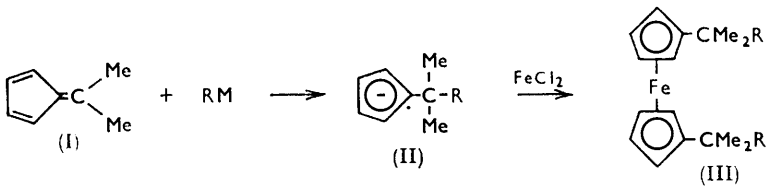
902. *Ferrocene Derivatives. Part X.*[1] *Their Preparation from Fulvenes.*[2]

By G. R. Knox and P. L. Pauson.

The conversion of fulvenes into substituted cyclopentadienide ions and thence by ferrous chloride into dialkyl- and alkenyl-ferrocenes is described. Azulene is shown to behave as a fulvene in these reactions.

In Part I[3] the preparation of ferrocene from cyclopentadienyl-lithium (or the corresponding Grignard reagent) and iron halides was extended to aryl- and alkyl-cyclopentadienes. One of the routes to such starting materials is from the readily accessible fulvenes. In special cases[3,4] these may be reduced by metallic sodium or, more generally, by lithium aluminium hydride[5] to s-alkylcyclopentadienes. In the latter reaction the substituted cyclopentadienyl-lithium or lithium aluminium hydride derivative (II; M = Li or $LiAlH_3$, R = H) is a probable intermediate and it appeared likely that treatment with ferrous chloride would convert this directly into the ferrocene derivative, the necessity of isolating the free cyclopentadiene being thus avoided.

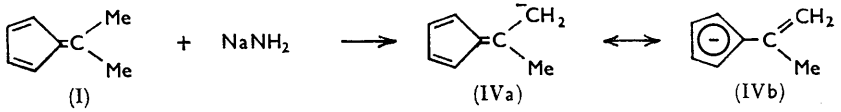


(I) (II) (III)

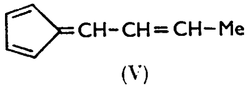
These expectations proved correct when dimethylfulvene (I) was treated with lithium aluminium hydride, followed by ferrous chloride, and di-isopropylferrocene (III; R = H) was isolated. Similarly 1,1′-dicyclohexylferrocene was obtained from pentamethylenefulvene (cyclopentadienylidenecyclohexane). The identification of " M " in this reaction as " $LiAlH_3$ " is suggested by the necessity of employing 1 mole of lithium aluminium hydride per mole of fulvene before the colour of the latter disappears.

The above formulation (I ⟶ II) has also been employed by Ziegler and Schäfer[6] for the addition of alkyl- or aryl-lithium to dimethylfulvene. Although these workers did not conclusively establish the structure of the product (II), this is adequately confirmed by its use in the present work to afford the 1,1′-di-t-alkylferrocenes (III; R = Me and Ph) by the above scheme (where M = Li). An analogous product was prepared from pentamethylenefulvene, phenyl-lithium, and ferrous chloride.

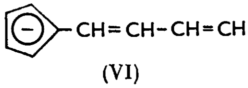
The quest for other anions (R^-) which might add in this way to fulvenes, led us to try sodamide, which was found to react in a different manner:



(I) (IVa) (IVb)



(V)



(VI)

Dimethylfulvene and related compounds behave as acids towards this strong base. The acidity, as that of other cyclopentadiene derivatives, may be ascribed to the formation

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[1] Part IX, preceding paper.

[2] For a preliminary communication see *Proc. Chem. Soc.*, 1958, 289

[3] Pauson, *J. Amer. Chem. Soc.*, 1954, **76**, 2187.

[4] Schlenk and Bergmann, *Annalen*, 1928, **463**, 1.

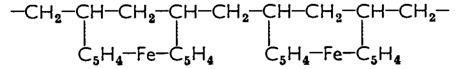
[5] Ziegler, Gellert, Martin, Nagel, and Schneider, *Annalen*, 1954, **589**, 91.

