

## Strained Heterocyclic Systems. VIII. The Mass Spectral Fragmentations of Some Arylquinolines and Quinoline *N*-Oxides (1)

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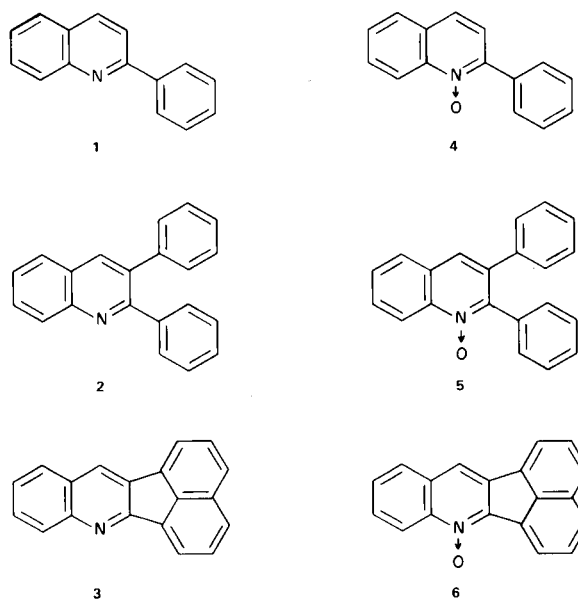
Received March 1, 1974

High resolution mass spectra of compounds **1-8** were investigated. For the quinolines (**1-3**) the absence of major peaks other than  $M^+$  and  $(M-1)^+$  reflects the stability of these systems. The *N*-oxides (**4-6**) all exhibit major peaks at  $M^+$ ,  $(M-16)^+$ , and  $(M-17)^+$ . In addition, **4** shows prominent fragmentations reflecting loss of hydrogen and carbon monoxide. The pathways are related to the geometries of the *N*-oxides; deuterated compounds (**7-8**) aided these assignments.

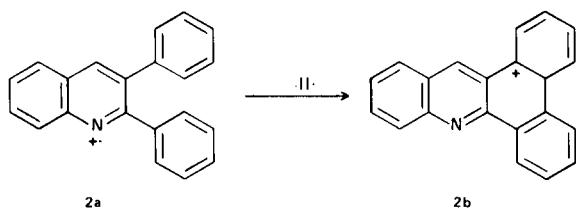
Under electron impact the particular modes of fragmentation exhibited by substituted quinolines are a function of the nature and position of the side chains. Although these relationships have been widely investigated during the past decade for alkyl derivatives (3), aryl substituted quinolines and their *N*-oxides have received much less attention. Only 2-phenylquinoline *N*-oxide and two derivatives have been reported (4,5,6); of these three compounds only the first has been discussed in terms of fragmentation pathways. It therefore seemed of interest to study the fragmentations of some 2,3-diarylquinolines and their *N*-oxides, including the strained acenaphtho[1,2-*b*]quinoline system in which the expected influence on basicity was observed (7). Accordingly, we have carried out mass spectrometric studies on 2-phenylquinoline (**1**), 2,3-diphenylquinoline (**2**), acenaphtho[1,2-*b*]quinoline (**3**), and their corresponding *N*-oxides (**4-6**). The group of three *N*-oxides constitutes an interesting series for assessing the involvement of the 2-aryl substituent *via* its *ortho* position in processes whereby a hydrogen or hydroxyl fragment is lost. The spectra of the parent heterocyclics serve as reference compounds for the *N*-oxides since the latter are known to undergo deoxygenation (6,8).

The fragmentation patterns and established metastable transitions of the six compounds are summarized in Tables I-IV (9).

