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50. Quadricyclanes. Part II: Electronic Structure and Chemical Reactivity

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(12. XI. 73)

Summary. The electronic structure of quadricyclane and 3-methylidenequadricyclane obtained by photoelectron spectroscopy, is used as a basis for the discussion of cycloadditions to these systems. The electronic structure of 3-heteroquadricyclanes, arrived at by theoretical calculations, agrees well with that expected from the above measured systems. A surprising outcome is that the orbital most responsible for the observed 2,4-cycloadditions to these heterosystems is *not* the HOMO but the third highest orbital which lies well below the former. This strongly suggests that these 2,4-cycloadditions proceed not in a concerted fashion but presumably involve as rate-determining step the formation of a resonance-stabilized zwitterionic intermediate. The nature of this intermediate is discussed and the feasability of its formation investigated on the basis of thermochemical considerations.

Introduction. – In the preceeding paper [1] the electronic structure of quadricyclane (**1**) and 3-methylidenequadricyclane (**2**) has been investigated by means of photoelectron spectroscopy. The present work describes some consequences concerning the interpretation of the chemical reactivity of quadricyclane systems which derive from these results.

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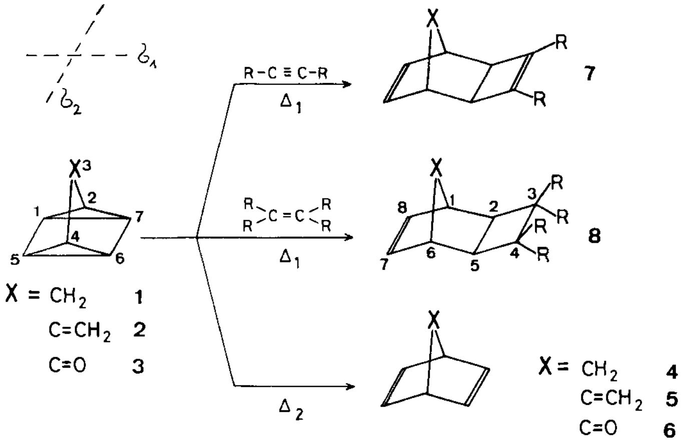
[1] 'Small Ring Compounds' part 10. Part 9 [1].

Cycloadditions to quadricyclane (**1**) *and 3-methylidenequadricyclane* (**2**). As shown in the above Scheme, **1**, **2** and **3** under mild conditions (Δ_1) suffer a 1,5-attack of the dienophile, leading to the tricyclic systems **7** and **8** [2] [3]. Since this *bishomo*-diene reaction exhibits remarkable *regio* – as well as *stereo*-specificity, it was concluded that it proceeds in a concerted fashion [3]. Only at elevated temperatures ($\Delta_2 > \Delta_1$) does the symmetry forbidden [$\sigma_s^2 + \sigma_s^2$]-cycloreversion to the norbornadienes **4**, **5** and **6**, resp. occur with *e.g.* E_a (**1**→**4**) = 33.5 kcal/mol [4]. It is important to note, however, that compounds of type **6** decarbonylate to benzene derivatives and that the trienes **5** are formed only to about 10%, the main product being an oxygen containing heterocycle [2]. Hence, in addition to the difference in reaction temperatures ($\Delta_2 > \Delta_1$) this provides further evidence that thermolysis and cycloaddition follow a different reaction path.



The PE.results discussed in [1] suggest that the correlation diagram of [3] needs to be looked at with caution. There, the two top occupied MO's of **1** where thought to be the out- and in-phase linear combinations of the C(1)-C(7)- and C(5)-C(6)-σ-bond orbitals of **1**. These were correlated with the out- and in-phase linear combinations of the C(2)-C(3)- and C(4)-C(5)-σ-bond orbitals of the cycloadduct **8**. Contrary to this view, the PE.analysis of **1** has shown that the two above mentioned orbitals lie energetically at the first and the *fourth* position (*cf.* fig. 5 in previous paper). In between these, two σ-orbitals of S(A)- and A(A)-symmetry are found which show in fact slight antibonding character for the bonds C(1)-C(7) and C(5)-C(6).