[6] Ziegler and Schäfer, *Annalen*, 1934, **511**, 101.

of the resonance-stabilised cyclopentadienide ion (IVb) which in this case has an additional canonical form (IVa). In other words, the acidity of fulvenes follows from that of cyclopentadiene itself by the principle of vinylogy. This consideration suggested further extension to such fulvenes as (V) and indeed this reacted readily with sodamide, presumably yielding the anion (VI). The only previous evidence for the acidity of fulvenes appears to be that Schlenk and Bergmann[7] observed the formation of triphenylmethane from dimethylfulvene and triphenylmethylsodium.

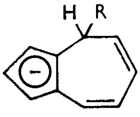
The anions (*e.g.*, IV and VI) produced with sodamide reacted smoothly with ferrous chloride, to give ferrocene derivatives bearing unsaturated side chains. These are rather difficult to isolate owing to the great ease with which they polymerize. For instance, Riemschneider and Helm[8] were unable to isolate di-isopropenylferrocene when it was prepared by another method. In the present work we were able to obtain this compound from the ion (IV) and ferrous chloride, albeit in low yield and accompanied by much polymer. Similar results were obtained when pentamethylenefulvene was employed as starting material to yield 1,1′-dicyclohex-1-enylferrocene. The structure of the latter was verified by reduction to dicyclohexylferrocene and dehydrogenation to the known diphenylferrocene; diphenylferrocene was also reduced to the dicyclohexyl derivative.

When, however, methylfulvene or propenylfulvene (V) was employed, the isolation of the expected divinyl- and dibutadienyl-ferrocene did not prove possible although polymeric ferrocenes which must clearly be derived from these products resulted. The low stability of the monomer is in contrast to the ready isolation of monovinyl-[9,10] and monobutadienyl-ferrocene[1] and suggests that the proximity of the unsaturated side chains assists polymerisation. It appears likely, therefore, that the polymers of, *e.g.*, divinylferrocene are of the form (VII) containing bridged rings.

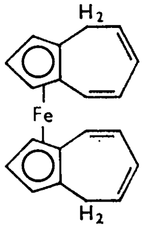
(VII) 

$$\begin{array}{l}-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-\\ \qquad\quad C_5H_4-Fe-C_5H_4 \qquad C_5H_4-Fe-C_5H_4\end{array}$$

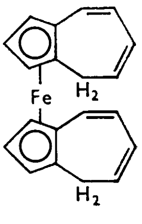
Azulene was included in the present study, since formally it contains a fulvene system. Hafner and Weldes[11] have shown that it adds alkyl-lithium, affording 4-alkyl-3α,4-dihydroazulenes, presumably by way of anions of type (VIII). Direct treatment with ferrous chloride converted these intermediates into the corresponding ferrocenes. A mixture of six stereoisomers (four racemates and two *meso*-forms) is theoretically possible, and not surprisingly a pure substance was not obtained when phenyl-lithium was employed. When R = H only two such isomers (1 *meso*, 1 racemic) are possible. This required addition of a hydride to azulene and although such additions had not been described, lithium aluminium hydride again proved successful though it added much more slowly than to fulvenes. From the oily product one component was isolated with m. p. 68°, but a sample with the melting range 47—53°, presumably containing both expected



(VIII)



(IXa



(IXb)

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[7] Schlenk and Bergmann, *Annalen*, 1930, **479**, 58.

[8] Riemschneider and Helm, *Chem. Ber.*, 1956, **89**, 155.

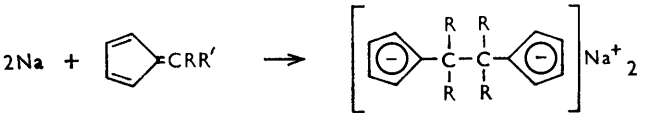
[9] Arimoto and Haven, *J. Amer. Chem. Soc.*, 1955, **77**, 6295.

[10] Hauser, Lindsay, and Lednicer, *J. Org. Chem.*, 1958, **23**, 358.

[11] Hafner and Weldes, *Annalen*, 1957, **606**, 90.

isomers (IXa and b), gave analyses in agreement with this composition and was characterised by hydrogenation to its octahydro-derivative.

After completion of the present work, Pruett and his co-workers[12] described an alternative use of fulvenes, which leads to bridged ferrocenes and is apparently based on the dimerisation of fulvenes by alkali metals first reported by Schlenk and Bergmann.[4]



EXPERIMENTAL

Unless otherwise stated, ligroin refers to the solvent of b. p. 60—80°. Alumina refers to Spence's grade H which had been exposed to air for 6 hr.

