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THERMAL DECOMPOSITION OF TROPYL ACETOALDEHYDE TOSYLHYDRAZONE

H. Tsuruta, K. Kurabayashi and T. Mukai
Department of Chemistry, Faculty of Science
Tohoku University, Sendai, Japan

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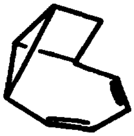
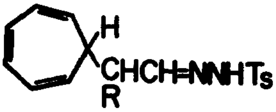
Intramolecular addition of a carbene to a double bond is very useful for the synthesis of highly strained hydrocarbons (1,2,3,4). Although the majority of this type of reaction concerns the addition to an isolated double bond, a few papers have been reported on the intramolecular addition of a carbene to conjugated double bonds (5,6). For example, Doering and Roth have synthesized barbaralone by the reaction of ketocarbene with the cycloheptatriene system and Jones and Scott reported the interesting thermal reaction of bicyclo[6.1.0]nona-2,4,6-triene-9-aldehyde tosylhydrazone giving bicyclo[4.2.2]deca-2,4,7,9-tetraene (5).

In an attempt to synthesize the strained hydrocarbons, I and II, we investigated the reaction of β-(7-tropyl)ethyl carbene (IV) and found that, in addition to formation of compound I, an intriguing rearrangement which may arise from compound II occurs.

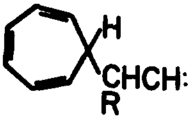
I



II



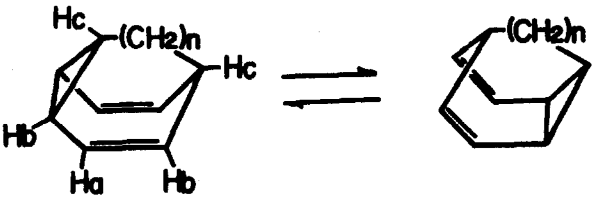
III R=H
VI R=C_6H_5



V R=H
VII R=C_6H_5

Pyrolysis of the tosylhydrazone (III), m.p. 130° (dec)(7), of tropyl acetoaldehyde (8) in dioxane at 90-95° afforded, on purification by means of extraction with aqueous silver nitrate and alumina column chromatography, an oily product in ca. 20 % yield, which, by v.p.c., was found to be a mixture of two hydrocarbons in a ratio 2:9. This oil, upon separation with the aid of preparative v.p.c. (20 % carbowax on chromosorb), provided two components, I and V. Both compounds have the same empirical formula C_9H_{10} and molecular weight 118 (mass spectra). The major product V, bp 73-74°/49 mm Hg, has the following data: infrared spectrum (neat) 3021, 2924, 2841, 1642, 1595, 1445, 732, 679, cm^{-1}; ultraviolet spectrum in cyclohexane, mμ (log ε), 259 (3.43), 268 (3.39), 278 (3.13)(sh); nmr in CCl_4(60 Mc), τ 8.71 (doublet, J=11.3 cps, 1H), 8.07 (triplet of doublet, J=11.3 and 6.2 cps, 1H), 6.92 (broaden triplet, J=6.2 cps, 2H), 4.87 (multiplet, 2H) and 4.12 (complex multiplet, 4H). When V was hydrogenated over platinum oxide in ether, it afforded bicyclo[4.2.1]nonane, m.p. 94-95° (9). These data confirm the structure assignment of V as bicyclo[4.2.1]nona-2,4,7-triene, previously synthesized by Cannell (10). The infrared spectrum of V was completely identical with that of an authentic sample (10).

On the other hand, the structure of the minor product I, m.p. 39-40° was elucidated from the following evidence: ultraviolet spectrum in cyclohexane; end absorption. The nmr spectrum (Table I) showed only four varieties of protons in a ratio 2:4:2:2. The chemical shifts of each group of signals are similar to that of barbaralone (6,11), dihydrobullvalene (12) and semibullvalene (13) except for C_9-protons, suggesting that I is tricyclo[3.3.1.0^{4,6}]nona-2,7-diene synthesized by Doering and Hartenstein (14) by reduction of barbaralone. As shown from this nmr specturm, compound I is in rapid equilibrium with its degenerate valence tautomers (Ia ⇌ Ib). The fact that a signal of methylene of I appeared in considerably high field may be ascribed to the anisotropic effect of the double bond. It should be noted that the chemical shift of Ha shifts to lower field as number of methylene group increased (n=0 → 2), while signals of other protons (Hb, Hc) to higher field.