The PE.spectrum of cyclobutane and MINDO/2-calculations for **8** (R=H, X=CH_2) also suggest that the highest lying σ-orbital of S-type of **8** is not related to the *Walsh*-b_{1g}-orbital of cyclobutane as implied in [3] but is that σ_S-orbital which together with the σ_A-HOMO forms a real representation to the degenerate highest lying *Walsh*-e_u-orbitals in cyclobutane [5–7]. The third orbital is again of A-type, its shape being reminiscent of the pseudo-π b_{1u}-orbital of cyclobutane. The fourth orbital of S-symmetry finally is derived from the b_{1g}-orbital of cyclobutane and has the shape indicated in [3].

From the proper correlation diagram of Fig. 1 it can be seen that there is still complete correlation between bonding levels and therefore a prediction of allowedness for concerted *exo*-cycloaddition to **1** as already found in [3]. Hence the final result is unchanged but has been arrived at by taking into account the true electronic structure of the reactants.

This problem has arisen because a *Woodward-Hoffmann* treatment of pericyclic reactions [8] requires the selection of only a few "critical" (high-lying) orbitals. The question whether an orbital shall be considered as "critical" or not cannot *a priori* be answered unambiguously. At this point it should be recalled that the *Dewar-Zimmermann* approach [9] is of purely topological nature and therefore less ambiguous in the choice of guidelines[2]).

Cycloadditions to 3-aza- (**9**) *and 3-oxa-quadricyclane* (**10**). Contrary to the above discussed case cycloaddition of a dienophile to the 3-heteroquadricyclanes **9** and **10** proceeds *via* 2,4-attack, yielding the tricyclic systems **13** [2] [10]. It is noticeable that the required temperature range is roughly that where unimolecular transformation of **9** and **10** to the azepine **11** and the oxepine **12** resp. occurs ($\Delta_2 \approx \Delta_1$).

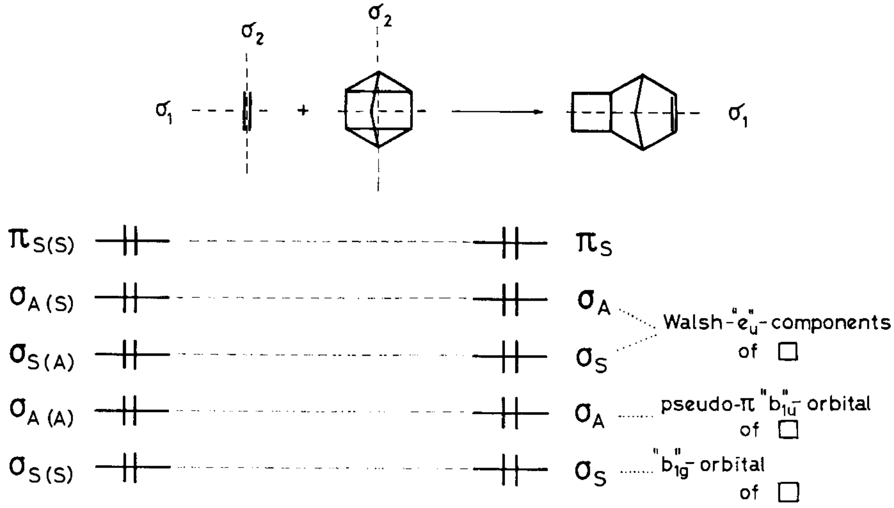
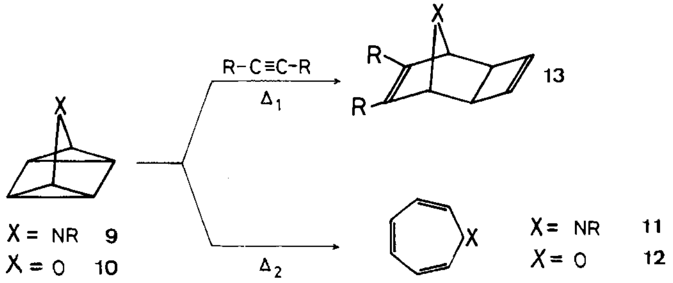


Fig. 1. *Modified orbital-correlation diagram for concerted 1,5-cycloadditions to quadricyclane*



X = NR **9**
X = O **10**

13

X = NR **11**
X = O **12**

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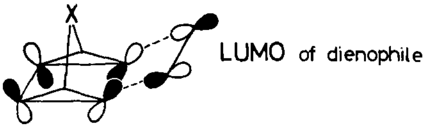
[2]) The infrequently observed 2,6-additions ('mixed additions') of a dienophile to some derivatives of **1** are obviously the result of a *non*-concerted pathway, in agreement with the fact that hitherto only tetracyanoethylene exhibits this kind of attack [10].

