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.

(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.

M. Nomura,[9] P. von R. Schleyer, A. A. Arz[10]
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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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.

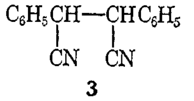
Preliminary results (Table I) indicate that treatment of sodiodiphenylmethane (**1′**, M = Na) (prepared from diphenylmethane and sodium amide in liquid ammonia) with solid potassium permanganate afforded 1,1,2,2-tetraphenylethane (**2**) in 42% yield (eq 1). Similar treatment of the corresponding potassio 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]

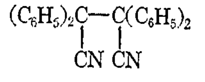
Table I. Oxidation of the Alkali Salts of Diphenylmethane by Various Oxidizing Agents in Liquid Ammonia

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



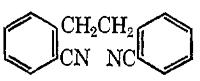
$C_6H_5CH(CN)\text{—}CH(CN)C_6H_5$

3



$(C_6H_5)_2C(CN)\text{—}C(CN)(C_6H_5)_2$

4



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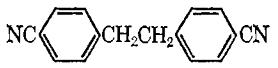

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Although optimum conditions have not yet been established, the best experimental procedure to date involves the addition of the active hydrogen compound to an ammonia solution of 1 molecular equiv of potassium amide, followed after 15 min by 1 molecular 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).

also to determine if various functional groups can be oxidized in these solvents.

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Edwin M. Kaiser
Department of Chemistry, University of Missouri
Columbia, Missouri 65201

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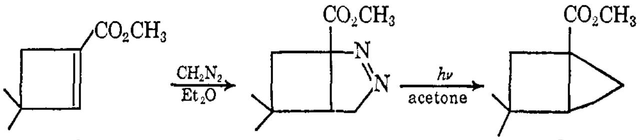
Substituted Bicyclo[2.1.0]pentanes

Sir:

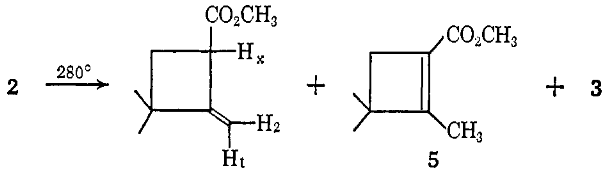
The pyrolytic or photolytic conversions of pyrazolines to cyclopropanes are valuable synthetic methods even though the mechanistic details of these reactions are still under active investigation.[1] These methods have been applied only to a limited extent to the preparation of fused ring cyclopropanes.[2–4] We wish to report a versatile high yield preparation of substituted bicyclo-[2.1.0]pentanes[5] using these methods.

Methyl 3,3-dimethylcyclobutene-1-carboxylate[6] (**1**) was converted to pyrazoline **2** in 93% yield by treatment with an excess of ethereal diazomethane at room temperature. The nmr spectrum of **2** exhibited the characteristic ABX pattern of a 3- or 5-substituted Δ^1-pyrazoline. Irradiation of **2** as a 1.5% solution in acetone[7] (irradiation in pentane solution produced a much more complex product mixture) caused an immediate evolution of nitrogen which was complete after 4 hr. Removal of solvent yielded a light yellow oil which consisted of 80% of one component by vpc analysis. Distillation (bp 34° (0.7 mm)) and final purification by gas chromatographic collection yielded ester **3** (ν_{CO} 1720 cm^{-1}) whose nmr spectrum exhibited three-proton singlets at 0.81, 1.26, and 3.57 ppm and two multiplets totaling five protons between 1.1 and 2.2 ppm. Hydrogenation of the ester[8] at room temperature using PtO_2–HOAc at 500 psi resulted in a slow uptake of hydrogen to produce methyl 3,3-dimethylcyclopentane-1-carboxylate whose nmr and mass spectra were identical with a sample prepared by a Favorskii reaction using 4,4-dimethylcyclohexanone.



1 2 3

In contrast to these photolytic results, pyrolysis of **2** yielded a three-major-component mixture containing **5** in largest quantity.[9]



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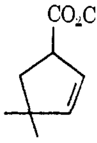
The structures of **4** and **5** follow clearly from spectral data. Compound **4** (ν_{CO} 1740 cm^{-1}, mol wt (mass spectroscopy) 154) showed proton resonance signals at 4.83 ppm (2 H, multiplet showing geminal and allylic coupling), the AB portion of an ABX centered at 2.0 ppm, a four-proton signal at 3.62 ppm (OCH_3 plus the X of the ABX pattern), and a six-proton singlet (perturbed) at 1.18 ppm. Compound **5** (ν_{CO} 1720 cm^{-1}) possessed an nmr spectrum containing signals at 1.12 (6 H, singlet), 3.62 (3 H, singlet), 1.85 (3 H, triplet, J = 2.0 cps), and 2.28 ppm (2 H, quartet, J = 2.0 cps).

