Table I. Summary of Nmr Data

| Proton | Chemical shifts,[a] $\tau$<br>II[b,e] in THF | VII-OMe in DME | III[f] in THF-$d_8$ | III in DME |
|---|---|---|---|---|
| $H_{1,5}$ | 7.43 | 7.26 | 7.55 | 7.51 |
| $H_2$ | 4.08 | 3.90 | 7.16 | 7.18 |
| $H_4$ | 7.83[c]<br>8.21[d] | ~6.7 | 7.16 | 7.18 |
| $H_3$ | 4.85 | 4.72 | 4.61 | 4.65 |
| $H_6$ | 4.35 | 4.18 | 6.33 | |
| $H_7$ | 3.82 | 3.57 | 6.33 | |
| $H_{8a}$ | 8.10 | 8.2 | 9.13 | 9.16 |
| $H_{8b}$ | 8.34 | | 9.58 | 9.58 |

[a] Relative to $\tau$ 6.40 and 8.25 signals for THF or $\tau$ 6.58 and 6.75 signals for DME. [b] Based partly on 60- and 100-Mc spectra of neat II and II-2,4,4-$d_3$. [c] *exo*. [d] *endo*. [e] $J_{2,3} = 10$ cps; $J_{8a,8b} = 9$ cps; $J_{6,7} = 5.6$ cps; $J_{1,8a} = J_{5,8a} = 4$ cps; $J_{1,7} = 2.8$ cps; $J_{5,6} = 2.6$ cps; $J_{3,4}$-*exo*, $J_{3,4}$-*endo*, $J_{1,8b}$, $J_{5,8b}$ all $<2$ cps. [f] $J_{8a,8b} = 8$ cps; $J_{2,3} = 6.7$ cps; $J_{1,2} = 5.3$ cps; $J_{1,8a} = 4$ cps; $J_{1,7}$, $J_{1,8b}$ both $<2$ cps.

signal in ordinary THF or DME, but this difficulty is largely avoided in THF-$d_8$ (Table I and Figure 1).

In the nmr spectrum of the anion III the signal for vinylic protons $H_{2,4}$ appears as a triplet at $\tau$ 7.16, shifted upfield by 3.1 ppm relative to $H_2$ in diene II. The signal for $H_{6,7}$ appears as a singlet at $\tau$ 6.33, upfield by an average of 2.3 ppm relative to $H_6$ and $H_7$ in II. On the other hand, the signal for $H_3$ appears as a triplet at $\tau$ 4.62, actually slightly downfield (*ca.* 0.2 ppm) from $H_3$ in II. For the bridgehead protons $H_{1,5}$ in the anion, the signal appears as a skewed triplet at $\tau$ 7.55, nearly the same position as in II ($\tau$ 7.43). The signals for the $H_8$ protons appear as a multiplet at $\tau$ 9.12 for $H_{8a}$ and a doublet at $\tau$ 9.58 for $H_{8b}$, an average of 1.1 ppm upfield relative to the values for $H_{8a,b}$ in II.

All the features of the nmr spectrum of the anion are very much in accord with a delocalized bishomocyclopentadienide structure III with an appreciable aromatic ring current. Very striking is the relatively large upfield shift of the $H_{6,7}$ signal on going from II to III, in contrast with the negligible effect on the bridgehead 1,5 protons. The upfield shift of the $H_{6,7}$ signal by an amount *ca.* two-thirds as large as that for $H_{2,4}$ indicates the substantial delocalization of negative charge to $C_6$ and $C_7$. The chemical shifts of the $H_{2,4}$, $H_{6,7}$, and $H_3$ protons relative to the values in II, namely 3.1, 2.3, and −0.2 ppm, respectively, are in just the $C_{2,4} > C_{6,7} > C_3$ order for the predicted[3] charge distribution in anion III. The slight negative shift for $H_3$ relative to $H_3$ in II can be ascribed to the fact that the appreciable deshielding due to the aromatic ring current more than offsets the shielding effect of the negative charge at $C_3$, the very atom expected[3] to bear the least negative charge. The substantial shielding of the $H_8$ protons in III relative to II by 1.1 ppm may also be ascribed at least partly to a ring-current effect.[9]