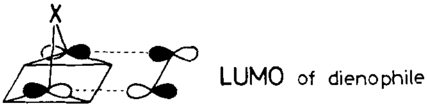
Although there are no PE.spectroscopical data for **9** and **10**, MINDO/2-calculations (fig. 2) indicate that the orbital electronic structure of these molecules for the three top occupied levels closely resembles that of **2**, the π-MO of the exocyclic double bond in the latter being replaced by a heteroatom lone pair orbital. While **2** and **9** (R=H) show quite similar orbital energies, those of **10** are at lower energies by 0.3–0.7 eV, due to the higher electronegativity of oxygen with respect to nitrogen. In support of this the π-IP of 7-oxanorbornene is shifted by 0.5 eV towards higher energies when compared with norbornene itself [11].

These points make it difficult to explain the difference in regioselectivity of dienophile-attack between heterosystems and hydrocarbons, assuming concertedness for both reactions. This is, because in both cases the dominant contribution to the stabilization of the activated complex will be the interaction of the HOMO of the quadricyclane moiety with the π^*-LUMO of the cycloaddend. Inspection of the shape of the respective HOMO's (fig. 2) reveals that this interaction is more effective for all systems if 1,5-attack occurs.



AS - HOMO

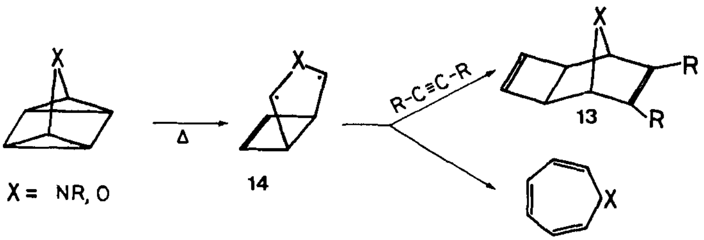
On the other hand, the highest lying MO exhibiting a suitable shape for a concerted 2,4-attack is situated in all systems about 1.1–1.3 eV below the HOMO.



AA - MO

Given that this AA-MO appearantly plays no decisive role for the steric course of the reaction in the case of the hydrocarbon **2**, the data in Fig. 2 do not provide any sound basis for the proposal that in the case of the heterosystems its importance overrides that of the HOMO.

Therefore the cycloadditions of the heterosystems may not be of concerted nature but may proceed *via* some *intermediate*. A conceivable structure for this species is the "1,3-biradical" **14**[3]), which has earlier been proposed as an intermediate in the ther-



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[3]) We shall later discuss this 'biradical' and its 'zwitterionic' nature.