This photolytic synthetic method is a general one. We have prepared 1-cyano-3,3-dimethylbicyclo[2.1.0]-pentane, 1-benzoyl-3,3-dimethylbicyclo[2.1.0]pentane, methyl-3,3,5-trimethylbicyclo[2.1.0]pentane-1-carboxylate (*exo*), methyl-3,3,5,5-tetramethylbicyclo[2.1.0]pentane-1-carboxylate, methyl-3-methylbicyclo[2.1.0]pentane-1-carboxylate, and methylbicyclo[2.1.0]pentane-1-carboxylate, among others, all in excellent yield. We have begun investigations of the chemical reactivity of these materials, particularly ring-opening reactions.

Pyrolysis[10] of **3** at 300° produced a nearly quantitative conversion to a 3:1 mixture of **6** and **7**.[11] Compound **6** (ν_{CO} 1740 cm^{-1}, mol wt (mass spectroscopy), 154) shows resonances at 1.05, 1.12, and 3.62 (each 3 H, singlets), 1.8–2.1 (2 H, multiplet), 3.3–3.7 (1 H, multiplet), and 5.35–5.7 ppm (2 H, multiplet). Compound **7** (ν_{CO} 1720 cm^{-1}, mol wt (mass spectroscopy) 154) possesses an nmr spectrum with resonances at 1.12 (6 H, singlet), 2.2–2.5 (4 H, multiplet), 3.67 (3 H, singlet), and 6.55 ppm (1 H, broadened singlet).



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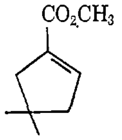

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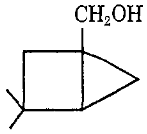

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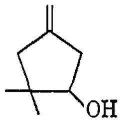

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(1) (a) T. V. Van Auken and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **84**, 3736 (1962); (b) D. E. McGreer, *et al.*, *Can. J. Chem.*, **43**, 1389, 1398, 1407 (1965); R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3768 (1965), and references cited therein; R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2587 (1966); P. Dowd, *ibid.*, **88**, 2589 (1966).

(2) K. Kocsis, P. G. Ferrini, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **43**, 2178 (1960); W. I. Awad, S. M. A. R. Omran, and M. Sobby, *J. Chem. U.A.R.*, **6**, 119 (1963); T. Shono, A. Oku, T. Morikawa, M. Kimura, and R. Oda, *Bull. Chem. Soc. Japan*, **38**, 940 (1965); W. Rundel and P. Kaestner, *Tetrahedron Letters*, 3947 (1965).

(3) See G. W. Krakower and H. A. Van Dine, *J. Org. Chem.*, **31**, 3467 (1966), for a discussion of the advantages of the ylide approach over the pyrazoline approach in certain steroidal systems.

(4) P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967).

(5) R. B. Turner, "Kekule Symposium on Theoretical Organic Chemistry," Butterworth & Co. (Publishers) Ltd., London, 1959, p 67, reports a very high 55.1-kcal/mole heat of hydrogenation for bicyclo-[2.1.0]pentane, indicative of its high degree of ring strain.

(6) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **29**, 801 (1964).

(7) Hanovia Type 673 A lamp using Pyrex apparatus.

(8) The mass spectrum of **3** exhibited a molecular ion at *m/e* 154 and intense fragment ions at *m/e* 139, 123, and 95 ($C_7H_{11}^+$, base peak). D. S. Weinberg and C. Djerassi [*J. Org. Chem.*, **31**, 3832 (1966)] have recently discussed the inherent stability of hydrocarbon ions derived from bicyclic compounds.

(9) Some mechanistic implications of these results are being studied further.

(10) M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962); J. P. Chesick, *ibid.*, **84**, 3250 (1962). These papers report pyrolysis studies of bicyclo[2.1.0]pentane and 2-methylbicyclo[2.1.0]-pentane.

(11) Pyrolysis at higher temperatures produces much larger quantities (>70%) of **7**. Control experiments indicate **6** is not appreciably isomerized to **7** under these higher temperature conditions.