183. *The Interaction of Diphenylketen and 2-Benzylidene-indan-1-one.*

By Neil Campbell, P. S. Davison, and H. G. Heller.

Diphenylketen and 2-benzylideneindan-1-one at 140° yield mainly 2-benzylidene-1-diphenylmethyleneindane (III), the structure of which has been established. The hydrocarbon, when exposed to sunlight in hexane, undergoes dehydrocyclisation to yield 5,10-diphenyl-11*H*-benzo[*b*]fluorene (VIII).

Diphenylketen reacts with αβ-unsaturated ketones to give β- or δ-lactones or their decomposition products.[1] We find that heating the keten with 2-benzylideneindan-1-one (I) at 140° gives the β-lactone (II) since the main product of the reaction is 2-benzylidene-1-diphenylmethyleneindane (III), obtained by the decarboxylation of the lactone. The hydrocarbon is a colourless crystalline substance, m. p. 139°, the structure of which follows from its ozonolysis to yield benzophenone and benzaldehyde, the formation of a Diels–Alder adduct with tetracyanoethylene, and smooth ring-closure to the diphenylbenzofluorene (VIII) (see below). Confirmation of the structure was supplied by reduction of the hydrocarbon with aluminium amalgam[2] to 2-benzyl-3-diphenylmethylindene (IV), whose ultraviolet spectrum resembled those of 2-benzylindene and 3-diphenylmethylindene and which was synthesised in the following manner. 2-Benzylideneindan-1-one with hydrogen and a palladium catalyst gave a good yield of 2-benzylindan-1-one (V) (benzylideneacetophenone likewise gave a good yield of benzylacetophenone). Reduction of the ketone to the alcohol, followed by dehydration, yielded 2-benzylindene (VI), identical with a sample prepared by another method.[3] Unlike 2-methylindene,[4] 2-benzylindene did not condense with benzaldehyde or anisaldehyde, but it formed a Grignard reagent with ethylmagnesium bromide,[5] thus confirming its indene structure. The Grignard compound

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[1] Staudinger and Kon, *Annalen*, 1911, **384**, 38; Staudinger and Endle, *ibid.*, 1913, **401**, 263.

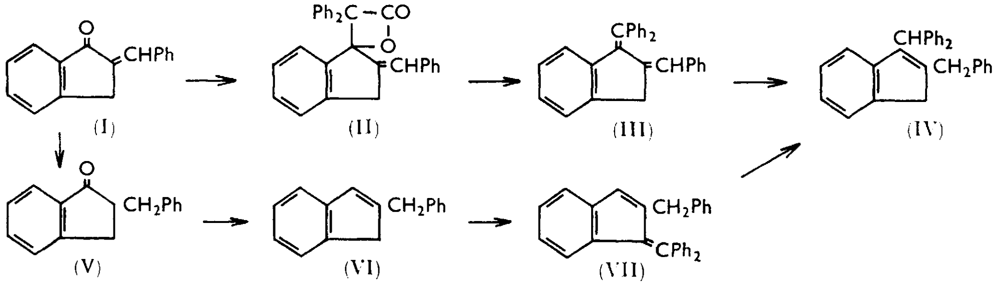
[2] Thiele and Bühner, *Annalen*, 1906, **347**, 249.

[3] Campbell and Heller, *J.*, 1962, 3006.

[4] von Braun, Kruber, and Danziger, *Ber.*, 1916, **49**, 2652.

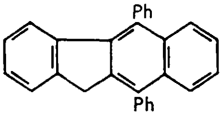
[5] Courtot, *Ann. Chim.* (*France*), 1915, **4**, 58, 76.

with benzophenone gave the corresponding alcohol, dehydration of which yielded the yellow benzofulvene, 2-benzyl-1-diphenylmethyleneindene (VII), whose ultraviolet spectrum resembled that of 1-diphenylmethyleneindene.[6] Reduction with aluminium amalgam,



used by Thiele and Merck[7] to reduce 1-diphenylmethyleneindene (see below) to 3-diphenylmethylindene, gave 2-benzyl-3-diphenylmethylindene (IV) identical with the product obtained as above.