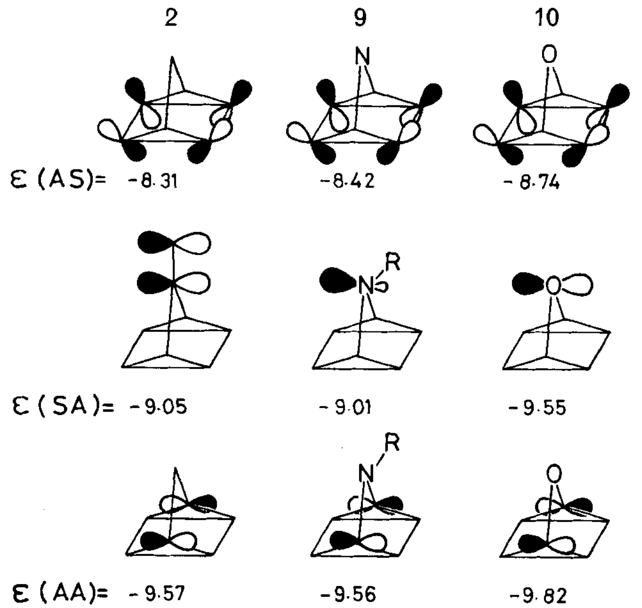
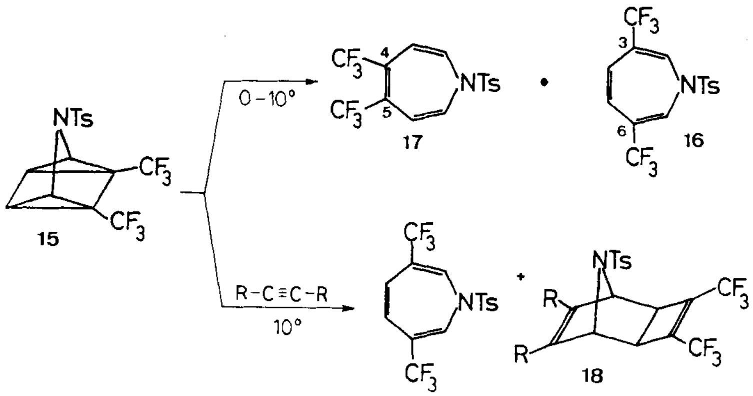


Fig. 2. *The shape and energy (in eV) of the three top occupied orbitals of* **2**, **9** *(R = H) and* **10**

molysis of **9** and **10** [10]. This species may also be generated in the rate-determining step of the cycloaddition as well.

In the presence of a dienophile, **14** will be trapped to yield the tricyclic adduct **13**; otherwise further bond rupture leads to the tropylidene system. This mechanism would also account for the similar temperature range observed for cycloaddition as well as for unimolecular transformation to the tropylidenes in the case of hetero-quadricyclanes (*vide supra*).

Some recent experimental observations by *Prinzbach & Markert* [13] are interpreted in support of a 'biradical'[3]) intermediacy[4]):



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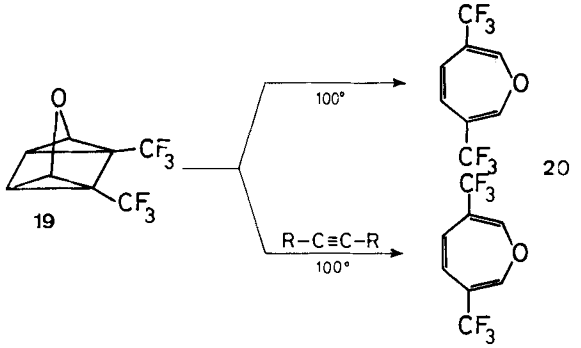
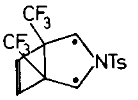
[4]) A detailed kinetic study of this reaction is in progress [12]. We are very grateful to Prof. *Prinzbach* for informing us prior to the publication of these results.

(*i*) Thermolysis of **15** yields the isomeric azepines **16** and **17** in a 3:2 ratio. Using the same reaction conditions but adding a dienophile still yields **16** but no **17**. Instead, the cycloadduct **18** is formed.



(*ii*) Thermal rearrangement of **19** leads almost exclusively to the 3,6-disubstituted oxepine **20**[5]). The presence of a dienophile does not decrease the yield of **20**.

Case (i) is explainable with an intermediacy of the 'biradicals'[3]) **21** and **22**, which are the precursers of **16** and **17** respectively.



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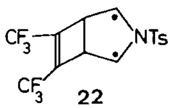

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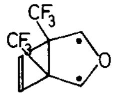

23

Added dienophile traps **22**, resulting in **18**. On the other hand **21** is not attacked because of steric hindrance. Hence **16** is still observed.

For (ii) rearrangement of **19** proceeds *via* the 'biradical' **23**, the reaction of which with the dienophile is again subject to steric hindrance.

In summary the chemistry exhibited by *homo-* and *hetero*-quadricyclanes follows different routes. Yet, this is not predicted from ground-state considerations nor from the "vertical" [14] behaviour of some of these systems in the PE.experiment. Given the *Bell-Evans-Polanyi*-principle [15], there must be an increased thermochemical driving force for formation of "biradical" intermediates in the case of the hetero-systems.