M. p.s were determined in sealed evacuated capillaries.

Ferrous chloride (anhydrous) employed in this and the following papers was freshly prepared by the method of Kovacic and Brace.[13]

1,1′-*Di-t-butylferrocene.*—Dimethylfulvene (2·12 g., 0·02 mole) in ether (10 ml.) was added to methyl-lithium, prepared in a nitrogen atmosphere from lithium (0·33 g., 0·05 g.-atom) and methyl iodide (3·15 g., 0·0248 mole). The mixture was stirred for 0·5 hr., ferric chloride (1·625 g., 0·01 mole) in ether (20 ml.) was added to the pale yellow precipitate to produce a blue mixture, and stirring was maintained for a further 2·5 hr. The ferricenium salt mixture was poured on ice (100 g.) and 12·5% titanous chloride solution (100 ml.), and the red-yellow ethereal solution was removed and dried over anhydrous sodium sulphate and zinc dust. Removal of the solvent in a nitrogen atmosphere afforded an oil (3·65 g.), which was chromatographed on alumina with ligroin as solvent; the eluate was evaporated, yielding a red-brown oil (2·8 g., 94%). 1,1′-Di-t-butylferrocene is an orange liquid, b. p. 108° (bath)/0·05 mm., $n_D^{21\cdot5}$ 1·550 (Found: C, 72·85; H, 8·8. Calc. for $C_{18}H_{26}Fe$: C, 72·6; H, 8·7%).

After our work,[2] Riemschneider and Nehring[14] prepared this compound, with m. p. 29—30°, from t-butylcyclopentadiene.

1,1′-*Di-(αα-dimethylbenzyl)ferrocene.*—Phenyl-lithium was prepared in ethereal solution (30 ml.) from lithium (0·33 g., 0·05 g.-atom) and bromobenzene (3·5 g., 0·021 mole), under nitrogen. Dimethylfulvene (2·12 g., 0·02 mole) in ether (10 ml.) was added dropwise, to produce a pale cream-coloured precipitate. Anhydrous ferric chloride (1·625 g., 0·01 mole) in ether (20 ml.) was added to the rapidly stirred suspension, and the mixture stirred for 2 hr., then poured on ice (100 g.), concentrated hydrochloric acid (2 ml.), and 12·5% titanous chloride solution (50 ml.). The organic material was separated with chloroform (150 ml.), washed with water, dried ($CaCl_2$), and evaporated, to leave a dark red oil (3·50 g., 83%) which solidified. Recrystallisation from ligroin–benzene afforded orange rods of 1,1′-*di-(αα-dimethylbenzyl)-ferrocene* (2·4 g., 57%), m. p. 133·5—134° (Found: C, 79·6; H, 7·3. $C_{28}H_{30}Fe$ requires C, 79·6; H, 7·2%).

In a similar reaction the use of anhydrous ferrous chloride and tetrahydrofuran increased the yield of crude material to 90%.

1,1′-*Di-(1-phenylcyclohexyl)ferrocene.*—Pentamethylenefulvene (cyclopentadienylidenecyclohexane)[15] (b. p. 118°/18 mm.; 2·92 g., 0·02 mole) in ether (15 ml.) was added dropwise to a stirred solution of phenyl-lithium (0·02 mole) in ether (30 ml.), under nitrogen, at a rate such that gentle refluxing was maintained. After 45 min. ferrous chloride [prepared from ferric chloride (3·3 g., 0·02 mole)] as a slurry in tetrahydrofuran (25 ml.) was added to the cream-coloured precipitate. The mixture was stirred under nitrogen at room temperature for 16 hr., poured into water (150 ml.) and titanous chloride solution (25 ml.), and extracted with ether (2 × 50 ml.). The combined ether extracts were washed with water (2 × 100 ml.), dried ($CaCl_2$), and evaporated to a brown oil (5·1 g., 100%) which solidified. Three recrystallisations

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[12] Union Carbide, Belgian P. 563,103; Ger. P. 1,052,401; Rinehart, Frerichs, Kittle, Westman, Gustafson, Pruett, and McMahon, *J. Amer. Chem. Soc.*, 1960, **82**, 4111.