The parent heterocyclics are all remarkably stable; Table I contains all species of **1-3** whose relative intensities are greater than 5%. The principal species in each case are the molecular ion and the  $M-1$  ion. For compound **3**, only the molecular ion is of major importance, a pattern



that is also observed for acenaphtho[1,2-*b*]quinoxaline (10). The site from which these arylquinolines lose a hydrogen atom is unknown. The fact that the base peak for **2** is the  $M-1$  ion may imply that the hydrogen is lost from the *ortho* position of the 2- (or 3-) phenyl substituent. Such a pathway (**2a**  $\rightarrow$  **2b**) could afford a dibenz[*a,c*]acridine structure and thereby alleviate the steric crowding which prevents the 2,3-diphenyl groups from attaining coplanarity with the quinoline ring. The same situation exists with *o*-terphenyl, for which the dihedral angles have been estimated at  $55^\circ$  (11). It is noteworthy that in the



mass spectrum of *o*-terphenyl the most prominent peak other than the molecular ion base peak occurs at M-1 (relative intensity *ca.* 60%), whereas the same peak for *m*- and *p*-terphenyl is substantially reduced (relative intensities *ca.* 10%) (12).

In an attempt to identify the site from which a hydrogen is lost in the M-1 ion of a 2-arylquinoline, the mass spectrum of 2-(pentadeuterophenyl)quinoline (**7**) was investigated (Table V). Although it was well known at the

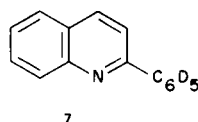


TABLE I

Major Fragments in the Mass Spectra of **1-3**

Species	Relative Intensities		
	<b>1</b>	<b>2</b>	<b>3</b>
M	100	54	100
M-1	69	100	10
M-2	9	6	11
M-3	3	8	2

TABLE II

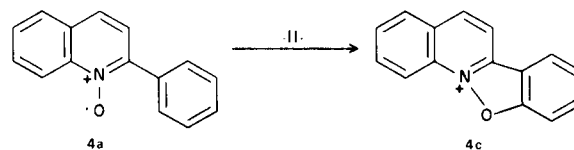
Major Fragments in the Mass Spectra of **4-6**

Species	Fragment Lost	Relative Intensities		
		<b>4</b>	<b>5</b>	<b>6</b>
M		93	70	100
M-1	H	100	2	2
M-16	O	75	53	98
M-17	HO	48	100	13
M-18	H <sub>2</sub> O	8	6	15
M-19	H <sub>3</sub> O	3	10	3
M-28	CO	28	0	6
M-29	HCO	23	3	14
M-54	C <sub>3</sub> H <sub>2</sub> O	29	0	1

time this study was initiated that complete hydrogen scrambling occurred in the molecular ions of pyridine and quinoline (13,14) and that considerable hydrogen randomization occurred over both rings in biphenyl (15,16), no systems involving deuterated arylquinolines had been reported. Compound **7**, however, did not resolve the issue, since the loss of one hydrogen atom was consistent with almost statistical amounts of protium and deuterium. This result was in accord with a subsequent report of hydrogen scrambling between the pyridine and phenyl moieties of various phenylpyridines (17).

The three quinoline *N*-oxides, **4-6**, show more complex fragmentation patterns. The data in Table II for **5** and **6** include all species with relative intensity greater than 5%; compound **4** produces additional peaks at lower *m/e* values for which **5** and **6** show no counterparts. The deoxygenation of the molecular ion to M-16 has been considered characteristic of many heterocyclic *N*-oxides (4,6,18), although subsequent work has shown that the loss of oxygen can be thermally induced (8). Consequently, the spectra of **4-6** were obtained using a direct introduction probe with as short a time delay and as low a source temperature as were practicable. This procedure afforded (M-16)<sup>+</sup>/M<sup>+</sup> ratios less than unity, which compared favorably to such values reported by Duffield and Buchardt (8). Although these data suggest that the thermal process for deoxygenation has been suppressed, it cannot be inferred that the observed loss of oxygen is a consequence of electron impact. Since the deoxygenation step is therefore ambiguous, further discussion is unwarranted.