Anomalous behaviour of the hydrocarbon (III), which is thermochromic, was observed when it was dissolved in organic solvents. Not only was the ultraviolet spectrum of such solutions unexpectedly different from that of 1,1,2,4-tetraphenylbutadiene, but the solutions assumed a yellow colour. It was thought at first that this might be due to isomerisation of the hydrocarbon to 2-benzyl-1-diphenylmethyleneindene (VII), but that was disproved as this compound has a characteristic diphenylbenzofulvene spectrum. When the n-hexane solution of the hydrocarbon (III) was exposed to sunlight for five hours the yellow colour disappeared and from the solution the diphenylbenzofluorene (VIII), identical with a sample prepared by the interaction of indene and 1,3-diphenylisobenzofuran,[8] separated. Evidently we are dealing with the photodehydrogenation of a butadiene derivative (IX), a reaction reminiscent of the conversion of dibenzylidenesuccinic acid into 1-phenylnaphthalene-2,3-dicarboxylic acid[9] or 1,4-diphenylbutadiene into 1-phenylnaphthalene.[10]



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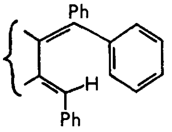
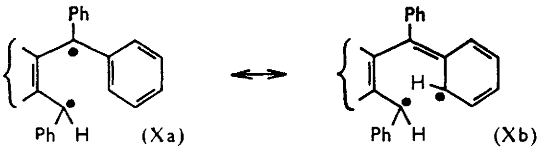
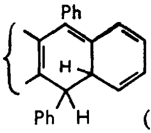


(IX)

The properties of the hydrocarbon (III) and particularly the ease with which one of its phenyl rings loses a hydrogen atom in the cyclodehydrogenation suggest that in solution it exists, partly at least, as a diradical (Xa and b). Cyclisation can then be pictured as free-radical attack of the benzene ring to give a dihydro-intermediate (XI)[11] which undergoes dehydrogenation, possibly by atmospheric oxygen.[12]





(XI)

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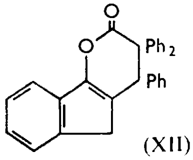
[6] Weizmann, Bergmann, and Sulzbacher, *J. Org. Chem.*, 1950, **15**, 918.
[7] Thiele and Merck, *Annalen*, 1918, **415**, 257.
[8] Weiss and Beller, *Monatsh.*, 1932, **59**, 143.
[9] Stobbe, *Ber.*, 1907, **40**, 3372; Baddar, El-Assal, and Gindy, *J.*, 1948, 1270.
[10] Fonken, *Chem. and Ind.*, 1962, 1327.
[11] Hugelshofer, Kalvoda, and Schaffner, *Helv. Chim. Acta*, 1960, **43**, 1322.
[12] Brockmann and Mühlmann, *Chem. Ber.*, 1949, **82**, 348.

The reaction between diphenylketen and 2-benzylideneindan-1-one yielded several other products, including a carbonyl compound, m. p. 190°, of unknown structure, the δ-lactone (XII), and a product, m. p. 230°, containing no carbonyl group but yielding diphenylketen on pyrolysis at 250°. We suggest that the last substance is an adduct of diphenylketen and the hydrocarbon (III) with structure (XIII) or (XIIIa)[13] and this is confirmed by the similarity of its ultraviolet spectrum to that of 2-benzyl-3-diphenylmethylindene (IV). If this is so, the reaction is unusual in furnishing an example, not only of a keten participating as a dienophile in a Diels–Alder reaction, but also of its doing this through the carbonyl double bond.[13] Ketens are known to react with one of the double bonds of conjugated dienes, and not at the 1,4-positions.[14] On the other hand, diphenylketen has been shown to form ring compounds with certain carbenes in which the keten-carbonyl double bond participates.[15] In view of this and our own work it is tempting to suggest that the interaction of ketens and diradicals or carbenes occurs through the carbonyl double bond; but this generalisation is too sweeping since we have found that the product from the photoreaction of phenanthraquinone with diphenylketen[16] contains the carbonyl group intact.



