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# HIGHLY STRAINED HYDROCARBONS.
# THE PHOTOLYSIS OF $\Delta^{2}$-CYCLOPENTENYLDIAZOMETHANE

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INTRAMOLECULAR addition of a divalent carbon atom to a carbon-carbon double bond has recently proven successful for the creation of systems incorporating a high degree of bond angle strain, e.g. bicyclobutane (1)[1] and the tricyclopentanones 2[2] and 3[3]. The present work represents an extension of this approach to a new hydrocarbon possessing the bicyclobutane skeleton: tricyclo$[2.1.1.0^{5,6}]$hexane (4).[4]

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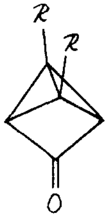
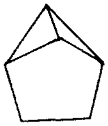


2 R = $C_6H_5$
3 R = $CH_3$



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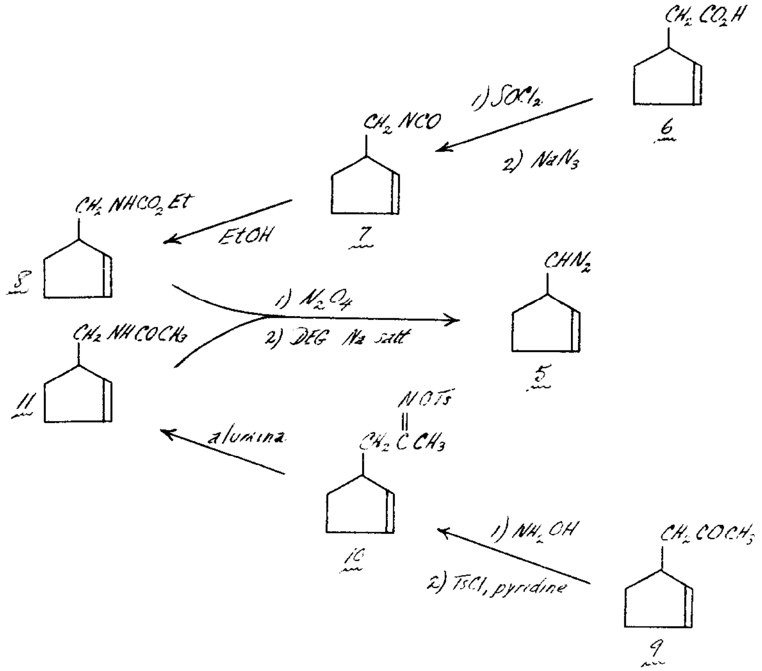
The key intermediate was $\Delta^{2}$-cyclopentenyldiazomethane (5), which was synthesized via each of the pathways shown in Chart I. Both $\Delta^{2}$-cyclopentenylacetic acid (6) and

$\Delta^2$-cyclopentenylacetone are available commercially, but the reaction sequence **9**-**5** proved to be the poorer route in terms of convenience and of yield. A major reason was that oximation of **9** yielded an oil containing much *anti* in addition to the desired *syn* isomer. Separation of isomers was not convenient at any stage; e.g. amide **11** was obtained as a sharply-boiling ~70:30 mixture with $\Delta^2$-cyclopentenyl-N-methylacetamide, the Beckmann rearrangement product of the tosylate isomeric with **10**. Hence diazomethane was presumably generated concurrently with **5**, and though the difference in volatility made separation easy the yield of **5** based on total nitrosoamide left much to be desired.

Accordingly, carboxylic acid **6** was transformed into the corresponding acyl azide, which rearranged *in situ* to isocyanate **7**. Addition of ethanol to the isocyanate function gave ethyl $\Delta^2$-cyclopentenylmethylcarbamate (**8**) as a colorless oil after distillation at 73-74° (0.2 mm.) (> 80% yield based on **6**). IR $\lambda_{max}^{neat}$ 3.02, 5.88, 6.52 $\mu$. *Anal.* Calcd. for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found: C, 63.83; H, 8.92; N, 8.32. The crude orange nitrosourethan (> 90% yield) prepared from **8** and dinitrogen tetroxide[5] was degraded by base to $\Delta^2$-cyclopentenyldiazomethane (50%). Yields suffered badly in this step unless addition of nitroso compound to the diethylene glycol (DEG) solution of DEG

