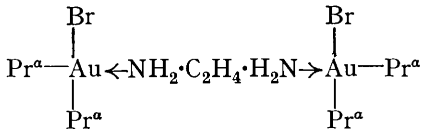
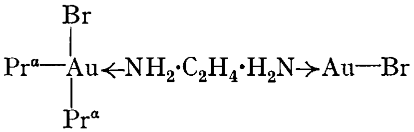
237. *The Organic Compounds of Gold. Part V. Cyano-compounds. Preliminary Experiments on the Production of Alkyl Radicals.*

By Abraham Burawoy, Charles S. Gibson, and (in part) Sidney Holt.

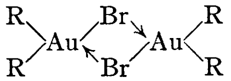
It has been shown (J., 1930, 2531; 1931, 2407; 1934, 860; this vol., pp. 217, 219) that the tervalent gold atom is always 4-covalent and has an effective atomic number of 84. The unique feature of the chemistry of gold is that in its compounds the valencies of the tervalent metal are always covalencies and gold is not a typical tervalent metal.* Monoethylenediaminodi-*n*-propyldibromodigold (II), produced by the elimination of two *n*-propyl groups from monoethylenediaminotetra-*n*-propyldibromodigold (I), contains a tervalent gold atom conforming to the above rules and a univalent gold atom which is 2-covalent and has an effective atomic number of 82 (this vol., p. 219). This is the first example of this type of complex compound to be described.

(I.) 

$$\mathrm{Pr^{a}—\overset{Br}{\underset{Pr^{a}}{Au}}\leftarrow NH_2\cdot C_2H_4\cdot H_2N\rightarrow\overset{Br}{\underset{Pr^{a}}{Au}}—Pr^{a}}$$

(II.) 

$$\mathrm{Pr^{a}—\overset{Br}{\underset{Pr^{a}}{Au}}\leftarrow NH_2\cdot C_2H_4\cdot H_2N\rightarrow Au—Br}$$


(III.)

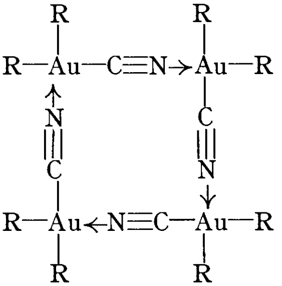
In view of the impossibility of existence of compounds having the empirical formula AuR_3 ($R = $ alkyl) (J., 1931, 2409), it was decided to study cyano-compounds, obtained from substances (III; R = Et and Pr^{a}), in which the tervalent gold atoms might be attached to three carbon atoms.† If they are so attached, the cyano-compounds cannot

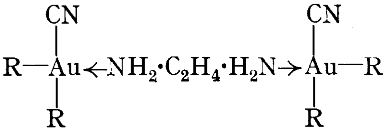
* In the compounds $(AlCl_3)_2$ and $(FeCl_3)_2$, the metals are also 4-covalent similar to gold in its trihalide and other derivatives; but iron and aluminium, unlike gold, yield tervalent kations.

† These compounds have been investigated by Kharasch and Isbell (*J. Amer. Chem. Soc.*, 1931, **53**, 2701), whose work on the dialkylmonobromo- and monoalkyldibromo-gold compounds, described by them as "auric bromides" and "auric dibromides" respectively, has been previously referred to (J., 1931, 2407; 1934, 860). In the case of the cyano-compounds, described by the above authors as "auric cyanides," no analytical figures are given for the diethyl compound and only the gold content is

be of type (III), since on stereochemical grounds the gold atom and the cyano-group must be linear. The investigation of these cyano-compounds, therefore, should furnish additional evidence of the correctness or otherwise of the general conclusions concerning the constitution of tervalent gold compounds and complex tervalent and univalent gold compounds. Preliminary experiments indicated an additional importance of the investigation, since the parent substances and their ethylenediamino-derivatives appeared to decompose similarly to (I).

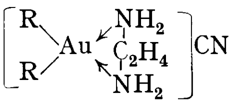
Diethylmonocyanogold and *di*-n-*propylmonocyanogold* are easily prepared from the analogous monobromo-compounds. They are colourless, highly crystalline non-electrolytes and their molecular weights in freezing bromoform are four times those required by the empirical formulæ. The compounds are therefore of a type not previously described, no compound containing more than two gold atoms in the molecule having so far been investigated. In such a compound the gold atoms must be attached to the carbon atoms of the cyano-groups and the nitrogen atoms must be co-ordinated to neighbouring gold atoms. Constitution (IV) ($R = Et$ and Pr^{α}), indicating a symmetrical twelve-atom planar ring structure, is the only one possible for such compounds; it affords additional support for the existence of co-ordinate linkages in complex molecules and is in keeping with the stereochemical configuration of the $-C{\equiv}N$ group.


(IV.)



$$R\text{—}\underset{R}{\overset{CN}{Au}}\leftarrow NH_2\cdot C_2H_4\cdot H_2N\rightarrow\underset{R}{\overset{CN}{Au}}\text{—}R$$

(V.)


(VI.)

These compounds yield with ethylenediamine colourless crystalline derivatives, which also are non-electrolytes, described as *monoethylenediaminotetraethyldicyanodigold* and *monoethylenediaminotetra*-n-*propyldicyanodigold* respectively. The constitution of these compounds follows from analytical and molecular-weight determinations and is represented by (V; $R = Et$ or Pr^{α}), corresponding to (I). Although (IV) and (V) are soluble in aqueous solutions of ethylenediamine, it has not been possible to isolate salts of type (VI) analogous to the monoethylenediaminodialkylgold bromides. Similarly, they are soluble in alcohol–pyridine, but attempts to isolate pyridine derivatives analogous to (V) and (VI) were also unsuccessful.