[13] Kovacic and Brace, *J. Amer. Chem. Soc.*, 1954, **76**, 5491.

[14] Riemschneider and Nehring, *Monatsh.*, 1959, **90**, 568.

[15] Kohler and Kable, *J. Amer. Chem. Soc.*, 1935, **57**, 917.

from ligroin gave orange-brown prisms of *1,1'-di-(1-phenylcyclohexyl)ferrocene* (4·9 g., 96%), m. p. 135—136° (Found: C, 81·4; H, 7·8. $C_{34}H_{38}Fe$ requires C, 81·3; H, 7·6%).

1,1'-Dicyclohexylferrocene.—Pentamethylenefulvene (2·92 g., 0·02 mole) in ether (10 ml.) was added dropwise, under nitrogen, to a stirred suspension of lithium aluminium hydride (0·76 g., 0·02 mole) in ether (10 ml.). A vigorous reaction ensued, and a thick white precipitate was formed. A solution of anhydrous ferric chloride in ether was added dropwise to the mixture until a permanent (10 min.) blue colour developed. The mixture was added to ice-water (100 ml.) and 12·5% titanous chloride solution (50 ml.) and extracted with ether (3 × 50 ml.). The combined ether extracts were dried ($CaCl_2$) and evaporated to an orange oil (2·0 g.) which rapidly became green in air. Ligroin (50 ml.) and zinc dust were added to the oxidised material, and the mixture was shaken for 0·5 hr., filtered, and chromatographed on alumina. The main orange band was eluted rapidly with ligroin, the eluent evaporated under a reduced atmosphere of nitrogen, and the residue distilled at 184° (bath)/0·08 mm. *1,1'-Dicyclohexylferrocene* (1·8 g., 77%) crystallised as fine orange-brown rods, m. p. 42·5°. The m. p. remained unchanged after six further distillations (Found: C, 76·6; H, 8·55. $C_{22}H_{30}Fe$ requires C, 75·4; H, 8·6%).

Solid 1,1'-dicyclohexylferrocene is stable in air but in solution the substance was oxidised, and owing to its great solubility in organic solvents did not recrystallise satisfactorily.

Catalytic Hydrogenation of 1,1'-Diphenylferrocene.—1,1'-Diphenylferrocene (0·1014 g., 0·0003 mole) was added in ether (15 ml.) to 10% palladium–charcoal (20 mg.; presaturated with hydrogen) in ether (10 ml.). After 16 hr. 5 ml. of hydrogen had been absorbed (theor. 3 ml.), and the ethereal solution was practically colourless. Continuous ether-extraction of the catalyst and evaporation of the extract left an orange oil (0·142 g.), which crystallised. Chromatography of this solid in ligroin yielded 1,1'-dicyclohexylferrocene (0·07 g., 66·7%), m. p. 42—43° after a single distillation. The other products were not investigated.

1,1'-Di-isopropylferrocene.—Dimethylfulvene (2·12 g., 0·02 mole) in ether (25 ml.) was added dropwise to a stirred suspension of lithium aluminium hydride (0·19 g., 0·02 mole) in ether (10 ml.) at room temperature under an atmosphere of nitrogen. After 15 min., anhydrous ferric chloride (1·625 g., 0·01 mole) in ether (40 ml.) was added dropwise, and the resulting blue mixture stirred for a further 12 hr. at room temperature, then poured on ice (100 g.) and titanous chloride solution (200 ml.). The organic phase was separated, combined with the ether extracts (3 × 100 ml.), dried, and evaporated. The residual oil (2·91 g.), after chromatography, gave *1,1'-di-isopropylferrocene* (2·0 g., 74%) as an orange-red liquid, b. p. 91°/0·025 mm., n_D^{20} 1·5604 (Found: C, 71·55; H, 8·0. $C_{16}H_{22}Fe$ requires C, 71·1; H, 8·2%).

