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BARBARALYLIDENE, A NEW TYPE OF NUCLEOPHILIC CARBENE$^{1)}$

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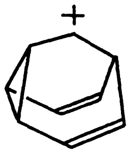
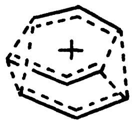
This study was carried out to elucidate the properties of barbaralylidene (II). Vacuum thermolysis of sodium salt of barbaralone tosylhydrazone (III) afforded mainly ethynylcycloheptatrienes (IV, V, and VI). The carbene (II), which was derived from III, did not add to electron-rich olefins, but instead added to electron-deficient olefins such as dimethyl fumarate, maleate or methyl acrylate to give spiro-cyclopropane derivatives (VII or XII) in addition to VIII or IX.

Although some considerations have been made on the singlet carbene possessing nucleophilic character,$^{2)}$ only a few species such as cyclopropenylidene,$^{3)}$ cycloheptatrienylidene$^{4)}$ and annulenylidenes$^{5)}$ have been studied in detail. In connection with the 9-barbaralyl cation (I), in which the peculiar stabilization due to D_{3h} symmetrical nonclassical cation (Ia) was emphasized experimentally$^{6)}$ and theoretically,$^{7)}$ we intended to examine the properties of barbaralylidene (II) under the expectation that II should be a nucleophilic singlet carbene as represented by formula IIa.

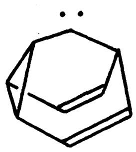
For the formation of II, thermolysis of sodium salt of barbaralone tosylhydrazone (III) was attempted.$^{8)}$ Thus, firstly the vacuum pyrolysis was carried out at 180°C and 7-, 3-, and 1-ethynylcycloheptatrienes (IV, V, and VI)$^{9)}$ were obtained in 32, 3, and 2% yields, respectively, in addition to seven aromatic hydrocarbons.$^{10)}$ The main product (IV) may be formed by a nonlinear cheletropic cleavage of the cyclopropane ring of the expected singlet carbene (II).11,12) The minor products, V and VI, are assumed to be derived from IV by thermal 1,5-hydrogen shifts.13)



