.3–4.2 (6 H, m, olefinic), and 6.81 (2 H, s, allylic);[8] uv (95% ethanol) λ_{max} 237 nm (ϵ 33,600); ir (KBr) 1697 cm^{-1} C=O)]. Hydrolysis (NaOH and then concentrated HCl) of **2f** afforded, after preparative vpc purification, a 20% yield of **1e** (colorless oil). The hydrazine **1e** was identified by comparison of its spectral characteristics with those of related bicyclo[4.2.1]nonatrienes described herein and by its independent synthesis from **1b**. The parent amine **1b** was allowed to react with hydroxylamine-*O*-sulfonic acid–KOH to afford a low yield (1.1% after purification) of **1e** which proved identical (nmr, ir, vpc) with the material prepared from **2f**. The hydrazine **1e** is best prepared from **2f**.

The hydrolysis of **2f** to **1e** was also effected with excess hydrazine in ethanol (1 hr) but the yield was lower. When **2f** was treated with excess hydrazine at room temperature for 3 min, examination of the crude mixture by nmr revealed the presence of small amounts of **1e**. We have been unable to detect the presence of **2e**. Com-

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(1) (a) C. H. DePuy and B. W. Ponder, *J. Amer. Chem. Soc.*, **81**, 4629 (1959); (b) E. H. Timms and E. Wildsmith, *Tetrahedron Lett.*, 195 (1971).

(2) (a) E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965); (b) see also, T. J. Katz, C. R. Nicholson, and C. A. Reilly, *ibid.*, **88**, 3832 (1966).

(3) Acylation of COT^{2-} affords mixtures of 1,2 and 1,4 adducts [T. S. Cantrell and H. Shechter, *ibid.*, **89**, 5868 (1967); **85**, 3300 (1963)]. Dichlorophenylphosphine reacts with COT^{2-} exclusively by 1,2 addition.[2b]

(4) A. G. Anastassiou, *ibid.*, **90**, 1527 (1968); **87**, 5551 (1965).

(5) S. Masamune and N. T. Castellucci, *Angew. Chem., Int. Ed. Engl.*, **3**, 582 (1964). The urethane **1c** is unchanged upon heating at 80° for at least 2 hr and further pyrolysis of **3c** affords a complex mixture from which some *N*-carbethoxyindole can be isolated (unpublished observations, this laboratory).

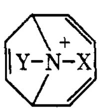
(6) This type of transformation was first observed in the phosphorus case reported by Katz.[2b] A sulfur example was reported recently [A. G. Anastassiou and B. Y-H. Chao, *Chem. Commun.*, 979 (1971)] and two carbon examples have also been reported [A. G. Anastassiou, R. P. Cellura, and E. Ciganek, *Tetrahedron Lett.*, 5267 (1970); D. Schönleber, *Chem. Ber.*, **102**, 1789 (1969)].

(7) D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Commun.*, 146 (1969). We thank Dr. Rees for the experimental details prior to publication.

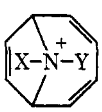
(8) The nmr spectrum is very similar to that of the corresponding phenylphosphorus derivative (P decoupled).[2b]

pared to **2c**[5] and **2d**,[4] **2f** proved to be quite stable thermally. At 78°, a sample of **2f** (degassed sample in benzene under vacuum, sealed ampoule) could be recovered unchanged after 24 hr. After heating a similarly prepared sample at ~115° for 3 hr, the nmr spectrum ($CDCl_3$) of the crude product revealed the presence of **2f**, a substance which appears to be **1f**, and other unidentified components. Besides the other resonances, the spectrum revealed signals expected for the ethylenic and bridgehead protons of **1f**: a sharp doublet ($J \sim 1$ Hz) at τ 4.51 and a broad doublet ($J \sim 4$ Hz) at 5.33, respectively. Without exception these signals are characteristic of all of the known nitrogen analogs of **1**. If the area of the resonances in the τ 2.0–2.5 region (aromatic) reflects total product concentration, the yields of **1f** and **2f** can be estimated to be ~30 and 17%, respectively. Unfortunately, we have been unable to isolate pure components from this mixture.

The reaction of **1a** with benzyl bromide affords a single hydroxylammonium salt (**4a** or **5a**, 89%, mp 143.0–143.5° dec). Structure **5a** is assigned to this salt because of the following experiments. Potassium carbonate treatment of the hydroxylammonium salt affords what is presumed to be the corresponding amine oxide (**5b**, 97%, mp 79–81° dec).[9] Both salt (**5a**) and oxide (**5b**) possess nmr spectral patterns characteristic of the other derivatives of **1** and both are convertible (zinc) to the benzylamine **1g** (54% from **5a**, mp 28.5–29.0°). The nmr spectrum ($CDCl_3$) of **5b** in the presence of a lanthanide-induced shift (LIS) reagent[10] relative to that in the absence of the LIS reagent reveals that the four diene protons are strongly shifted downfield and that the two ethylenic protons are only slightly shifted. This suggests that the oxide moiety lies over the 1,3-diene bridge and that therefore the oxide and the salt be assigned as **5b** and **5a**, respectively.[10] The epimeric oxide **4b** (97%, mp 93.0–94.0°) was prepared by the action of hydrogen peroxide on **1g**. The nmr spectrum of **4b** in the presence of the LIS reagent[10] showed a downfield shift of the ethylenic proton resonances (diene proton resonances only slightly shifted) as expected.[11]