Reaction between Azulene, Phenyl-lithium, and Ferrous Chloride.—Azulene (2·56 g., 0·02 mole) in ether (25 ml.) was added to phenyl-lithium (*ca.* 0·02 mole) in ether (30 ml.), and the mixture stirred under nitrogen for 4 hr. at room temperature. Decolorisation was not complete. Ferrous chloride [from ferric chloride (4·875 g., 0·03 mole)], added in tetrahydrofuran (10 ml.) to the brown mixture, caused an immediate exothermic reaction and colour change to burgundy-red. After 13 hr. the mixture was filtered, and the solid residue washed with ether (50 ml.) and methanol (15 ml.), and digested with chloroform (2 × 50 ml.) at room temperature. The combined filtrate and organic phases were washed, dried ($CaCl_2$), and evaporated to a dark red oil (4·66 g., 100%). About 0·6 g. of this oil was dissolved in ligroin (10 ml.) and benzene (5 ml.) and placed on alumina (130 × 2 cm.). Elution with ligroin (900 ml.) removed a trace of azulene, followed by a diffuse pink band, whose ingredients were not separated. Evaporation left an oil, presumably containing the mixed isomers of di-(8,9-dihydro-8-phenylazulenyl)-iron(II). Sublimation did not succeed, but the residue, on trituration with ligroin, gave a solid, m. p. 103—107° (Found: C, 81·4; H, 5·9. $C_{32}H_{26}Fe$ requires C, 82·4; H, 5·6%).

Bis-(3α,4-*dihydroazulenyl*)*iron* (IX).—Azulene (1·28 g., 0·01 mole) and lithium aluminium hydride (0·40 g., *ca.* 0·01 mole) were suspended in ether (50 ml.; dried by lithium aluminium hydride) under nitrogen and the whole was shaken for 60 days. To the resulting colourless solution (which contained a brown suspension) was added anhydrous ferrous chloride [from anhydrous ferric chloride (1·625 g., 0·01 mole)] in tetrahydrofuran (100 ml.). An exothermic reaction took place and the mixture became red. After 36 hr. under nitrogen, methanol (10 ml.) was added and the mixture filtered and added to water (100 ml.). The dried organic phase was evaporated, the residue passed in benzene down a column of alumina, and the residue of the red mobile band rechromatographed on alumina (25 × 2·5 cm. column) in ligroin (b. p. 40—60°). Azulene (0·16 g.) was recovered from the first band. The second band was not resolved by slow elution and yielded a red solid (0·52 g., 17%). This was twice recrystallised from ligroin (b. p. 40—60°) and twice sublimed at 60°/0·02 mm., the sublimate being washed with ligroin and recrystallised from the same solvent, to yield red needles of one isomer of bis-(3α,4-dihydroazulenyl)iron (IX), m. p. 68°. The mother liquors from the first recrystallisation were evaporated, and the residue was sublimed. The oily sublimate was partially resublimed twice, the most volatile fraction being retained each time; this finally yielded material, m. p. 18°, which did not crystallise when seeded with a crystal of the higher-melting isomer. A sample of the mixed isomers, having m. p. 47—53°, gave the expected analyses (Found: C, 76·4; H, 6·2. Calc. for $C_{20}H_{18}Fe$: C, 76·45; H, 5·8%).

Bis(hexahydroazulenyl)iron(II).—The crude mixed isomers of bis-(3α,4-dihydroazulenyl)-iron(II) (*ca.* 0·07 g.) were rapidly hydrogenated in methanol over Adams catalyst, changing in colour from red to yellow. The solution was filtered and evaporated. The residue was recrystallised twice from absolute ethanol, yielding golden-orange prisms of *bis(hexahydroazulenyl)iron*, m. p. 52—54° (Found: C, 74·8; H, 8·3. $C_{20}H_{26}Fe$ requires C, 74·5; H, 8·1%).