## CHART I

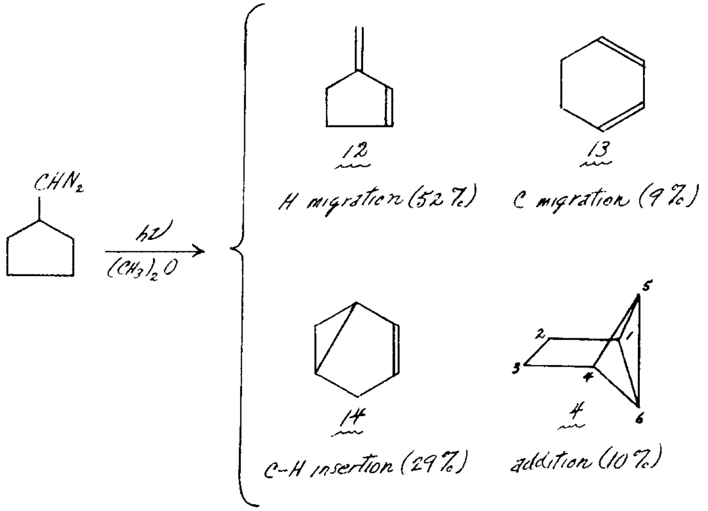


Ts = *p*-toluenesulfonyl

sodium salt was carried out at very low pressures. Under these conditions 5 distilled as it was formed into a trap cooled by liquid nitrogen, and redistillation was performed below 100 microns. The diazoalkene content of the resulting distillate, which also contained ethanol and water formed in the nitrosourethan decomposition, dropped off rather rapidly if the mixture was warmed to room temperature without being diluted. Measurement of the nitrogen evolved when acetic acid was injected into a dilute toluene solution of the product constituted a convenient assay for the diazo compound.

$\Delta^2$-Cyclopentenyldiazomethane was photolyzed in dimethyl ether, a solvent of such high volatility that product isolation occasioned no difficulty. Solutions (~2%) were irradiated until colorless at -78° using a Hanovia 450 watt Type L mercury lamp equipped with a Pyrex filter. They were then allowed to evaporate slowly until they reached room temperature, whereupon the volatile portion of the residue was distilled into a cold trap (~65% yield). Gas-liquid chromatography (g.l.c.) of these distillates on a dimethylsulfolane/firebrick column gave three well-resolved peaks with relative areas 10:29:61 (in order of increasing retention time). Prolonging the period of irradiation failed to alter the product ratio significantly, thus indicating that none of the products was formed or destroyed by secondary photochemical processes.

The largest g.l.c. peak, which was somewhat unsymmetrical, was shown by n.m.r. spectroscopy to correspond to a 1:6 mixture of 1,3-cyclohexadiene (13) and 3-methylenecyclopentene (12). Two slightly split singlets of equal area at $\delta$ = 2.12 and 5.77 were identical in position and contour with the spectrum of authentic 1,3-cyclohexadiene.[c] The remainder of the n.m.r. spectrum (slightly split singlets at $\delta$ = 2.49 and 6.09 and a multiplet centered at 4.75 with relative areas 2:1:1, attributable to methylene, vicinal olefinic and geminal olefinic protons, respectively) was indistinguishable from the spectrum of authentic 12.[7] Comparison of the mixture's infrared and ultraviolet spectra and g.l.c. retention time with those of the known diene samples confirmed the assigned composition.



The photolysis product of intermediate retention time exhibited complex n.m.r. absorption in the $\delta$ = 0.5-3.0 region and a pair of multiplets centered at $\delta$ = 5.29 and 5.84 (relative areas, 6:1:1). Thus both vinyl and cyclopropyl protons were present, an inference which pointed strongly to the structure 14. When subjected to the

Simmons-Smith reaction, cyclopentadiene afforded authentic bicyclo[3.1.0]-2-hexene; its identity with the photolysis product was clear from a comparison of retention times and spectra (infrared, n.m.r.).