Quenching of the carbanion III solutions in $CH_3OH$ or $CH_3OD$ produces essentially quantitatively the diene II containing <0.5% of tricyclic hydrocarbon IV or tetracyclic V. The identity of the diene from the $CH_3OH$ quench was confirmed by vpc and by the nmr spectrum of the recovered material. The data show that kinetic control in the protonation of III favors $C_{2,4}$ very strongly.[10] As regards possible stereospecificity of the protonation, the nmr spectrum of the diene II recovered from the $CH_3OD$ quench shows the presence of both *exo*- and *endo*-4-D in comparable amounts. Thus, no appreciable stereospecificity is evident in protonation of III, as was also indicated by the behavior of diene II in the deuterium exchange study.[5a]

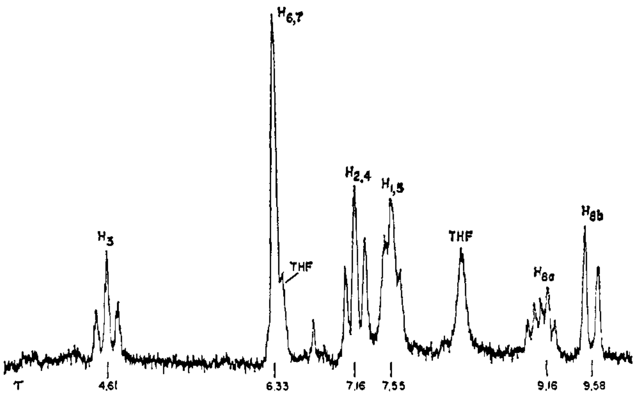

Figure 1. Nmr spectrum of bicyclooctadienide anion III in THF-$d_8$ (Varian A-60 spectrometer).

We are now employing carbanion III in the synthesis of homocounterparts of cyclopentadienyl complexes.

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[9] *E.g.*, S. Winstein, C. G. Kreiter, and J. I. Brauman, *J. Am. Chem. Soc.*, **88**, 2047 (1966).

[10] Appreciable amounts of tricyclic IV and tetracyclic V are detected in the products from Na–$NH_3$(l) reduction of tricyclic or tetracyclic halides or from preparation and hydrolysis of the corresponding Grignard reagents.[4c,5a] Thus, as we already surmised,[4c] these latter conversions do not proceed entirely *via* carbanion III.

[11] National Science Foundation Postdoctoral Fellow, 1965–1966.

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## Alkyladamantanes by Rearrangement from Diverse Starting Materials

*Sir:*

When Nujol (refined petroleum oil) is heated with aluminum halide catalysts, a mixture of polysubstituted alkyladamantanes is formed in yields of up to 11%. A variety of other substances, including cholesterol, cholestane, abietic acid, cedrene, caryophyllene, camphene, cyclohexene, cyclohexanol, cyclohexane, squallene, squallane, and dodecane, also give similar alkyladamantane mixtures (Table I).

These reactions were most successfully carried out in pressure bottles agitated by a wrist-action shaker at 110–130° for 2–5-day periods. Various catalysts were effective. The best were $AlBr_3$[1,2] and $AlCl_3$[3] "sludge" catalysts which facilitated contact when used in excess. To a lesser degree, $AlBr_3$ and $AlCl_3$ also worked. Solvents were not needed, but $CS_2$ could be

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[1] (a) V. Z. Williams, Jr., A.B. Thesis, Princeton University, 1965; (b) V. Z. Williams, Jr., P. von R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *J. Am. Chem. Soc.*, **88**, 3862 (1966).

[2] A. Schneider, R. W. Warren, and E. J. Janoski, *J. Org. Chem.*, **31**, 1617 (1966).

[3] Prepared from $AlCl_3$ and *t*-BuBr following Williams[1] by M. Nomura.