The fragmentation of 2-phenylquinoline *N*-oxide (**4**) is the most complex of the three *N*-oxides in this study (*cf.* Tables II, IV). Its spectrum has been reported previously (4,5) and the M-1 ion (**4c**) was accounted for

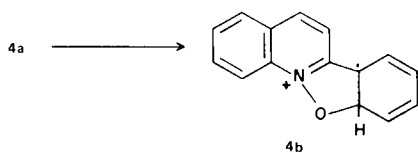


by attack of the oxygen atom at the *ortho* position of the 2-phenyl substituent. Furthermore Buchardt, Duffield and Shapiro postulated that loss of carbon monoxide occurred from both the molecular ion and the M-1 ion (5). The existence of these pathways has been established by the present metastable studies. The major fragmentations involve sequential losses of carbon monoxide and acetylene from the molecular ion and from the M-1 ion. The M-17 ion can be considered to arise from **4c** via loss of oxygen in accord with an earlier interpretation (5). Alternately, the direct loss of hydroxyl from the molecular ion is a possibility, since such a pathway is operative in the case of **5** (Table IV).

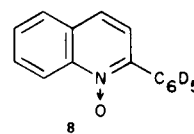
TABLE III  
Metastable Transitions in the Mass Spectra of **1-3**

Compound	Transition	Relative Intensity (%) (a)	
<b>1</b>	$204^+ \rightarrow 178^+ + \text{CN}/\text{C}_2\text{H}_2$	0.1	
	$204^+ \rightarrow 177^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.4	
	$203^+ \rightarrow 176^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.3	
	$178^+ \rightarrow 152^+ + \text{CN}/\text{C}_2\text{H}_2$	0.7	
	$178^+ \rightarrow 128^+ + \text{C}_4\text{H}_2$	0.1	
	$177^+ \rightarrow 151^+ + \text{CN}/\text{C}_2\text{H}_2$	0.2	
	$177^+ \rightarrow 150^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.05	
	$154^+ \rightarrow 128^+ + \text{C}_2\text{H}_2$	0.9	
	$154^+ \rightarrow 127^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.02	
	$153^+ \rightarrow 126^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.05	
	$129^+ \rightarrow 102^+ + \text{HCN}$	0.06	
	$128^+ \rightarrow 101^+ + \text{HCN}$	0.2	
	<b>2</b>	$280^+ \rightarrow 254^+ + \text{C}_2\text{H}_2$	0.04
		$280^+ \rightarrow 253^+ + \text{C}_2\text{H}_3\cdot$	0.09
$280^+ \rightarrow 252^+ + \text{H}_2\text{CN}/\text{C}_2\text{H}_4$		0.3	
$280^+ \rightarrow 203^+ + \text{C}_6\text{H}_5\cdot$		0.01	
$203^+ \rightarrow 176^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$		0.13	
$177^+ \rightarrow 151^+ + \text{CN}/\text{C}_2\text{H}_2$		0.42	
$176^+ \rightarrow 150^+ + \text{CN}/\text{C}_2\text{H}_2$		0.02	
<b>3</b>		$253^+ \rightarrow 226^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.33
	$252^+ \rightarrow 225^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.48	
	$253^+ \rightarrow 214^+ + \text{C}_3\text{H}_3$	0.03	
	$253^+ \rightarrow 201^+ + \text{C}_3\text{H}_2\text{N}/\text{C}_4\text{H}_4$	0.02	
	$251^+ \rightarrow 224^+ + \text{HCN}$	0.22	
	$251^+ \rightarrow 200^+ + \text{C}_3\text{HN}/\text{C}_4\text{H}_3$	0.02	
	$249^+ \rightarrow 199^+ + \text{C}_3\text{N}/\text{C}_4\text{H}_2$	0.01	
	$228^+ \rightarrow 201^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.02	
	$227^+ \rightarrow 200^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.11	
	$226^+ \rightarrow 199^+ + \text{HCN}/\text{C}_2\text{H}_3\cdot$	0.13	

(a) The intensity (%) of the metastable ion precursor relative to the daughter fragment.