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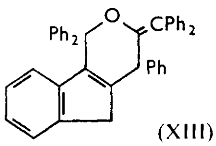

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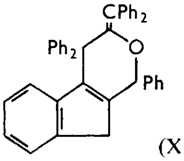
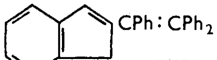


(XIIIa)

In one experiment, heating equimolecular quantities of diphenylketen and 2-benzylideneindan-1-one gave none of the usual product, m. p. 139°, but a hydrocarbon of m. p. 220° with a bright blue fluorescence and a spectrum not unlike that of 1,1,2,4-tetraphenylbutadiene. It is suggested that this hydrocarbon is 2-indenyltriphenylethylene (XIV).

2-Benzylidene-1-diphenylmethylene-3,3-dimethylindane (XV) was synthesised and found to possess the characteristic properties of hydrocarbon (III), readily undergoing cyclodehydrogenation to give 11,11-dimethyl-5,10-diphenylbenzo[*b*]fluorene, identical with a specimen prepared by the interaction of 1,3-diphenylisobenzofuran and the formate of 3,3-dimethylindan-1-ol. Since hydrocarbons (III) and (XV) exhibit similar properties and, since the two methyl groups in the latter substance exclude isomerisation, confirmation is obtained that the striking characteristics in solution of hydrocarbon (III) cannot be attributed to tautomerism.



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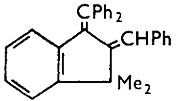
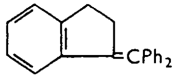


(XV)

(XVI)



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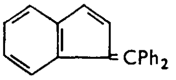

(XVIII)

Wohl–Ziegler bromination of 1-diphenylmethyleneindane (XVII) resulted in spontaneous dehydrobromination and the formation of 1-diphenylmethyleneindene (XVIII).[17] The diphenylmethyleneindene (XVII) was prepared by dehydration of the alcohol (XVI)[18]

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[13] Campbell and Davison, *Chem. and Ind.*, 1962, 2012.

[14] Alder and Rickert, *Annalen*, 1940, **543**, 15; Young, *J. Amer. Chem. Soc.*, 1949, **71**, 1346; Vogel and Müller, *Annalen*, 1958, **615**, 29.

[15] Yates and Robb, *J. Amer. Chem. Soc.*, 1957, **79**, 5760; Gulbins and Hamann, *Chem. Ber.*, 1961, **94**, 3287.

[16] Schönberg and Mustafa, *J.*, 1947, 999.

[17] Courtot, *Ann. Chim.* (*France*), 1915, **4**, 215.

[18] Courtot, *Ann. Chim.* (*France*), 1916, **5**, 66.

which can be prepared either by dehydrogenation of the corresponding indene-alcohol[19] or by the interaction of 1-benzoylindane and phenylmagnesium bromide.

EXPERIMENTAL

Ultraviolet spectra were measured for n-hexane solutions unless otherwise indicated.

2-*Benzylindene*.—2-Benzylideneindan-1-one on ozonolysis in carbon tetrachloride–n-hexane yielded benzaldehyde and homophthalic acid. The ketone (11 g.) in ethanol was hydrogenated at 5 atm. with a palladium–barium sulphate catalyst.[20] The theoretical amount of hydrogen was absorbed in 1 hr. and removal of the catalyst and solvent yielded 2-benzylindan-1-one (8·65 g.), b. p. 206°/12 mm. (Found: C, 86·3; H, 6·3. Calc. for $C_{16}H_{14}O$: C, 86·4; H, 6·35%) [2,4-*dinitrophenylhydrazone*, red plates (from acetic acid), m. p. 196—197° (Found: N, 13·1. $C_{22}H_{18}N_4O_4$ requires N, 13·9%)]. The ketone (10 g.) with aluminium isopropoxide in isopropyl alcohol gave 2-*benzylindan*-1-*ol* (8·2 g.), needles (from light petroleum), m. p. 104—105° (Found: C, 85·9; H, 7·4. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%). The alcohol (7 g.) was heated with 90% formic acid (25 ml.) for 1 hr. and diluted with water (250 ml.). Extraction with ether and removal of the ether after washing with sodium carbonate and water gave 2-benzylindene (45%), m. p. and mixed m. p. 48° (lit.,[3] 48°).