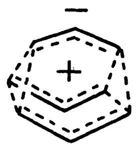
I



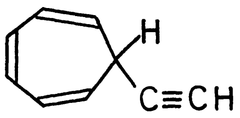
Ia



II

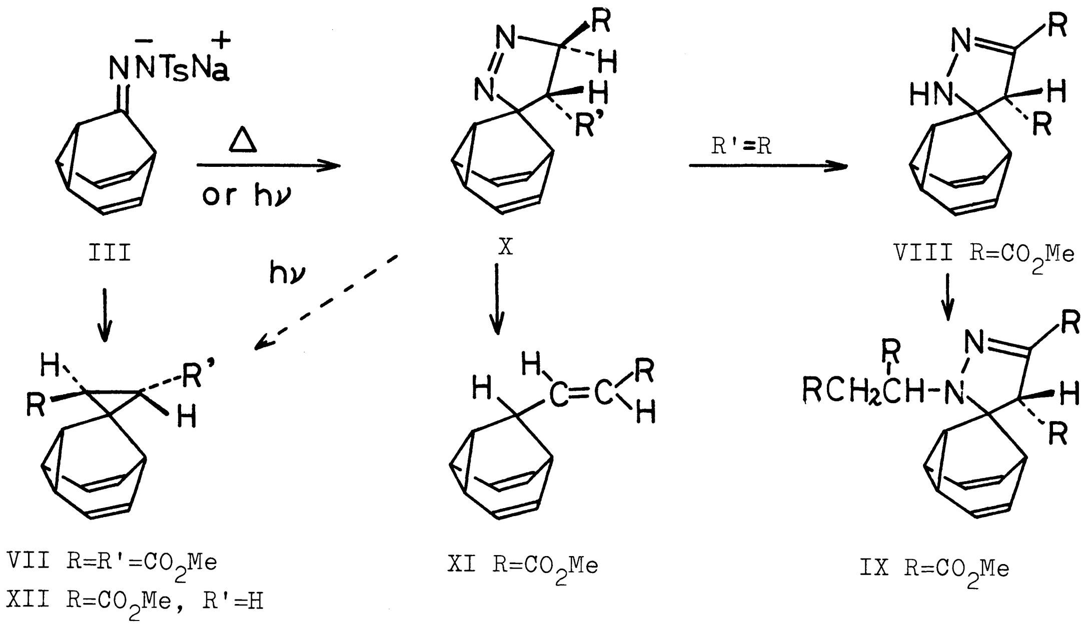


IIa



IV

When the thermolysis of III was carried out in diglyme at 150-170°C, in the presence of electron-rich olefins such as cyclohexene and styrene, adducts possessing the cyclopropane ring could not be detected except for the formation of a trace of V. Contrary to this finding, the thermal decomposition of III in the presence of electron-deficient olefins, such as dimethyl fumarate or maleate, afforded three products, VII, mp 135°C, VIII, mp 122°C, and IX, mp 117°C,14) in yields shown in the Table. The structures of the spiro compound with a cyclopropane ring (VII) and the spiro-type pyrazoline (VIII) were based on their ir (in KBr, 1710 and 1735 cm^{-1}), mass (M^{+}, 260 and 288) and nmr spectra.15,16) The nmr spectrum of VII15) shows the presence of two trans protons in the cyclopropane ring and suggests the occurrence of a degenerate Cope rearrangement in the barbaralane moiety, while that of VIII16) indicates that the equilibrium of VIII shifts to one structure, because of asymmetry of the molecule. The formation of only the trans bis(methoxycarbonyl) derivative VII from dimethyl maleate could be explained by the cis-trans isomerization of the olefin4b) or by the intervention of an intermediate in which bond rotation is allowed during the addition.4i,17) The formation of the pyrazoline derivative VIII should be attributed to the rapid prototropy of the preformed cyclic azo-compound X. The nmr spectrum of IX is too complicated to elucidate, but that of its adduct with tetracyanoethylene, mp 225-227°C, exhibits signals similar to those of the corresponding adduct of barbaralone.18) Furthermore, the addition of VIII to dimethyl maleate led to the formation of IX, supporting the structure of IX.



III

X

VIII $R=CO_2Me$

VII $R=R'=CO_2Me$
XII $R=CO_2Me$, $R'=H$

XI $R=CO_2Me$

IX $R=CO_2Me$

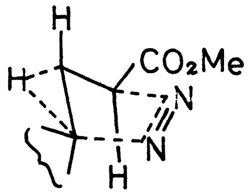
Table. Products from the Reaction of III with Dimethyl Fumarate or Maleate.

Starting olefins	(equiv.)	Conditions	(react. time)	Products, % VII	VIII	IX
Fumarate	(1.2)	155° C	(30 min)	12	25	-
Maleate	(1.2)	155° C	(30 min)	9	39	-
Fumarate	(1.2)	170° C	(30 min)	25	11	-
Maleate	(1.2)	170° C	(30 min)	23	10	-
Maleate	(3.0)	155° C	(30 min)	5	-	46
Fumarate	(1.2)	hν,[a] r.t.	(5 hr)	-	6	7[b]
Fumarate	(3.0)	hν,[a] r.t.	(20 hr)	-	36	6

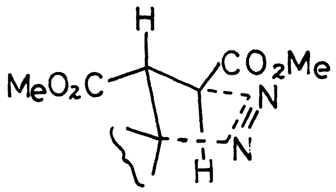
a) Direct irradiation with Toshiba H-400p Hg lamp.

b) With recovery of 18% of barbaralone tosylhydrazone.

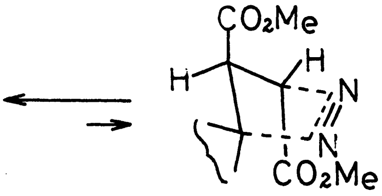
The thermal reaction of III with methyl acrylate was also carried out, in which case an α,β-unsaturated ester XI was obtained (30% yield) in addition to an expected spiro-cyclopropane derivative XII (15%). The structure of XII was deduced by a comparison of its spectral properties with those of VII; XI was assigned to methyl trans-β-9-barbaralylacrylate by its ir (neat, 1725 cm^{-1}) and nmr spectra.[19)] It should be noted here that no pyrazoline-type products were found, but instead unsaturated ester XI became the major product. Such a result would be accomodated by a transition state possessing a folded pyrazoline-type structure XIII, in which nitrogen is easily extruded in a concerted manner accompanied by a 1,2-hydrogen shift.[20] In contrast to this, the transition state with dimethyl fumarate should be a structure having two equatorial methoxycarbonyl groups (XIVa) rather than that with two axial groups (XIVb). Such a conformer XIVa is unsuitable for a concerted 1,2-hydrogen shift leading to an unsaturated ester, and instead it may convert into VIII by prototropy.