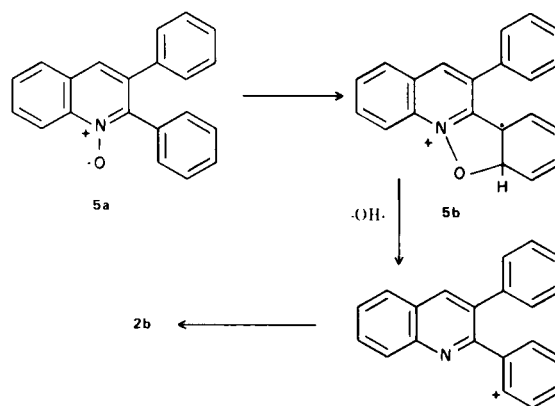


It seems likely, therefore, that ion **4b** could be the precursor of M-1, M-17, and M-28 by the loss of hydrogen, hydroxyl, and carbon monoxide, respectively. This type of intramolecular rearrangement occurs readily, despite the fact that the two rings may not be coplanar (19). In a system such as benzo[*a*]phenazine 12-oxide in which coplanarity is assured, the M-28 ion is the base peak (20). A zwitterion analogous to cation radical **4b** has been invoked as an intermediate in the base-catalyzed rearrangement of *N*-aryloxypyridinium salts (21). Additional evidence for an initial intermediate such as **4b** came from 2-(pentadeuterophenyl)quinoline *N*-oxide (**8**). Whereas the parent heterocycle (**7**) showed almost complete



protium/deuterium randomization prior to the loss of one hydrogen atom, the corresponding *N*-oxide exhibited a high selectivity toward deuterium (Table V).

In contrast to **4**, the mass spectrum of **5** is remarkably simple. There are only three major peaks which correspond to the molecular ion and the losses of oxygen and hydroxyl. The M-17 ion is of note for two reasons: it is the base peak and it is formed directly from the molecular ion. The absence of other major fragments is consistent with an extraordinarily stable M-17 ion, for which a reasonable structure is **2b**. This process permits the



sterically crowded phenyl rings to be converted to a planar delocalized cationic system *via* initial interaction of the oxygen atom at the *ortho* position of the adjacent phenyl ring (**5b**) and subsequent loss of hydroxyl.

The mass spectrum of **6** is also relatively simple compared to **4**, but it differs from **5** as well. Besides the molecular ion base peak, the only other major peak corresponds to deoxygenation. The diminished abundance of ions involving loss of hydroxyl (M-17) or carbon monoxide (M-28) is a consequence of the molecular

