561. *Oxidations of Organic Compounds by Cupric Salts. Part III.*[1] *The Oxidation of Propargyl Alcohol.*

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Acetylenes are oxidised to diynes in the absence of oxygen by cupric acetatein pyridine solution. Kinetic studies with propargyl alcohol show that the reaction requires the presence of copper(I) and becomes of zero order with respect to copper(II) at high $Cu^I : Cu^{II}$ ratios and that its rate depends on the basicity of the solution.

From the observed rate-dependences on copper(I) and acetylene concentrations a reaction mechanism is formulated in which the velocity depends on the rate of formation of the cuprous acetylide, oxidation of the latter involving a one-electron transfer through a ligand acetate group:

$$R\cdot C\equiv C\cdot Cu^I + AcO\cdot Cu^{II}\cdot OAc \longrightarrow R\cdot C\equiv C\cdot + 2Cu^IOAc$$

In the preceding Parts it was shown by Marshall and Waters that oxidation of acetoin and of benzoin by cupric salts required the presence of a cuprous compound and were reactions of zero order with respect to copper(II).[2] Similar kinetic features were first noted by Calvin for the oxidation of hydrogen by cupric chloride in quinoline solution.[3] To discover whether this catalysis by a copper(I) compound is a general feature of oxidations of organic compounds by cupric compounds we have investigated the oxidation of acetylenes, $R\cdot C\equiv CH$ to diynes, $R\cdot C\equiv C\cdot C\equiv C\cdot R$ and now report that this reaction too exhibits the same kinetic features.

It has long been known that the oxidation $2R\cdot C\equiv CH \xrightarrow{-2e} R\cdot C\equiv C\cdot C\equiv C\cdot R + 2H^+$ is best effected by the use of cuprous acetylides, but, preparatively, the best yields of diynes are obtained by oxidising the acetylide by free oxygen rather than by cupric salts. However,

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[1] Part II, Marshall and Waters, *J.*, 1961, 1579.

[2] Marshall and Waters, *J.*, 1960, 2392.

[3] Calvin, *Trans. Faraday Soc.*, 1938, **34**, 1181; *J. Amer. Chem. Soc.*, 1939, **61**, 2230.

cupric acetate in pyridine or pyridine–methanol can be used, without the addition of a cuprous salt, as an oxidant of acetylenes [4,5] and the simple reaction mechanism

$$\mathrm{R{\cdot}C{\equiv}CH \rightleftharpoons R{\cdot}C{\equiv}C^- + H^+}$$

$$\mathrm{R{\cdot}C{\equiv}C^- + Cu^{II} \longrightarrow R{\cdot}C{\equiv}C{\cdot} + Cu^{I}}$$

$$\mathrm{2R{\cdot}C{\equiv}C{\cdot} \longrightarrow R{\cdot}C{\equiv}C{-}C{\equiv}C{\cdot}R}$$

has been put forward by Keblanski, Grachev, and Kustnetsova [6] for the oxidation of 2-methylbut-3-yn-2-ol in aqueous ammonia. They reported that the oxidation was of first order with respect to both copper(II) and the acetylene, but they did not control rigorously the pH of their reacting solutions and used conditions in which the cuprous acetylide was insoluble. In our opinion it is important to investigate kinetically this type of oxidation under homogeneous conditions at a controllable pH.

Preliminary tests showed that, although alkaline aqueous solutions of cupric salts, *e.g.*, Fehling's solution, can be used to oxidise water-soluble acetylenic compounds, such as sodium pent-4-ynoate, in the absence of oxygen, yellow cuprous acetylides are soon precipitated. However, homogeneous oxidations can be effected by the use of cupric acetate dissolved in pyridine and their course can be followed spectrographically in the absence of air. The acidity of these solutions can be controlled by adding piperidine, a stronger base than pyridine, and acetic acid as the other buffer component. Test oxidations of phenylacetylene by this reagent gave, after purification, an 87% yield of diphenylbutadiyne. For kinetic measurement, however, it was more convenient to use propargyl alcohol, $\mathrm{H{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}OH}$, as the oxidisable substrate, for a wide range of concentrations could then be examined.