**Table I.** Summary of Various Better Alkyladamantane Rearrangement Runs

| Reactant | Wt, g | Solvent, g | Catalyst | Wt, g | Time, hr | Temp, °C ± 10° | Wt dist product[a] | Product analysis,[b] % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Me | $Me_2$ | $Me_3$ | $Me_4$ | MeEt | $Me_2Et$ | $Me_3Et$ | Other |
| Cholesterol | 10 | CH,[g] 25 | $AlBr_3$[c] | 80 | 75 | 130 | 4.5 | 1 | 16 | 26 | 35 | Tr | 3 | 12 | 7 |
| Cholesterol | 10 | None | $AlBr_3$[c] | 80 | 47 | 130 | 0.8 | 3 | 18 | 25 | 43 | | 1 | 3 | 7 |
| Cholesterol | 11 | $CS_2$, 22 | $AlBr_3$[c] | 90 | 75 | 120 | 1.1 | 1 | 7 | 21 | 2'52 | Tr | 2 | 7 | 10 |
| Cholestane | 10 | None | $AlBr_3$[c] | 50 | 70 | 120 | 1.0 | 2 | 15 | 30 | 35 | Tr | 2 | 6 | 10 |
| Nujol | 10 | None | $AlBr_3$[c] | 50 | 90 | 130 | 1.1 | 1 | 12[d] | 28[d] | 33[d] | | 4 | 14 | 8 |
| Nujol | 20 | None | $AlCl_3$ | 50 | 170 | 145 | 0.9 | 2 | 10 | 16 | 13 | 4 | 13 | 20 | 22 |
| Cedrene | 15.5 | None | $AlBr_3$[c] | 62 | 64 | 120 | 5.2 | 2 | 24 | 11 | 12 | | 2 | 43 | 6 |
| Cedrene | 31 | None | $AlCl_3$[c] | 90 | 66 | 120 | 13.6 | 1 | 7 | 4 | 3 | | 3 | 76[e] | 6 |
| Abietic acid | 10 | $CS_2$, 20 | $AlBr_3$[c] | 80 | 75 | 120 | 0.2 | Tr | 7 | 19 | 64 | | 12 | 5 | 3 |
| Camphene | 10 | None | $AlBr_3$[c] | 10 | 53 | 110 | 0.9 | | | M[f] | M[f] | | | | |
| Cyclohexane | 10 | None | $AlBr_3$[c] | 41 | 69 | 110 | 1.9 | | | | M[f] | | | | |
| Cyclohexene | 11 | CH,[g] 10 | $AlCl_3$ | 20 | 70 | 110 | 3.0 | | | | M[f] | | | | |
| Caryophyllene | 11 | None | $AlBr_3$[c] | 41 | 86 | 110 | 1.4 | | | | M[f] | | | | |
| Squallene | 15 | None | $AlCl_3$[c] | 107 | 90 | 120 | 0.8 | | | M[f] | M[f] | | | | |

[a] Boiling point range generally 75–110° (10 mm). [b] With 300 ft Golay DC-200 column. The alkyl groups are all at bridgehead positions. [c] Sludge catalyst. [d] Compounds isolated by preparative vpc and identified by nmr and mass spectroscopy. [e] Compound isolated by fractional distillation and identified by nmr. [f] Main products. [g] CH = cyclohexane.

used. Originally, cyclohexane was tried as a solvent, and some apparently excellent yields of alkyladamantanes were observed, but it was later found that cyclohexane itself would rearrange to alkyladamantane mixtures under similar conditions. The sludge catalysts[1-3] consist partially of organic materials as polymerized olefins, but these are not found to rearrange to alkyladamantanes.

The reaction products were worked up by petroleum ether extraction and vacuum distillation. Provided the reaction time was adequate, the fraction boiling in the 75–110° range at 10 mm consisted almost exclusively of a mixture of various alkyladamantanes! Adamantane itself was never observed, and 1-methyladamantane and 1-methyl-3-ethyladamantane were, at best, minor products. The major components usually were 1,3,5,7-tetramethyladamantane, 1,3,5-trimethyladamantane, and 1,3-dimethyladamantane (Table I). These last three compounds were separated by preparative gas chromatography from one of the Nujol products and were positively identified by comparison of their spectra with those of authentic materials.[1,2,4,5] The major product from cedrene was 1,3,5-trimethyl-7-ethyladamantane;[4b] it could be separated by fractional distillation. For the most part the very characteristic gas chromatographic retention times[1a,2,4c] were used for the identification of the alkyladamantanes; direct comparisons were made with a "standard mixture" containing all of the various components.

The yields reported in Table I are not to be considered optimum, since we were chiefly interested in surveying the nature of compounds which might rearrange to alkyladamantanes. This class appears to be quite large.

A number of years ago we carried out experiments similar to those described here.[6] Camphene and other $C_{10}$ hydrocarbons were heated with aluminum halide catalysts in hopes of obtaining adamantane. While many peaks appeared in the gas chromatograms of the products of these reactions, no adamantane was present and the studies were abandoned. At that time reference samples of the various polyalkyladamantanes were not available, and so the reactions described herein were not discovered. As can be seen from Table I, adamantane is indeed not formed from camphene, but almost 9% of alkyladamantanes can be obtained.