XIII



XIVa



XIVb

For comparison with the thermal reactions, photolysis of III was carried out in the presence of dimethyl fumarate. The results are shown in the Table. It should be noted that pyrazolines VIII and IX could be isolated, but the spirocyclopropane VII was not detected. In general, cyclic azo-compounds such as X are known to decompose to cyclopropanes and nitrogen on irradiation more readily than by heating.[21] Thus, it seems unreasonable that the cyclopropane adduct VII originates only from the cyclic azo-compound X. It is rather plausible that, under the thermal conditions, diazo-barbaralane, as a precursor of X, partially decompose to barbaralylidene (II), besides affording X; and II adds to electron-deficient olefins to give VII. This explanation is supported by the fact that yield of the spiro-cyclopropane VII increased, whereas that of the pyrazoline VIII decreased, when the thermal reaction of III with the olefins was carried out at higher temperatures (see Table). Thus, it may be concluded that II is likely a nucleophilic singlet carbene. However, it is noteworthy that the reaction of III with electron-deficient olefins is a little different from that of sodium salt of tropone tosylhydrazone, which provided only spiro[2.6]nonatriene and no pyrazoline derivatives.[4]

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9) The structures of IV, V, and VI were deduced by inspection of their spectral properties. As an example, those of IV are presented here; ir (neat), 3300 and 2120 cm^{-1}; nmr (60 MHz, CCl_4, δ), 6.54 (t, H_3, H_4), 6.05 (d,t, H_2, H_5), 5.20 (d,d, H_1, H_6), 2.6-2.1 (m, H_7), and 2.00 (d, -C≡CH); J values (Hz), $J_{1,2}=J_{5,6}=9$, $J_{2,3}=J_{4,5}=3$, $J_{1.7}=J_{7,6}=6$, and $J_{7,-C\equiv CH}=2.5$

10) They are toluene, phenylallene, allylbenzene, β-methylstyrene, styrene, phenylmethylacetylene, and benzylacetylene. The formation of these products will be discussed elsewhere.

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14) Elemental analyses were satisfactory for all new compounds except for V and VI.

15) Nmr of VII (60 MHz, $CDCl_3$, δ); 3.67 (s, $COOCH_3$), 2.28 (s, cyclopropane-H), 5.73 (m, H_3 and H_7), 4.10 (m, H_2, H_4, H_6, and H_8), and 2.50 (m, H_1 and H_5).

16) Nmr of VIII (100 MHz, $CDCl_3$, δ); 3.76 (d,d,d, H_3 and H_7), 5.02 (d,d, H_4 and H_6), 3.23 (d,d, H_2 and H_8), 2.60 (t,t,d, H_5), and 2.40 (t,d, H_1); J value (Hz), $J_{1,2}$=7.0, $J_{2,3}$=6.5, $J_{3,4}$=8.5, $J_{4,5}$=6.5, $J_{1,5}$=3.0, and $J_{3,5}$=1.5.

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19) Nmr of XI (100 MHz, $CDCl_3$, δ); 3.69 (s, $COOCH_3$), 5.78 and 6.73 (olefinic protons in side-chain, J=15.5, 8.0, and 1.0 Hz), 5.69 (m, H_3 and H_7), 4.04 (m, H_2, H_4, H_6, and H_8), 2.32 (d,t, H_1 and H_5) and 2.02 (d,d,t, H_9); J value (Hz), $J_{1,2}$=5.5 and $J_{1,9}$=2.5. This spectrum shows that XI is also in equilibrium between two degenerated isomers.

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