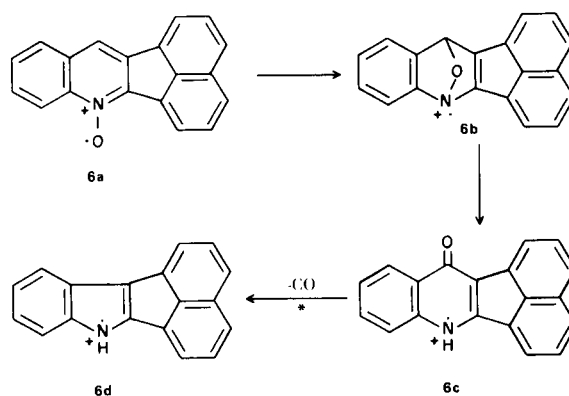


TABLE IV

Metastable Transitions in the Mass Spectra of **46**

Compound	Transition	Relative Intensity (%) (a)	
<b>4</b>	221 <sup>+</sup> → 193 <sup>+</sup> + CO	0.9	
	221 <sup>+</sup> → 180 <sup>+</sup> + C <sub>2</sub> HO	0.08	
	220 <sup>+</sup> → 192 <sup>+</sup> + CO	0.4	
	220 <sup>+</sup> → 166 <sup>+</sup> + C <sub>3</sub> H <sub>2</sub> O	0.6	
	219 <sup>+</sup> → 191 <sup>+</sup> + CO	0.3	
	219 <sup>+</sup> → 165 <sup>+</sup> + C <sub>2</sub> NO	0.4	
	203 <sup>+</sup> → 177 <sup>+</sup> + CN-/C <sub>2</sub> H <sub>2</sub>	0.4	
	203 <sup>+</sup> → 176 <sup>+</sup> + HCN/C <sub>2</sub> H <sub>3</sub> ·	0.2	
	202 <sup>+</sup> → 175 <sup>+</sup> + HCN	0.2	
	193 <sup>+</sup> → 167 <sup>+</sup> + C <sub>2</sub> H <sub>2</sub>	1.8	
	192 <sup>+</sup> → 166 <sup>+</sup> + CN-/C <sub>2</sub> H <sub>2</sub>	1.9	
	192 <sup>+</sup> → 165 <sup>+</sup> + HCN	0.8	
	178 <sup>+</sup> → 128 <sup>+</sup> + C <sub>4</sub> H <sub>2</sub>	0.1	
	166 <sup>+</sup> → 139 <sup>+</sup> + HCN	0.2	
	154 <sup>+</sup> → 128 <sup>+</sup> + C <sub>2</sub> H <sub>2</sub>	0.4	
	128 <sup>+</sup> → 102 <sup>+</sup> + CN-/C <sub>2</sub> H <sub>2</sub>	0.2	
	128 <sup>+</sup> → 101 <sup>+</sup> + HCN	1.1	
<b>5</b>	297 <sup>+</sup> → 280 <sup>+</sup> + HO·	4.0	
	297 <sup>+</sup> → 268 <sup>+</sup> + CHO·	0.22	
	296 <sup>+</sup> → 279 <sup>+</sup> + HO·	0.11	
	296 <sup>+</sup> → 267 <sup>+</sup> + CHO·	0.11	
	295 <sup>+</sup> → 278 <sup>+</sup> + HO·	0.13	
	281 <sup>+</sup> → 254 <sup>+</sup> + C <sub>2</sub> H <sub>3</sub> ·	0.01	
	280 <sup>+</sup> → 253 <sup>+</sup> + C <sub>2</sub> H <sub>3</sub> ·	0.04	
	280 <sup>+</sup> → 252 <sup>+</sup> + H <sub>2</sub> CN-/C <sub>2</sub> H <sub>4</sub>	0.04	
	278 <sup>+</sup> → 251 <sup>+</sup> + HCN/C <sub>2</sub> H <sub>3</sub> ·	0.04	
	269 <sup>+</sup> → 254 <sup>+</sup> + CH <sub>3</sub> ·	0.003	
	268 <sup>+</sup> → 253 <sup>+</sup> + CH <sub>3</sub> ·	0.005	
	203 <sup>+</sup> → 176 <sup>+</sup> + HCN	0.002	
	177 <sup>+</sup> → 151 <sup>+</sup> + C <sub>2</sub> H <sub>2</sub>	0.02	
	<b>6</b>	269 <sup>+</sup> → 241 <sup>+</sup> + CO	1.0
		269 <sup>+</sup> → 214 <sup>+</sup> + C <sub>3</sub> H <sub>3</sub> O-/C <sub>2</sub> HNO	0.02
268 <sup>+</sup> → 240 <sup>+</sup> + CO		1.1	
268 <sup>+</sup> → 213 <sup>+</sup> + C <sub>3</sub> H <sub>3</sub> O-/C <sub>2</sub> HNO		0.03	
253 <sup>+</sup> → 227 <sup>+</sup> + C <sub>2</sub> H <sub>2</sub>		0.23	
253 <sup>+</sup> → 226 <sup>+</sup> + HCN/C <sub>2</sub> H <sub>3</sub> ·		0.37	
252 <sup>+</sup> → 225 <sup>+</sup> + HCN/C <sub>2</sub> H <sub>3</sub> ·		0.25	
251 <sup>+</sup> → 224 <sup>+</sup> + HCN/C <sub>2</sub> H <sub>3</sub> ·		0.29	
241 <sup>+</sup> → 215 <sup>+</sup> + CN-/C <sub>2</sub> H <sub>2</sub>		0.14	
241 <sup>+</sup> → 214 <sup>+</sup> + HCN/C <sub>2</sub> H <sub>3</sub> ·		0.27	
240 <sup>+</sup> → 213 <sup>+</sup> + HCN/C <sub>2</sub> H <sub>3</sub> ·	0.37		

(a) The intensity (%) of the metastable ion precursor relative to the daughter fragment.