2-*Benzyl*-1-*diphenylmethyleneindene*.—2-Benzylindene (2·06 g.) in toluene (8 ml.) and ether (3 ml.) was added to ethylmagnesium bromide prepared from ethyl bromide (0·8 ml.), magnesium (0·25 g.), and ether (8 ml.). Ether was distilled off and the mixture heated on a water-bath (3½ hr.) and then boiled (3 hr.). Benzophenone (1·8 g.) was added to the cooled mixture and the whole was then heated for ½ hr. Dilute hydrochloric acid was added and the mixture extracted with ether. Solvent was removed from the ether layer by distillation and the residual oil heated for 1 hr. with 90% formic acid. Working-up the solution in the usual way gave an orange oil, which was chromatographed on alumina with benzene as solvent and light petroleum (b. p. 60—80°) as developer. A yellow band yielded 2-*benzyl*-1-*diphenylmethyleneindene*, prisms (from ethanol), m. p. 126° (Found: C, 94·2; H, 6·05. $C_{29}H_{22}$ requires C, 94·0; H, 6·0%), $\lambda_{max.}$ 253, 285, and 350 mμ (log ε 4·40, 4·13, and 4·11) [cf. 1-diphenylmethyleneindene, $\lambda_{max.}$ 244—245, 284, and 340 mμ (log ε 4·44, 4·24, and 4·29].

2-*Benzyl*-3-*diphenylmethylindene*.—Reduction of benzyldiphenylmethyleneindene (0·03 g.) with aluminium amalgam in moist ether for 7 hr. gave 2-benzyl-3-diphenylmethylindene, m. p. 115—116°, undepressed when admixed with the compound prepared as below.

Interaction of Diphenylketen and 2-*Benzylideneindan*-1-*one*.—Equimolecular proportions of diphenylketen (9·2 g.) and 2-benzylideneindan-1-one (10·3 g.) were heated under nitrogen in a sealed-tube at 140—145° for 3½ hr. Trituration of the product with ether yielded yellow crystals (5·5 g.) and a filtrate (A). The crystals were boiled with light petroleum (200 ml.), giving an insoluble solid, prisms (from benzene–light petroleum), m. p. 190° (Found: C, 87·0; H, 6·2%), ν 1705 (CO) and 1605 cm.$^{-1}$ (C:C), and the filtrate, on cooling, yielded 2-*benzylidene*-1-*diphenylmethyleneindane*, crystals (from ethanol), m. p. 139° (orange melt) (Found: C, 93·75; H, 6·1. $C_{29}H_{22}$ requires C, 94·0; H, 6·0%). The latter became yellow when exposed to light or heated, and failed to give an adduct with maleic anhydride; but when heated (4 hr.) with tetracyanoethylene in benzene it gave an *adduct* of high m. p., which was crystallised from benzene (Found: C, 84·2; H, 4·5; N, 10·8. $C_{35}H_{22}N_4$ requires C, 84·3; H, 4·55; N, 11·15%), $\lambda_{max.}$ 265 mμ (log ε 4·19), $\lambda_{min.}$ 248 mμ (log ε 4·07) in $CHCl_3$. The ultraviolet spectrum of the adduct is similar to that of 2-benzyl-3-diphenylmethylindene, proving that addition had occurred at the 1,4-positions of the diene system and not at a double bond. Reduction of the hydrocarbon with aluminium amalgam and moist ether for 3 days at room temperature gave 2-*benzyl*-3-*diphenylmethylindene* having m. p. 115—116°, after crystallisation from ethanol and then from light petroleum (Found: C, 93·5; H, 6·5. $C_{29}H_{24}$ requires C, 93·5; H, 6·5%), and $\lambda_{max.}$ 261 (log ε 4·29), $\lambda_{min.}$ 240 mμ (log ε 3·99).