As a result of our early experiments, we had "adopted the working hypothesis that saturated tricyclic compounds of ten or more carbon atoms were most likely to rearrange to isomers containing the adamantane skeleton."[6] While this limited class of compounds probably do undergo adamantanoid rearrangements most readily,[1,2,4,6] it is now clear that a much wider variety of starting materials can be employed: functionalized acyclic, monocyclic, and polycyclic. For the preparation of specific compounds, the isomerization of saturated precursors is still to be preferred. Cedrane is converted cleanly to 1,3,5-trimethyl-5-ethyladamantane,[4b] but cedrene (Table I) gives this product in lower yield and only as the major component of a mixture. However, the possibility of the production of alkyladamantanes from crude hydrocarbon mixtures suggests that these reactions may have commercial potential.

It would be interesting to learn the details of the mechanisms whereby simple alkanes are converted into alkyladamantanes, but obviously this would be a difficult problem to study. One can speculate that acyclic hydrocarbons crack to form olefins which then cyclize. Further fragmentation, alkylation, and cyclization eventually give polycyclic adamantane precursors and then alkyladamantanes themselves. It is known that higher alkyladamantanes are subject to fragmentation and rearrangement reactions whereby side chains are lost or are converted to bridgehead methyl groups.[1b,2,4] The end products of such processes—the polymethyladamantanes—are the chief components of the mixtures observed here. The reaction conditions employed are rather destructive; all other compounds evidently are either polymerized or converted to tar and/or volatile materials. The alkyl-

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(4) (a) Review: R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, 64, 277 (1964); (b) P. von R. Schleyer, G. J. Gleicher, and C. A. Cupas, *J. Org. Chem.* 31, 2014 (1966); (c) S. Goscin, A.B. Thesis, Princeton University, 1965; (d) R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, 30, 789 (1965).

(5) We wish to thank Dr. W. Ando for his assistance in showing us microtechniques. A 50 ft × 0.25 in. 25% SE-30 column at 125° proved effective.

(6) P. von R. Schleyer and R. D. Nicholas, *Tetrahedron Letters*, 305 (1961); R. D. Nicholas, Ph.D. Thesis, Princeton University, 1960.

adamantanes alone seem to be sufficiently stable to resist these conditions, and their isolation in virtually uncontaminated form is possible.

Adamantane, various alkyladamantanes, and other diamondoid molecules are found in crude petroleum.[4a,7,8] The fact that simple hydrocarbons can be made to rearrange to alkyladamantanes may well relate to the question of how the latter compounds came to be present in petroleum, and to the origin of petroleum itself.[8]

**Acknowledgments.** The National Science Foundation provided funds for the purchase of the MS-9 mass spectrometer used in this research.

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(7) S. Hála, S. Landa, and V. Hanuš, *Angew. Chem. Intern. Ed. Engl.*, 5, 1045 (1966).

(8) R. Robinson, *Nature*, 212, 1291 (1966).

(9) On leave from Kyoto Technical University.

(10) National Science Foundation Undergraduate Research Participant, 1966–1967; A.B. Thesis, Princeton University, 1967.

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## Oxidative Dimerization of Carbanions in Liquid Ammonia

*Sir:*

Anhydrous liquid ammonia is known to be an excellent solvent for condensation reactions of anions with electrophilic reagents.[1,2] In addition, it is routinely employed to dissolve alkali and alkaline earth metals, the solutions of which constitute powerful reducing agents.[3] However, ammonia is not recognized as a medium for effecting oxidations of organic compounds, but this is not surprising in view of the fact that it is reported to be slowly oxidized to nitrogen and various inorganic ions by permanganate.[4]

It has now been found that carbanions prepared in liquid ammonia by means of alkali amides can be smoothly and conveniently dimerized by a variety of oxidizing agents. Such oxidative dimerizations appear to be not only instantaneous but also are unaccompanied by side reactions since recovered starting material is the only contaminant.