Kinetic Results.—The oxidation, under nitrogen, of propargyl alcohol (0·1M) by cupric acetate (0·01M) in pyridine shows self-retardation (Fig. 1). This is due to the production of acetic acid in the oxidation: $\mathrm{2H{\cdot}C{\equiv}C{\cdot}CH_2{\cdot}OH + 2Cu(OAc)_2 \longrightarrow (HO{\cdot}CH_2{\cdot}C{\equiv}C{\cdot})_2 + 2CuOAc + 2HOAc}$; for when the acidity of the solution is stabilised by adding a piperidine–acetic acid buffer mixture the course of the oxidation changes to a reaction of autocatalytic type (Fig. 2), which eventually appears to be a reaction of zero order with respect to copper(II) when the buffer concentration is adequate.

If cuprous acetate is added in at least 5-fold excess over copper(II) the oxidation of propargyl alcohol by cupric acetate in buffered pyridine solution becomes a reaction of zero order with respect to copper(II) (see Table 1), and its velocity can be expressed quantitatively by an equation of the type

$$-\mathrm{d}[\mathrm{Cu^{II}}]/\mathrm{d}t = a[\mathrm{Cu^{I}}]/(1 + b[\mathrm{Cu^{I}}]) \qquad (A)$$

in regard to the cuprous salt concentration (Fig. 3); and by a similar equation

$$-\mathrm{d}[\mathrm{Cu^{II}}]/\mathrm{d}t = c[\mathrm{R{\cdot}C{\equiv}C{\cdot}H}]/(1 + d[\mathrm{R{\cdot}C{\equiv}C{\cdot}H}]) \qquad (B)$$

in regard to the acetylene concentration (Fig. 4). The rate increases with the basicity of the solution in the manner shown in Table 2.

TABLE 1.

Oxidation of propargyl alcohol by $\mathrm{Cu^{II}}$ in the presence of an excess of $\mathrm{Cu^{I}}$ at 40°.

The reaction mixture contained propargyl alcohol (0·1M), $\mathrm{Cu^{II}}$ acetate (0·008M), $\mathrm{Cu^{I}}$ acetate (0·096M), piperidine (1·2M), and acetic acid (0·2M).

Time (min.)	3	6	9	12	15	18	21	24
$[\mathrm{Cu^{II}}]$ (10^{-3}M)	7·2	6·4	5·7	4·8	4·0	3·2	2·5	1·7

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[4] Eglinton and Galbraith, *J.*, 1959, 889.

[5] Sondheimer, Amiel, and Wolovsky, *J. Amer. Chem. Soc.*, 1959, **81**, 1771.

[6] Keblanski, Grachev, and Kustnetsova, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 3008.

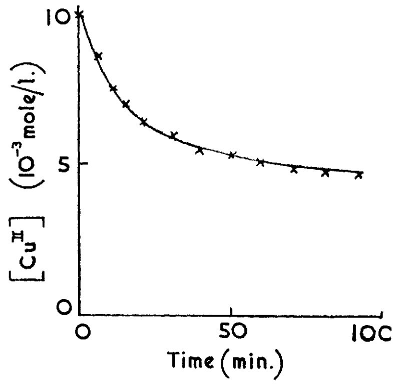


FIG. 1. Oxidation of propargyl alcohol by cupric acetate in pyridine at 40°. Initial [propargyl alcohol] 0·1M; initial [cupric acetate] 0·01M. No buffer present. Nitrogen atmosphere.

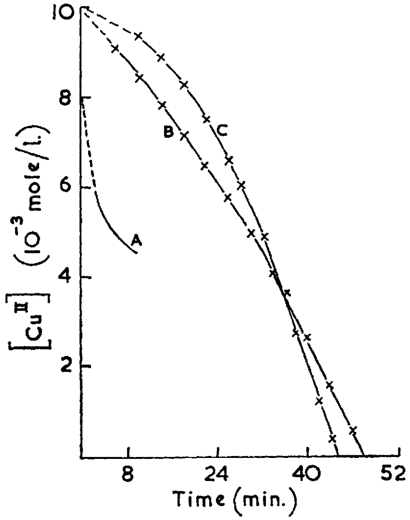


FIG. 2. Oxidation of propargyl alcohol by cupric acetate in buffered pyridine solutions at 40°. Initial [propargyl alcohol] 1·0M; initial [cupric acetate] 0·01M.