1,1′-*Di-isopropenylferrocene*.—Sodamide was prepared from sodium (1·38 g., 0·06 g. atom) and liquid ammonia (150 ml.) containing a trace of ferric nitrate. Dimethylfulvene (6·36 g., 0·06 mole) was added, and the mixture stirred under nitrogen at the temperature of refluxing ammonia, assuming in 3 hr. a dark red colour. Anhydrous ferrous chloride [from ferric chloride (3·47 g., *ca.* 0·02 mole)] was added portionwise. The mixture was stirred for a further 18 hr. under nitrogen. The ammonia was allowed to evaporate, and ethanol (50 ml.), ice (150 g.), and ligroin (100 ml.; b. p. 40—60°) were added; the ligroin phase was separated, and the aqueous phase extracted with ligroin (3 × 100 ml.; b. p. 40—60°). The combined extracts were dried by passage down a column of calcium chloride and sodium sulphate, evaporated to small volume *in vacuo* at room temperature, and immediately chromatographed on alumina. The eluate of the main orange-red band, which was eluted after a small quantity of dimethylfulvene, was concentrated to small volume *in vacuo* at room temperature, rapidly filtered, and cooled to −70°. Orange-red crystals of 1,1′-*di-isopropenylferrocene* separated. An analytically pure sample had m. p. 58—59° after one recrystallisation (Found: C, 72·35; H, 7·0. $C_{16}H_{18}Fe$ requires C, 72·2; H, 6·8%). The material polymerised extremely rapidly in solution, and in contact with air in the solid state. Consequently yields varied considerably; they never exceeded 65%.

1,1′-*Dicyclohex*-1-*enylferrocene*.—Pentamethylenefulvene (4·38 g., 0·03 mole; n_D^{21} 1·568) was added to sodamide [from sodium (0·69 g.) and ferric nitrate] in liquid ammonia (150 ml.). After 4·5 hr. the mixture had assumed a dark red colour, and ferrous chloride [from anhydrous ferric chloride (4·95 g.)] was added portionwise in 10 min. The mixture was stirred for 13·5 hr. under nitrogen as the ammonia evaporated, then treated with ethanol (50 ml.), poured into water (500 ml.), and extracted with ether (4 × 100 ml.). The combined ether extracts were dried (soda-lime) and evaporated under a reduced pressure of nitrogen. The residue was chromatographed in ligroin (b. p. 40—60°) on alumina (20 × 3 cm.). The largest, first, orange band was eluted with the same solvent, the eluate filtered and evaporated (under nitrogen), and the residual red oil (3·7 g., 71%) distilled. The excess of pentamethylenefulvene distilled first, followed by 1,1′-*dicyclohex*-1-*enylferrocene*. This redistilled at 180° (bath)/0·15 mm., as a deep red oil, n_D^{24} 1·6215, which crystallised *in vacuo* as red prisms, m. p. 44° (Found: C, 75·8; H, 7·5. $C_{22}H_{26}Fe$ requires C, 76·3; H, 7·6%). Although polymerising rapidly in solution, or when an oil, solid 1,1′-dicyclohex-1-enylferrocene (unlike 1,1′-di-isopropenylferrocene) was unchanged in appearance after storage for six months in a sealed bottle.

Catalytic Hydrogenation of 1,1′-*Dicyclohex*-1-*enylferrocene*.—Freshly distilled 1,1′-dicyclohex-1-enylferrocene (*ca.* 0·85 g., 0·00246 mole) was hydrogenated overnight in pure ether (25 ml.) and over 10% palladium–charcoal (57 mg.). The solution was filtered, the catalyst washed with ether (5 × 10 ml.), and the filtrate evaporated to an orange oil (0·69 g.) which was distilled [b. p. 160° (bath)/0·07 mm.]. The distillate cooled to orange-brown needles, m. p. 39°; a mixed m. p. with 1,1′-dicyclohexylferrocene prepared from lithium aluminium hydride, pentamethylenefulvene, and anhydrous ferric chloride, was 42°.

Dehydrogenation of 1,1′-*Dicyclohex*-1-*enylferrocene*.—1,1′-Dicyclohex-1-enylferrocene (*ca.* 1·0 g., 0·003 mole) was heated with 10% palladium–charcoal (*ca.* 300 mg.) at 220—240° under nitrogen for 5·25 hr. Loss of material by sublimation was prevented by employing a water-condenser (100 cm.) plugged with cotton wool. The mixture was allowed to cool and extracted with ether, and the extract was filtered and evaporated. The red oil (0·85 g.) was chromatographed in ligroin on alumina (44 × 2·5 cm.). Two bands developed, yielding successively unchanged 1,1'-dicyclohex-1-enylferrocene and 1,1'-diphenylferrocene. A single recrystallisation from ligroin gave 1,1'-diphenylferrocene (0·39 g., 40%) as red plates, m. p. and mixed m. p. 153—154°.

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