Consider the relative stabilities (E^{stab}) of the open-chain products formed in the reactions depicted in Tab. 1 (p. 478).

The heat of reaction ΔH (**24** → **25**) is about 54 kcal/mol [16]. In **25**, the radical centers are not significantly stabilized [16] [17]. In fact theoretical calculations do not even indicate a minimum for **25** on the C_3H_6-singlet energy surface [18]. Therefore we take ΔH (**24** → **25**) = 54 kcal/mol as a reference value for generating an unstabilized 1,3-diradical (E^{stab} = 0) from a three-membered ring precurser.

According to MINDO/2-calculations [19], trimethylidenemethane (**27**) [20] has the lowest energy singlet structure **27a** with ΔHf (**27**) = 63 kcal/mol [21]. We prefer the value obtained with the *Benson*-formalism [16]; ΔHf (**27**) = 75.6 kcal/mol, since the MINDO/2-method generally yields too low heats of formation. This with ΔHf (**26**) = 47.9 kcal/mol [22] yields ΔH (**26** → **27**) = 27.7 kcal/mol. E^{stab} (**27**) = 14.6 kcal/mol is obtained by comparing this latter value with ΔH

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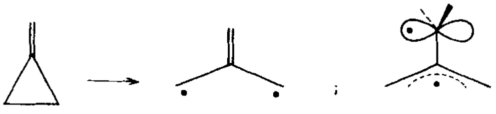
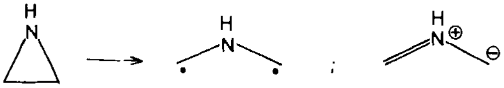
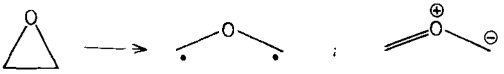
[5]) **20** may well exist in equilibrium with its valence isomer benzene oxide.

Tab. 1. *Estimated enthalpies (ΔH) of reaction for the ring opening of three-membered ring compounds.* Stabilization energies (E^{stab}) for the open-chain products with respect to trimethylene.

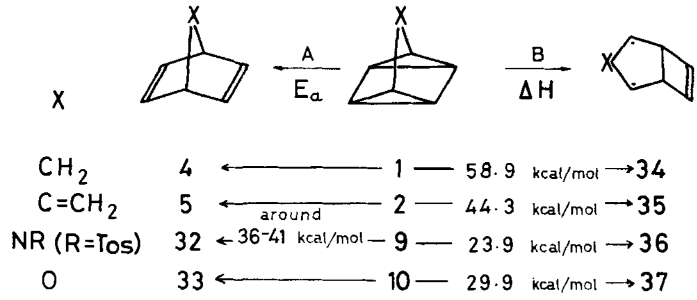
	ΔH (kcal/mol)	E^{stab} (kcal/mol)
 24 → 25	54	0
 26 → 27 ; 27a	27.7	14.6
 28 → 29 ; 29a	19	35
 30 → 31 ; 31a		(29)

(**24** → **25**), in addition correcting for the greater strain energy of **26** with respect to **24** ($\Delta E^{strain} = 11.7$ kcal/mol). Note that E^{stab} is roughly equal to the resonance energy of allyl radical, an outcome not unexpected in view of the MINDO/2-structural prediction **27a**.

The ring opening of a substituted aziridine (**28**) by flash photolysis yielded a free energy of reaction of 8 kcal/mol ($T = 393°K$) [23]. The resonance energy of the open-chain product is reported as 22 kcal/mol, implying that **29** is more rigid than **25**. ΔS (**24** → **25**) amounts to 10 e.u. [16], but ΔS (**28** → **29**) is smaller by ~5 e.u., *i.e.* by the entropy of restricted motion of allyl radical [16]. Therefore ΔH (**28** → **29**) = 19 kcal/mol after correcting for the stabilizing effect of two methoxycarbonyl substituents (9 kcal/mol [16]) attached to **28** in the kinetic study [23]. Since the strain energies of **28** and **24** are virtually identical [16] this figure can be directly compared with ΔH (**24** → **25**) yielding E^{stab} (**29**) = 35 kcal/mol. This large stabilization shows that in **29** a strong interaction between the radical lobes *via* the N-lone pair prevails, rendering the system allyl-anion like. In the valence bond formalism this signals increased importance of '*zwitterionic*' structures (**29a**) contributing to the ground state. This is also supported by MO-calculations [24] as well as by chemical evidence [25].