(A) No buffer. (B) 0·4M-Piperidine + 0·08M-acetic acid as buffer. (C) 1·0M-Piperidine + 0·2M-acetate acid as buffer.

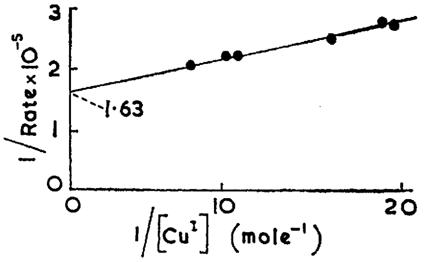


FIG. 3. Dependence of $1/\{d[Cu^{II}]/dt\}$ on $1/[Cu^{I}]$. Each reaction mixture contained propargyl alcohol 0·1M, piperidine 1·2M, acetic acid 0·2M, and Cu^{II} initially about 0·01M (rates computed in mole l.$^{-1}$ sec.$^{-1}$). Slope of the line = (1/1·87) × 10^{-4}.

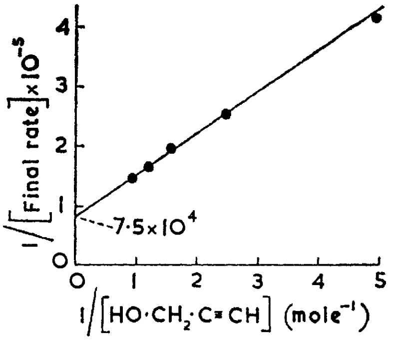


FIG. 4. Dependence of $1/\{d[Cu^{II}]/dt\}$ on $1/[R{\cdot}C{\equiv}CH]$. Each reaction mixture contained cupric acetate 0·01M, piperidine 1·0M, acetic acid 0·2M (rates for the final zero-order reaction in mole l.$^{-1}$ sec.$^{-1}$). Slope of the line = (1/1·43) × 10^{-5}.

TABLE 2.

Rate-dependence on piperidine concentration.

The concentrations at which the experimental final rates were taken were propargyl alcohol (1·0M), Cu^{I} acetate (0·01M), acetic acid (0·2M), and Cu^{II} acetate tending to zero.

[Piperidine] (M)	0·4	0·6	0·8	1·0	1·2
Final rates (10^{-6} mole l.$^{-1}$ sec.$^{-1}$):					
expt.	4·0	5·0	6·2	6·8	7·8
calc. from (*E*)	3·98	5·09	5·98	6·79	7·64

Discussion.—(*a*) *Reaction kinetics.* The solvent is a buffer system in which pyridine acetate Py,HOAc can be regarded as the weak acid component and piperidine (always used in excess over the acetic acid) and the base (*B*). Thus we may write

$$(\text{Py,HOAc}) + \text{B} \overset{K_1}{\rightleftharpoons} \text{BH}^+ + \text{OAc}^- + \text{Py}$$

and since $[\text{BH}^+] = [\text{OAc}^-]$ for electrical neutrality and $[\text{Py,HOAc}] = [\text{HOAc}]$, it follows that $[\text{BH}^+] = (K_1[\text{B}][\text{HOAc}])^{\frac{1}{2}}$.

The reaction kinetics, as for the oxidation of acyloins, correspond to a sequence involving the slow formation and rapid oxidation by copper(II) of a cuprous compound, *i.e.*:

$$\text{(1)}\quad \text{R·C≡CH} + \text{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R·C≡C}^- + \text{BH}^+$$

$$\text{(2)}\quad \text{R·C≡C}^- + \text{CuOAc} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{R·C≡C·Cu} + \text{OAc}^-$$

$$\text{(3)}\quad \text{R·C≡CCu} + \text{Cu(OAc)}_2 \xrightarrow{k_3} \text{R·C≡C·} + \text{2CuOAc}$$