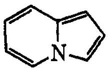
4



5

a, $X = CH_2C_6H_5$; $Y = OH$
b, $X = CH_2C_6H_5$; $Y = O^-$
c, $Y = CH_2C_6H_5$; $X = CH_3$

Interestingly, titanium trichloride reduction of **1a**[1b] in methanol affords, besides **1b**, pyrrocoline (**6**).[12]



6

The possibility that this rearrangement may *formally* be proceeding through the intermediacy of **1i** is being examined. We hope to report on other studies concerning the chemistry of **1**, **4**, and **5** in the near future.

The remarkable effect of the group X on the thermal reorganization pathway of **2** is most interesting. It is possible to explain these results as arising from electronic effects,[4] but we defer further discussion until more experimental information becomes available.[13]

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[9] In one instance, a solid sample of **5b** decomposed violently on heating at near its melting point. At room temperature in ether, **5b** rearranges to a new substance after standing for less than 1 day.

[10] Eu-Resolve-II from Alfa-Ventron Inorganics; R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 93, 1522 (1971).

[11] Reaction of the benzylamine **1g** with methyl iodide afforded a single ammonium salt tentatively assigned structure **5c** (85%, mp 147.0–147.5°). Reaction of the methylamine **1h** (prepared in a way similar to that of **1g**) with benzyl iodide afforded a single substance (88%, mp 139.0–139.5°) tentatively assigned as the epimeric salt **4c**. For examples of stereospecific alkylations of bridged amines, see G. Fodor, R. V. Chastain, Jr., D. Frehel, M. J. Cooper, N. Mandava, and E. L. Gooden, *ibid.*, 93, 403 (1971).

[12] V. Boekelheide and W. Feely, *J. Org. Chem.*, 22, 589 (1957).

[13] NOTE ADDED IN PROOF. In a recent paper [W. L. Mock and P. A. H. Isaac, *J. Amer. Chem. Soc.*, **94**, 2749 (1972)], the preparation of **1b** and the *N*-nitroso compound (**1**, X = NO) was reported. The latter can be converted in good yield to **1e**.

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Poly-*tert*-butylcyclobutenes. Novel Rearrangements to a Cyclopropene

Sir:

The solvolysis of cyclopropenylcarbinyl alcohol derivatives is known to give products derived from the cyclobutenyl cation *via* ring expansion.[1] The reverse rearrangement (*i.e.*, cyclobutene to cyclopropene) has heretofore not been reported.

As part of a research project designed to generate suitable precursors to poly-*tert*-butylcyclobutadienes, we have prepared 1,2,3-tri-*tert*-butyl-3,4-dichlorocyclobutene (**1**) and tri-*tert*-butylcyclobutadieneiron tricarbonyl (**2**). We now wish to report that both the solvolysis of **1** and the oxidation of **2** afford a cyclopropene derivative **6** as the sole product and present evidence that the former rearrangement proceeds *via* a carbonium ion pathway.

Addition of tri-*tert*-butylcyclopropenium fluoroborate[2] to a slight excess of dichloromethyllithium[3] in tetrahydrofuran at −65° gave 1,2,3-tri-*tert*-butyl-3-dichloromethylcyclopropene (**3**)[4,5] (Scheme I). Although stable for prolonged periods at room temperature, **3**,

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[1] R. Breslow, J. Lockhart, and A. Small, *J. Amer. Chem. Soc.*, **84**, 2793 (1962); R. Breslow and M. Battiste, *ibid.*, **82**, 3626 (1960); R. Breslow, H. Bozimo, and P. Wolf, *Tetrahedron Lett.*, 2395 (1970); W. J. Gensler, J. J. Langone, and M. B. Floyd, *J. Amer. Chem. Soc.*, **93**, 3828 (1971).

[2] J. Ciabattoni and E. C. Nathan, *ibid.*, **91**, 4766 (1969); J. Ciabattoni, E. C. Nathan, A. E. Feiring, and P. J. Kocienski, *Org. Syn.*, submitted for publication.

[3] G. Kobrich and W. Drischel, *Angew. Chem., Int. Ed. Engl.*, **3**, 513 (1964).

[4] A related synthesis in the trimethylcyclopropenium ion series has been reported. G. L. Closs and V. N. M. Rao, *J. Amer. Chem. Soc.*, **88**, 4116 (1966).

[5] All new compounds gave satisfactory elemental analyses (except for 3) and were further characterized by infrared, nuclear magnetic resonance, and mass spectroscopy.