The chromatographic peak of shortest retention time corresponded to a hydrocarbon isomeric with the other three (Anal. Calcd. for $C_6H_8$: C, 89.94; H, 10.06. Found: C, 89.84; H, 10.06. Mass spectral mol. wt., 80). No double bond absorption was discernible in the infrared spectrum, but a prominent band at 3.28 µ ( $CCl_4$) indicated the presence of C-H bonds possessing a high degree of s character. Clear-cut evidence for structure 4, tricyclo-[2.1.1.$0^{5,6}$]hexane, was provided by the n.m.r. spectrum (Fig. I). The three signals at $\delta$ = 1.23, 1.63 and 2.00

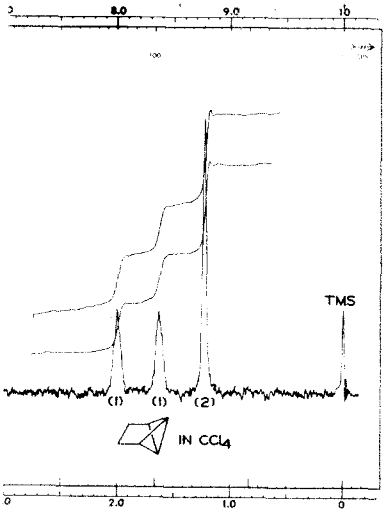
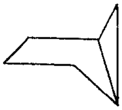


Fig. I

(relative areas 2:1:1) are attributable to the methylene protons at C.2 and C.3, the C.1 and C.4 methine protons and the C.5 and C.6 methine protons, respectively.[8] It is apparent from the line breadths that the two pairs of methine protons are coupled, albeit weakly.

Hydrogenation of 4 in diglyme solution over 10% palladium-on-charcoal proceeded with no inflection in the absorption curve until 1.95 moles had been consumed. The sole product was methylcyclopentane. Since the logical intermediates 15 and 16 were shown to be stable under the hydrogenation conditions, it is probable that two bonds are hydrogenolyzed simultaneously.[9] The possibility that rearrangement occurs during hydrogenation, as it does with the isomeric tricyclohexane 17,[10] has not been excluded, however.



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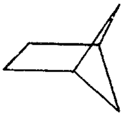

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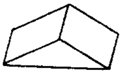

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## REFERENCES AND FOOTNOTES

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2. S. Masamune, ibid., 86, 735 (1964).
3. W. von E. Doering and M. Pomerantz, Tetrahedron Letters, No. 17, p. 961 (1964).
4. Representatives of this ring system have been synthesized by J. Meinwald, C. Swithenbank and A. Lewis (J. Am. Chem. Soc., 85, 1880 (1963)) and by A. Small (Ibid., 86, 2091 (1964)).
5. E. H. White, ibid., 77, 6008 (1955).
6. All n.m.r. spectra were measured in carbon tetrachloride solution containing tetramethylsilane as internal standard.
7. Alkaline hydrolysis of the amide 11 gave $\Delta^2$-cyclopentenylmethylamine, which was completely methylated and subjected to the Hofmann elimination in order to provide authentic 3-methylenecyclopentene. See I. N. Nazarov and N. V. Kuznetsov, J. Gen. Chem. U.S.S.R. (Eng. transl.) 29, 754 (1959).
8. Assignment of the methine protons is based on analogy to the homolog of 4 prepared by W. R. Moore, H. R. Ward and R. F. Merritt (J. Am. Chem. Soc., 83, 2019 (1961)) and to the derivative of 4 synthesized by Meinwald and his coworkers (ref. 4).
9. Similar behavior was observed by Meinwald in the hydrogenolysis of tricyclo[2.1.1.0$^{5,6}$]hexane-5-t-butylcarboxamide (ref. 4).
10. D. M. Lemal and K. S. Shim, J. Am. Chem. Soc., 86, 1550 (1964).