$$\text{(4)}\quad \text{2R·C≡C·} \xrightarrow{k_4} \text{R·C≡C–C≡C·R}$$

where reactions (3) and (4) are much faster than (1) or (2). In the above equations, CuOAc, Cu(OAc)_2, and R·C≡CCu are used briefly to denote copper compounds with attached pyridine ligands in equilibrium with the solvent. Clearly reaction (1), the heterolysis of a C–H bond, may require a significant amount of activation energy. Reaction (2) represents S_N2 displacements at Cu^{I} centres and not reactions at ion-pairs of Cu^+; it is evidently reversible since in the absence of copper(II) the product R·C≡CCu does not accumulate so as eventually to be precipitated, but steady-state equations for the oxidation of R·C≡CH can be formulated if this back-reaction is neglected, *i.e.*:

if $$k_3[\text{Cu(OAc)}_2] \gg k_{-2}[\text{OAc}],$$

then $$[\text{R·C≡C}^-] = k_1[\text{R·C≡C·H}][\text{B}]/(k_{-1}[\text{BH}^+] + k_2[\text{CuOAc}])$$

and $$[\text{R·C≡CCu}] = k_2[\text{R·C≡C}^-][\text{CuOAc}]/k_3[\text{Cu(OAc)}_2]$$

$$= \frac{k_1k_2[\text{R·C≡CH}][\text{B}][\text{CuOAc}]}{k_3[\text{Cu(OAc)}_2](k_{-1}[\text{BH}^+] + k_2[\text{CuOAc}])}$$

so that the rate of consumption of copper(II) becomes

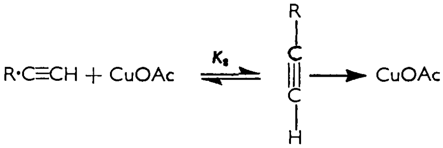
$$-\text{d}[\text{Cu(OAc)}_2]/\text{d}t = k_3[\text{R·C≡CCu}][\text{Cu(OAc)}_2]$$

$$= \frac{[k_1k_2[\text{R·C≡CH}][\text{B}][\text{CuOAc}]}{(k_{-1}[\text{BH}^+] + k_2[\text{CuOAc}])}, \qquad (C)$$

which is of zero order with respect to copper(II), shows the correct type of dependence on copper(I), and is very largely dependent on the slow rate of ionisation of the acetylene in the basic solvent.

Expression (*C*), however, indicates that the reaction should be of first order with respect to the acetylene, which is not the case. The measured reaction, in which the reciprocal of the reaction velocity varies as the reciprocal of the acetylene concentration (Fig. 4), corresponds to the common circumstance in which a fraction of a reactant has been removed, in a rapidly reversible equilibrium, by a complexing agent.

Now complexing between copper(I) and the π-orbitals of an acetylenic bond has been postulated in solid cuprous acetylides,[7] and so it is rational to formulate an equilibrium:



$$\mathrm{R{\cdot}C{\equiv}CH + CuOAc} \underset{}{\overset{K_2}{\rightleftharpoons}} \mathrm{R{-}C{\equiv}C{-}H \longrightarrow CuOAc}$$

Now if $[\mathrm{Cu^I}]$ denotes the total cuprous compound concentration, then $[\mathrm{CuOAc}] = [\mathrm{Cu^I}]/(1 + K_2[\mathrm{R{\cdot}C{\equiv}CH}])$ under our conditions when the acetylene is present in large excess over copper(I). By substituting for [CuOAc] and $[\mathrm{BH^+}]$ in the previous kinetic expression one derives that

$$-\mathrm{d}[\mathrm{Cu^{II}}]/\mathrm{d}t = \frac{k_1k_2[\mathrm{R{\cdot}C{\equiv}CH}][\mathrm{B}][\mathrm{Cu^I}]}{k_{-1}(K_1[\mathrm{B}][\mathrm{HOAc}])^{\frac{1}{2}}(1 + K_2[\mathrm{R{\cdot}C{\equiv}CH}]) + k_2[\mathrm{Cu^I}]}, \qquad (D)$$

which accords with experimental findings concerning the reaction order with respect to the acetylene. By inserting numerical values derived from Figs. 3 and 4 it can be calculated that