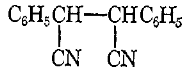
Preliminary results (Table I) indicate that treatment of sodiodiphenylmethane (**1′**, M = Na) (prepared from diphenylmethane and sodium amide in liquid ammonia) with solid potassium permanganate afforded 1,1,2,2-tetraphenylethane (**2**) in 42% yield (eq 1). Similar treatment of the corresponding potassio salt (**1′**, M = K) with this oxidizing agent afforded **2** in 69% yield. Treatment of the sodio salt **1′** (M = Na) with cupric bromide or potassium ferricyanide, or of the potassio salt **1′** (M = K) with molecular iodine, potassium dichromate, potassium perchlorate, or with air[5] also gave hydrocarbon **2**, but the yields were lower.

$$\underset{\mathbf{1}}{2(C_6H_5)_2CH_2} + \underset{(M\ =\ Na,\ K)}{MNH_2} \xrightarrow{NH_3} \underset{\mathbf{1'}}{2(C_6H_5)_2CHM} \xrightarrow{KMnO_4} \underset{\mathbf{2}}{(C_6H_5)_2CH_2CH_2(C_6H_5)_2} \quad (1)$$

That the oxidative dimerization is not limited to hydrocarbons was demonstrated by oxidation of various nitriles. Thus, treatment of the potassio salts of phenyl- and diphenylacetonitrile in ammonia with solid potassium permanganate afforded dimers **3** and **4** in 67 and 77% yield, respectively. Similar treatment of the potassio salts of *o*- and *p*-tolunitrile gave dimers **5** and **6** in 50 and 47% yield, respectively.[6]

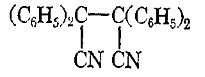
**Table I.** Oxidation of the Alkali Salts of Diphenylmethane by Various Oxidizing Agents in Liquid Ammonia

| Base | Oxidizing agent | Yield of dimer, % |
|---|---|---|
| $NaNH_2$ | $KMnO_4$ | 42 |
| $NaNH_2$ | $CuBr_2$ | 31 |
| $NaNH_2$ | $K_3Fe(CN)_6$ | 31 |
| $KNH_2$ | $KMnO_4$ | 69 |
| $KNH_2$ | $I_2$ | 51 |
| $KNH_2$ | $K_2Cr_2O_7$ | 4 |
| $KNH_2$ | $KClO_4$ | 5 |
| $KNH_2$ | Air | 3 |



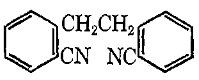
$$\underset{CN}{C_6H_5CH}\text{—}\underset{CN}{CH}C_6H_5$$

**3**

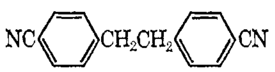


$$(C_6H_5)_2\underset{CN}{C}\text{—}\underset{CN}{C}(C_6H_5)_2$$

**4**



**5**



**6**

Although optimum conditions have not yet been established, the best experimental procedure to date involves the addition of the active hydrogen compound to an ammonia solution of 1 molecular equiv of potassium amide, followed after 15 min by 1 molecular equiv of solid potassium permanganate. Regardless of the color of the carbanion, a brilliant intense green color forms immediately, followed by a deep blue color. After 1 hr, the reaction mixture is treated with excess ammonium chloride and the product is then isolated using standard techniques.[2]

These results are to be contrasted with other base-catalyzed oxidative dimerizations of such compounds as *o*- and *p*-nitrotoluene which do not require an external oxidizing agent,[7] and of various autoxidation reactions which employ molecular oxygen as the oxidizing agent and which lead to oxygenated products.[8]

A broad study is in progress not only to assess the possible oxidative dimerizations of other mono- and multiple anions in liquid ammonia and amines, but

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(1) H. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, Inc., New York, N. Y., 1963, pp 286–291.

(2) See, for example, C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, 80, 6360 (1958), and later papers; this series of papers illustrates such condensations of carbanions.

(3) Reference 1, pp 151–285.

(4) R. Stewart in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 26.

(5) The fact that oxidation of **1′** (M = K) with air afforded **2** in only 3% yield negates its use as a synthetic method. It has been reported that such oxidation of the sodio salt (**1′**, M = Na) in ammonia proceeded smoothly, but neither conditions nor yields were reported; see C. B. Wooster, *Chem. Rev.*, 11, 1 (1932).

(6) All of the dimers reported are known compounds. In some cases, the present method of dimerization appears to be superior to those previously described; for example, see F. H. Rash, S. Boatman, and C. R. Hauser, *J. Org. Chem.*, 32, 372 (1967).

(7) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, 89, 300 (1967).

(8) See, for example, G. A. Russell and A. G. Bemis, *ibid.*, 88, 5491 (1966).