Ozone was passed through benzylidenediphenylmethyleneindane (0·3 g.) in n-hexane (50 ml.) and carbon tetrachloride (25 ml.) until the ozonide separated. Steam-distillation gave first solvent and then benzophenone, identified by its m. p., mixed m. p., infrared spectrum, and dinitrophenylhydrazone. Ozone was passed through a separate portion of the hydrocarbon

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[19] Courtot, *Ann. Chim.* (*France*), 1915, **4**, 131.

[20] Breitner, Roginski, and Rylander, *J. Org. Chem.*, 1959, **24**, 1855.

(0·75 g.) in carbon tetrachloride (100 ml.), cooled in ice, until the yellow solution became colourless (25 min.). Steam-distillation yielded benzaldehyde, detected by odour, dinitrophenylhydrazone, and oxidation ($KMnO_4$) to benzoic acid.

The filtrate (A), on evaporation, left a residue which was triturated with light petroleum, giving yellow crystals (3 g.) and a filtrate (B). Repeated crystallisation of the crystals from benzene and light petroleum gave the δ-lactone, 2,3,4,5-*tetrahydro*-3,3,4-*triphenylindeno*[1,2-*b*]-*pyran*-2-*one* (XII), needles, m. p. 222° (Found: C, 86·4; H, 5·4. $C_{30}H_{22}O_2$ requires C, 86·9; H, 5·4%), ν 1775s (C=O) and 1670 cm.$^{-1}$, $\lambda_{\text{max.}}$ 250 and 278 mμ (log ε 4·09 and 3·99), $\lambda_{\text{min.}}$ 239 and 269 mμ (log ε 4·07 and 3·97).

The filtrate (B) and the combined filtrates from the crystallisation of the δ-lactone gave on evaporation, a residue which was boiled with ethanol. The solid insoluble therein crystallised from benzene–light petroleum in prisms, m. p. 239°, probably the adduct, 3-*diphenylmethylene*-1,3,4,5-*tetrahydro*-1,1,4-*triphenylindeno*[1,2-*c*]*pyran* (XIII) (Found: C, 89·8; H, 5·3. $C_{42}H_{32}O$ requires C, 91·5; H, 5·7%), $\lambda_{\text{max.}}$ 267 mμ (log ε 4·40), $\lambda_{\text{min.}}$ 239 (log ε 4·4).

5,10-*Diphenyl*-11H-*benzo*[*b*]*fluorene*.—The hydrocarbon (III) (0·1 g.) in n-hexane (500 ml.) gave a colourless solution after exposure to sunlight for 2 days. Evaporation of the solution gave 5,10-diphenyl-11*H*-benzo[*b*]fluorene, m. p. 199° (lit.,[8] 199°), $\lambda_{\text{max.}}$ 270, 310, and 323 mμ (log ε 4·82, 4·25, and 4·28).

Compound, M. p. 220°.—In one instance, heating equimolecular quantities of diphenylketen and 2-benzylideneindan-1-one in a sealed tube at 140° for 3½ hr. gave a product which was chromatographed in ethyl acetate on alumina with ethyl acetate–light petroleum (1 : 10 v/v) as developer. Elution of a yellow band gave a solid which was boiled with light petroleum (b. p. 60—80°). The insoluble material crystallised in plates (from benzene–light petroleum), m. p. 220° (Found: C, 93·8; H, 5·9. $C_{29}H_{22}$ requires C, 94·0; H, 6·0%), $\lambda_{\text{max.}}$ 242, 261, 271, 277, 280, 324, and 339—340 mμ (log ε 4·35, 4·56, 4·51, 4·34, 4·31, 4·60, and 4·45), similar to that of 1,1,2,4-tetraphenylbutadiene, $\lambda_{\text{max.}}$ 255—260 and 335 mμ (log ε 4·18, 4·44), $\lambda_{\text{min.}}$ 285 mμ (log ε 4·00). Efforts to repeat the experiment were unsuccessful.