$$-\mathrm{d}[\mathrm{Cu^{II}}]/\mathrm{d}t = \frac{8{\cdot}84 \times 10^{-4}[\mathrm{R{\cdot}C{\equiv}CH}][\mathrm{B}][\mathrm{Cu^I}]}{[\mathrm{B}]^{\frac{1}{2}}[\mathrm{HOAc}]^{\frac{1}{2}}(1 + 1{\cdot}49[\mathrm{R{\cdot}C{\equiv}CH}]) + 17{\cdot}3[\mathrm{Cu^I}]}, \qquad (E)$$

from which it follows that the value for the equilibrium constant K_2 is 1·49 at 40°.

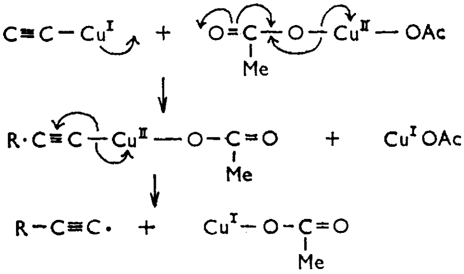
Again, from the above equation it should follow that

$$-\mathrm{d}[\mathrm{Cu^{II}}]/\mathrm{d}t = (8{\cdot}84 \times 10^{-6})[\mathrm{B}]/(0{\cdot}173 + 1{\cdot}13[\mathrm{B}]^{\frac{1}{2}})$$

for the reaction conditions under which the base-dependence was followed, *i.e.*, propargyl alcohol (1·0M), $\mathrm{Cu^I}$ acetate (0·01M), and acetic acid (0·2M). Table 2 shows that this expression does represent the effect of changing the composition of the buffer mixture. Thus the general kinetic expression (*D*) has been confirmed experimentally with reference to each component of the system.

Again $k_1 = (8{\cdot}84 \times 10^{-4})/17{\cdot}3 = 5{\cdot}18 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ at 40° which is a reasonable value for the velocity of ionisation of such a weak acid as an acetylene.

(*b*) *Reaction mechanism.* The actual oxidation step, written as reaction (4) above, seems to be an electron transfer between cuprous acetylide and cupric acetate. This can be formulated rationally as proceeding through an acetate bridge:



This gives an unstable cupric acetylide which rapidly decomposes to acetylenic radicals and cuprous acetate There is no reason why this one-electron transfer reaction of the $\mathrm{Cu^I}$ compound $\mathrm{R{\cdot}C{\equiv}CCu}$ should not be faster than the two-electron transfers of reaction (2). Similar reactions can be formulated with other ligand groups, *e.g.*, chloride. From

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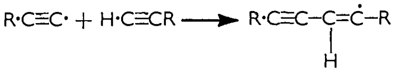
[7] Coates and Parkin, *J. Inorg. Nuclear Chem.*, 1961, **22**, 59.

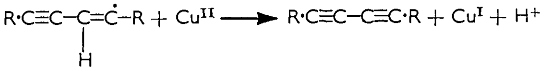
these the dimer R·C≡C·C≡C·R must be formed rapidly, perhaps by direct radical combination:

$$(5)\quad 2\mathrm{R{\cdot}C{\equiv}C{\cdot}} \longrightarrow \mathrm{R{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}R}$$

or possibly by the following sequence of fast reactions:

(6) 

$$\mathrm{R{\cdot}C{\equiv}C{\cdot} + H{\cdot}C{\equiv}CR \longrightarrow R{\cdot}C{\equiv}C{-}\underset{H}{\underset{|}{C}}{=}\dot{C}{-}R}$$

(7) 

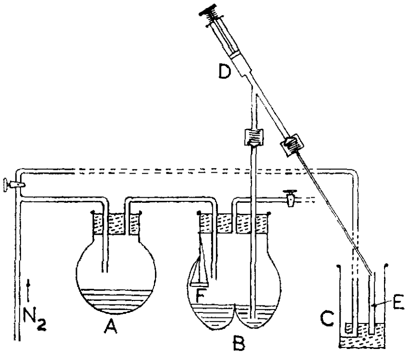
$$\mathrm{R{\cdot}C{\equiv}C{-}\underset{H}{\underset{|}{C}}{=}\dot{C}{-}R + Cu^{II} \longrightarrow R{\cdot}C{\equiv}C{-}C{\equiv}C{\cdot}R + Cu^{I} + H^{+}}$$