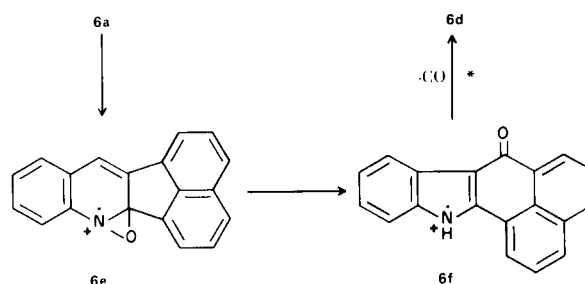
geometry. The strain of the acenaphtho[1,2-*b*]quinoline system is known to influence the basicity (7), and the more distant C-6 of the acenaphthyl moiety precludes facile attack by oxygen. Although the M-28 and M-29 ions are of low intensity, it is interesting to speculate about their generation. It is not unreasonable that a pathway analogous to that proposed for acridine *N*-oxide is operative (22). Intramolecular rearrangement of the molecular ion **6a** via endoxide **6b** can afford a quinolone

TABLE V

Selected Fragments in the Mass Spectra of **7** and **8**

Species	7	8
M	100	81
M-1	37	19
M-2	24	73
M-16		100
M-17		36
M-18		27

**6c** suitable for decarbonylation to an acenaphtho[1,2-*b*]indole ion **6d**. Alternately, a pathway that has photochemical analogies (23) involves initial formation of oxaziridine **6e** followed by rearrangement and ring expansion to **6f** prior to decarbonylation. Loss of hydrogen from any of the intermediates (**6b**, **6c**, **6e**, **6f**) can lead to a corresponding M-29 ion.



## EXPERIMENTAL.

## General.

Melting points, uncorrected, were obtained on a modified Hershberg apparatus with total immersion Anschütz thermometers. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921. Deuterium analyses were performed by J. Nemeth, Urbana, Illinois 61801.

## Materials.

The preparation of compounds **1**, **2**, and **3** has been reported (7). The *N*-oxides **4**, **5**, and **6** were prepared from the parent heterocyclics by oxidation with *m*-chloroperbenzoic acid by the previously described method (24): **4**, recrystallized from ethyl acetate, m.p. 144-145° [lit. (25) 144-145°]; **5**, recrystallized from ethyl acetate, m.p. 198.8-200°; **6**, recrystallized from absolute ethanol, m.p. 247.2-247.5°.

Anal. Calcd. for C<sub>21</sub>H<sub>15</sub>NO (**5**): C, 84.82; H, 5.08; N, 4.71. Found: C, 84.65; H, 4.95; N, 4.86. Calcd. for C<sub>19</sub>H<sub>11</sub>NO (**6**): C, 84.87; H, 4.12; N, 5.20. Found: C, 84.62; H, 4.10; N, 5.20.

Compound **7** was prepared by the reaction of the Grignard reagent derived from bromobenzene-d<sub>5</sub> with quinoline *N*-oxide by the method of Kato and Yamanaka (25) and recrystallized from ethanol-water, m.p. 83.6-84.2° [lit. (25) 80-82° for **1**].

Oxidation of **7** by the method used above gave **8**, recrystallized from benzene-ligroine (b.p. 60-90°), chromatographed on alumina (neutral, activity I) and eluded with chloroform, m.p. 142.6-144.1° [lit. (25) 144-145° for **4**].

*Anal.* Calcd. for C<sub>15</sub>H<sub>6</sub>D<sub>5</sub>N (**7**): atom % excess D, 45.45. Found: atom % excess D, 44.35. Calcd. for C<sub>15</sub>H<sub>6</sub>D<sub>5</sub>NO (**8**): atom % excess D, 45.45. Found: atom % excess D, 43.85.

#### Spectra.

Mass spectra were obtained with a CEC 21-110B mass spectrometer using the direct introduction probe and an ionizing voltage of 70 eV. Source temperatures for compounds **1-6** were 75°, 100°, 100°, 100°, 170°, and 160°, respectively. Exact mass measurements were made with a resolution exceeding 10,000; perfluorokerosene was used to provide reference mass. Metastable transitions were established by uniquely determining the precursor ions employing the ion accelerator decoupling technique (26).

#### Acknowledgements.

The mass spectrometer was purchased with funds from the National Science Foundation (Grant GP-5323). Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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