Interaction of 2-*Benzylidene*-3,3-*dimethylindan*-1-*one*.—3,3-Dimethylindan-1-one (4 g.) [2,4-*dinitrophenylhydrazone*, red prisms, m. p. 270° (Found: N, 15·9. $C_{17}H_{16}N_4O_4$ requires N, 16·5%)], benzaldehyde (2·7 g.), and potassium hydroxide (1 g.) in ethanol (20 ml.) were boiled for 15 min. and then poured into water. The oil solidified and separated from light petroleum in yellow crystals (1·1 g.) of 2-*benzylidene*-3,3-*dimethylindan*-1-*one*, m. p. 79—80° (Found: C, 86·9; H, 6·3. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%), ν 1700s (C=O), 1620s (C:C), and 1320m cm.$^{-1}$ (CMe_2) [2,4-*dinitrophenylhydrazone*, orange needles and crimson plates (from acetic acid), m. p. 218° (Found: N, 12·9. $C_{24}H_{20}N_4O_4$ requires N, 12·6%)]. This indanone (0·76 g.) and diphenylketen (0·59 g.) were heated under nitrogen in a sealed tube for 3 hr. at 160°. The product in ether was chromatographed on alumina and developed with light petroleum, to give an orange band which yielded 2-*benzylidene*-1-*diphenylmethylene*-3,3-*dimethylindane*, needles (from benzene–light petroleum), m. p. 223°, giving yellow solutions in organic solvents (Found: C, 93·3; H, 6·6. $C_{31}H_{26}$ requires C, 93·4; H, 6·6%). The filtrates, on storage, deposited 11,11-dimethyl-5,10-diphenylbenzo[*b*]fluorene, m. p. 230°, not depressed when admixed with a synthetic sample (see below). The benzylidene derivative also underwent dehydrocyclisation when exposed to light in n-hexane.

11,11-*Dimethyl*-5,10-*diphenylbenzo*[b]*fluorene*.—The above indanone was reduced by aluminium isopropoxide and propyl alcohol to 3,3-dimethylindan-1-ol which did not crystallise. The gum, when heated with formic acid, yielded an impure oily formate, with a characteristic odour, b. p. 60—70°/0·5 mm. (Found: C, 79·3; H, 7·9. Calc. for $C_{12}H_{14}O_2$: C, 75·3; H, 7·4%), ν 1720s (C=O), 1350m (CMe_2), and 1175s cm.$^{-1}$ (formate), which reduced ammoniacal silver nitrate. The ester (1 g.) and 1,3-diphenylisobenzofuran (1 g.) were suspended in ethanol (10 ml.), and hydrogen chloride was passed through the suspension for 1 hr. 11,11-*Dimethyl*-5,10-*diphenylbenzo*[b]*fluorene* separated; it formed plates (from ethanol), m. p. 230° (Found: C, 93·3; H, 6·9. $C_{31}H_{24}$ requires C, 93·9; H, 6·1%), $\lambda_{\text{max.}}$ 260, 272, 308, and 322 mμ (log ε 4·70, 4·87, 4·35, and 4·41), $\lambda_{\text{min.}}$ 240, 265, 293, and 315 mμ (log ε 4·51, 4·69. 4·05, and 4·22).

1-*Diphenylmethyleneindene*.—An excess of diphenylcadmium in benzene was added during ½ hr. to indane-1-carbonyl chloride (9 g.) in benzene, and the stirred mixture was boiled for 2 hr. Working-up gave 1-benzoylindane, b. p. 130—170°/2 mm., ν 1680s cm.$^{-1}$ (C=O). The gum in ether was added with stirring to an excess of phenylmagnesium bromide, to give 1-indanyldiphenylmethanol (39%), m. p. 85° (lit.,[19] 90°) unchanged after repeated crystallisation (Found:

C, 88·0; H, 6·8. Calc. for $C_{22}H_{20}O$: C, 88·0; H, 6·7%). With ethanol and hydrochloric acid the alcohol yielded 1-diphenylmethyleneindane, which (1·42 g.) with *N*-bromosuccinimide (0·89 g.) in carbon tetrachloride underwent a vigorous reaction with evolution of hydrogen bromide. Evaporation gave a quantitative yield of crude 1-diphenylmethyleneindene, yellow needles (from ethanol), m. p. 114—115° (lit.,[17] 116°).

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THE UNIVERSITY, EDINBURGH.

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