Some free radicals are known to be able to add to acetylenes,[8] and the oxidation of radicals by cupric salts has been well established.[9] The mechanism (6, 7) is attractive in that it can give some indication of how vinylacetylenes may be formed from acetylenes and cuprous salt catalysts in acid solution.[10] However, under the conditions of our oxidation we were not able to catalyse the radical polymerisation of vinyl cyanide by our oxidising mixtures.

EXPERIMENTAL

Materials.—Anhydrous cupric acetate was prepared by refluxing hydrated material with acetic anhydride and washing the insoluble product with dry ether [11] (Found: $\mathrm{Cu^{II}}$, 35·1. Calc. for $\mathrm{C_4H_6CuO_4}$: Cu, 35·0%). Cuprous acetate was produced by dissolving cupric acetate (5 g.) in a mixture of acetic acid (25 ml.), water (75 ml.), and ammonium acetate (25 g.) and adding 64% aqueous hydrazine dropwise until the mixture became colourless. The white precipitate of cuprous acetate was collected under nitrogen and washed successively with 25% aqueous acetic acid, methanol, and dry ether (Found: Cu, 52·7. Calc. for $\mathrm{C_2H_3CuO_2}$: Cu, 52·8%). It was stable in dry air and dissolved in pyridine to give a clear solution though some oxidation to the cupric state could not be avoided.

FIG. 5. Apparatus for preparing reaction mixtures and for filling spectrophotometer cells under nitrogen.



Propargyl alcohol was fractionated and collected at 52—53°/50 mm. Pyridine was dried (KOH) and fractionated at 115—115·5°. Piperidine, similarly dried, was fractionated 3 times before use. The nitrogen used was British Oxygen Company's " white spot " gas which was dried with sulphuric acid.

Kinetic Procedure.—The solutions were made up in a divided flask B (250 ml.) (Fig. 5) through which nitrogen saturated with pyridine vapour was passed from flask A, both flasks being immersed in a thermostat-bath at 40°. One section of flask B was charged with a solution

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[8] Raphael, " Acetylenic Compounds in Organic Synthesis," Butterworths Scientific Publns., London, 1955, p. 43.

[9] Haines and Waters, *J.*, 1952, 3108.

[10] Aktar and Weedon, *Proc. Chem. Soc.*, 1958, 303.

[11] Späth, *Sitzungber. Akad. Wiss. Wien*, 1911, **120**, 1117.

of cupric acetate in pyridine; the other with propargyl alcohol and the requisite piperidine–acetic acid buffer mixture in pyridine. In some experiments solid cuprous acetate was added, in weighed amounts, from the suspended boat F, and in these cases it was found that before all the air had been removed from B sufficient oxidation of the cuprous acetate occurred in the presence of solvent vapours to produce enough cupric ions for the kinetic experiments requiring high Cu^{I} concentrations initially. Because of this oxidation it was impossible to obtain a series of kinetic experiments in which the cuprous concentrations were the same. To find the dependence on the propargyl alcohol and piperidine concentrations, therefore, the final rates of autocatalytic reactions (Fig. 2) were compared.

Flask B was thoroughly flushed with nitrogen, the contents were then mixed by shaking, and samples of the mixture were extracted by means of an automatic syringe pipette D, into a deep cylinder C which was continously flushed with nitrogen. A few early samples were rejected. Then a spectrophotometer cell E was filled with the reacting mixture, and was rapidly closed, whilst still in C, with a Polythene stopper lubricated with silicone grease, wiped, and transferred to a thermostat-controlled block at 40° that fitted into a Unicam S.P. 500 spectrophotometer. The decrease of absorption at 660 mμ, due to copper(II) was then followed. At this wavelength the mixture of reaction products had negligible light absorption.

Attempts to follow the reaction titrimetrically were unsuccessful, for it was found that the large amount of pyridine that has to be used interfered with the copper(II)–iodide reaction.

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