The ring opening of substituted oxiranes (**30**) has been reported recently [26], but no thermodynamic parameters were given. A rough estimate of E^{stab} (**31**) is obtained by plotting E^{stab} of **25** and **29** against the percentage of dipolar character of these species, calculated in [24] and then linearly interpolating for **31**. On this basis, E^{stab} (**31**) = 29 kcal/mol is found, which needs no further correction since the strain energy of **30** is equal to that of **24** and **28** [16]. Note that E^{stab} (**31**) < E^{stab} (**29**) as expected since oxygen has a higher electronegativity than nitrogen. In a MO-picture this results in less depression of the O-lone pair by the symmetric combination of the radical p-lobes. In a VB-description, the 'zwitterionic' valence structure where the O-atom carries a positive charge will contribute less.

Now a clear thermochemical driving force for "biradical" formation (process B) in the case of the heterosystems becomes discernible.



The concurrent valence isomerisation for the dimethoxycarbonyl derivatives of **1**, **2**, **9** and **10** (process A) requires at least $E_a(A) \approx 25$–30 kcal/mol [27]. Since **1** has $E_a(A) = 38$ kcal/mol [28] in MeCN-solution, whereas its 1,5-dimethoxycarbonyl derivative has $E_a(A) = 27$ kcal/mol [27] we use simply $E_a(A) \approx 36$–41 kcal/mol as an E_a-range common to the four unsubstituted quadricyclanes.

Unfortunately we have no means to estimate E_a of the B-processes. However, $\Delta H(B)$ can be estimated in a straightforward manner. Using the *Benson*-increments [16] $\Delta \mathrm{Hf}$ (**34**) = 119.4 kcal/mol is obtained. This together with $\Delta \mathrm{Hf}$(**1**) = 60.5 kcal/mol [29] leads to ΔH(**1**→**34**) = 58.9 kcal/mol. In order to arrive at the ΔH-values for the other three B-processes, ΔH(**1**→**34**) is corrected by E^{stab} (Tab. 1) of the corresponding "biradical" product. The results are given in the scheme above.

Since $\Delta H(B)$ is a lower bound to $E_a(B)$, it is clear that for the two hydrocarbons **1** and **2**, process B can never compete with A. On the other hand, $\Delta H(B)$ for the *hetero*-systems **9** and **10** lies significantly below $E_a(A)$ so that here – *in principle* – route B may compete with route A. In summary: **9**→**36** and **10**→**37** cannot be excluded from consideration whereas **1**→**34** and **2**→**35** are clearly impossible.

Having thus provided further support for a "biradical" intermediacy we draw attention to the experimental observation that the thermal stability of **9** increases with increasing electron-withdrawing ability of substituents attached to the N-atom [10]. This parallels the fact that the feasibility of the quadricyclane→tropylidene rearrangement ($X{=}CH_2$, NR, O) also depends strongly upon the electron-donating power of the X-group [10]. This latter feature has been cited in support of a (formally allowed) concerted reaction mechanism, the analysis of which also requires – in addition to the usual symmetry-correlation procedure – the decisive consideration of topological aspects and spatial definitions of the crucial MO's [30]. From the above discussion, however, the cited trends strongly support a *stepwise* process. Thus, a less electron-demanding substituent R of the group NR makes the heteroatom lone-pair more available for the stabilization of the intermediate "biradical", thereby increasing the driving force of the reaction. The same is true along the series $X{=}CH_2$, O, NR as discussed previously (*cf.* Tab. 1).

After this work was submitted a paper by *Tanny & Fowler* [31] appeared in which the mechanism of cycloaddition to heteroquadricyclanes was also discussed. The conclusions reached by these author are essentially identical to ours.

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