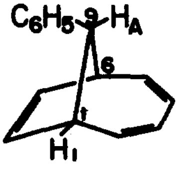
Ia : n=1 Ib : n=1

TABLE I. Nmr Spectra of I and Related Compounds.

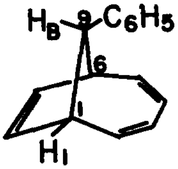
	Ha	Hb	Hc	-CO- or $-(CH_2)_n-$	Ref
barbaralone	τ 4.3	τ 5.8	τ 7.3	-CO-	6, 11
semibullvalene	4.92	5.83	7.03	n=0	13
I*	4.45	6.10	7.72	$-CH_2-$ τ 8.98	This work
dihydrobullvalene	4.37	6.32	8.1	$-CH_2CH_2-$ ~8.1	12

* Nmr spectrum of I was measured in CCl_4 on Varian A 60. The following coupling constants were obtained by decoupling technique using Varian HA 100; J_{ab} ~ 8.0, J_{bc}=7.0 and J_c, methylene proton=2.5 cps.

Similar to the decomposition of III, the tosylhydrazone (VI), m.p. 166°, of α-phenyl-α-(7-tropyl)acetoaldehyde affords hydrocarbons in 33 % yield, which contain two components in a ratio 10:1. The major hydrocarbon $C_{15}H_{14}$ (VIII), m.p. 22-25°, has the following physical data: infrared spectrum (neat); 3030, 2933, 1605, 1499, 1456, 725, 678 cm^{-1}; ultraviolet spectrum in cyclohexane mμ (log ε), 255 (3.35)(sh), 261 (3.39)(sh), 264 (3.40), 271.5 (3.38), 283 (3.17)(sh); nmr in CCl_4 (60 Mc), τ 7.18 (singlet, 1H) 6.90 (broaden doublet, J=6.5 cps, 2H), 4.83 (multiplet, 2H) and 3.65 ~ 4.35 (complex multiplet, 4H) and 2.93 (singlet, 5H). The similarity of the above data to those of V suggests that VIII is the 9-phenyl derivative of bicyclo[4.2.1]nona-2,4,7-triene, in which both exo (VIIIa) and endo-forms (VIIIb) are possible.



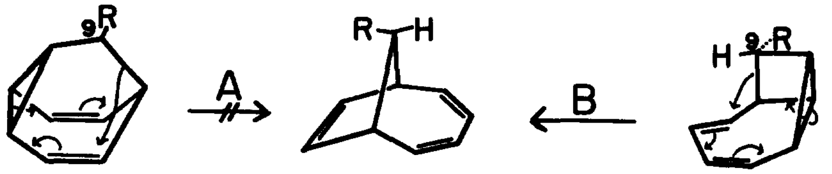
VIIIa



VIIIb

In the nmr spectrum of VIII, the signal of the proton at the 9 position appears as a singlet at τ 7.18, suggesting $J_{1,9}=J_{6,9}=0$, that is, the dihedral angle between the two protons of the 1 and 9 or 6 and 9 positions is nearly 90°. Inspection of the Dreiding Model of VIIIa and VIIIb indicates that the dihedral angle between $H_{1(6)}$ and H_A is 90° but that between $H_{1(6)}$ and H_B is 30°. These facts safely confirm the structure of VIII as exo-form VIIIa.

The formation of compound I clearly could be explained by the intramolecular addition of the carbene to the C_3-C_4 double bond of IV (6). On the other hand, compound V or VIII could be formed from compound I or IX (path A) or from the highly strained intermediate II or X (path B) by thermal rearrangement as depicted in the following scheme. However, path A can be discarded, because heating I in refluxing dioxane for two hours did not result in formation of V. Futhermore, the stereospecific formation of VIII from VI can be explained by assuming that the stable intermediate (X), having phenyl group situated behind the cyclobutane ring, forms stereospecifically and that X rearranges to VIII through the path B without change of the configuration at 9 position.



I R=H
IX R=C6H5

V R=H
VIII R=C6H5

II R=H
X R=C6H5

Further study for elucidation of the mechanism for the formation of V or VIII is in progress.

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