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given for the di-*n*-propyl compound: the constitutions assigned to the compounds cannot be correct. The melting points of both compounds as given are incorrect, and the phenomena accompanying the change from the solid to the liquid state are described as a slight decomposition in the one case and are not mentioned in the other. What is more remarkable is the statement (p. 2705), "The compounds $R_2Au(CN)$ when freshly prepared are soluble in benzene. Many of these compounds, particularly the compounds from the benzyl radical, upon standing for a period of time become insoluble in benzene, although the empirical formula of the compound remains the same." The diethyl compound is specifically described also as being soluble in benzene when new and insoluble on standing (p. 2709). It is shown in the present communication that the cyano-compounds undergo a definite chemical change on standing which is the same as, but takes place more slowly than, that which they undergo on melting. This change results, of course, in the production of chemical compounds having empirical formulæ and chemical properties different from those of the parent substances.

Kharasch and Beck (*J. Amer. Chem. Soc.*, 1934, **58**, 2057) still use the general formula $RAuCl_2$ for the dichloro-compounds. In the light of the investigations carried out in these laboratories, it is difficult to understand how it is possible for a compound "cyanophenyl auric dichloride," having the assumed constitution $(3)CN\cdot C_6H_4\cdot AuCl_2(1)$, to react with aqueous acids and bases to yield benzonitrile and inorganic auric compounds, and with pyridine to give benzonitrile and "a varying mixture of pyridine-auric-chloride compounds" (p. 2060).

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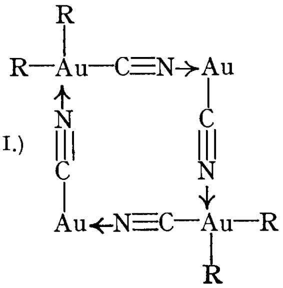
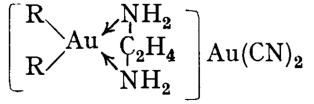
When the cyano-compounds (IV) are heated, they lose half their alkyl groups on melting, a definite compound (VII) being produced; this is converted at a higher temperature into aurous cyanide by loss of the remaining alkyl groups.

The diethyl compound (IV) when freshly prepared is readily soluble in such solvents as ether, chloroform and benzene. At the ordinary temperature it gradually loses weight, the gold content increasing and the compound becoming insoluble in the above solvents. This corresponds to the first of the above changes. A solution of the diethyl compound (IV) in ether may be boiled for a short time without obvious change; but when a clear solution in chloroform or benzene is heated for a short time on the water-bath an almost colourless substance is precipitated. This is *diethyldicyanodigold,* mixed with a small quantity of aurous cyanide due to the decomposition having partly proceeded too far. Diethyldicyanodigold, obtained pure from its ethylenediamine derivative (see below), is identical with the product formed when the parent substance melts with evolution of gas. When heated slowly to 100—120°, it loses its ethyl groups slowly and quantitatively and without explosion, leaving a residue of aurous cyanide. If it is heated quickly to a higher temperature, it decomposes explosively and this may happen in a melting-point tube after the first decomposition of the parent substance. Owing to the very low solubility of the compound, its molecular weight cannot be determined and therefore its constitution cannot be stated with certainty. Since it is formed by elimination of half the ethyl groups from compound (IV; R = Et), and the gold atoms and $-C\equiv N$ groups must be linear, constitution (VII; R = Et) may reasonably be suggested for it. This constitution indicates the presence of two tervalent gold atoms conforming to the general rules and two univalent gold atoms each being 2-covalent and having an effective atomic number of 82. Compound (II) also is such a complex tervalent and univalent gold compound and, actually, constitution (VII) is the simplest which is in accordance with the general rules concerning tervalent and univalent gold compounds. Compound (VII; R = Et) is a chemical individual and not an equimolecular mixture of diethylmonocyanogold and aurous cyanide, since it is colourless and practically insoluble in most solvents, including water, whereas aurous cyanide is yellow and diethylmonocyanogold is readily soluble in many organic solvents; it also forms an ethylenediamine derivative, which is described below.

(VII.)





(VIII, R = Et or Pr^{a}.)

Di-*n*-propylmonocyanogold (IV; R = Pr^{a}) is more stable than its ethyl analogue; unlike this, it does not undergo explosive decomposition on mere rubbing. *Di-*n*-propyldicyanodigold* (VII; R = Pr^{a}) has been obtained from it under conditions similar to those employed for the preparation of its ethyl analogue.

The following decompositions of compounds (IV) and (VII) (R = Et and Pr^{a}) have been observed quantitatively:

(a) $(R_2AuCN)_4 = 4AuCN + 8R'$ (b) $(R_2AuCN\cdot AuCN)_2 = 4AuCN + 4R'$

The volatile products have not yet been identified as free radicals, but they have been collected as butane (from the ethyl compounds) and hexane (from the *n*-propyl compounds) (see below).

The compounds (V; R = Et and Pr^{a}) are more stable than the parent substances (IV). They undergo similar changes to the latter on being heated, but without explosion.

At their melting points (both below 100°) gas is evolved and a non-volatile substance is produced having the empirical formula $R_2Au_2(CN)_2en$ ($R = Et$ or Pr^a, en = ethylenediamine):

$$\text{(c)}\quad R_2Au(CN)\,.\,en\,.\,(CN)AuR_2 = R_2Au_2(CN)_2en + 2\,R'$$

Here, again, the volatile products have only been collected as butane and hexane from the ethyl and the *n*-propyl compound respectively.

The non-volatile product $R_2Au_2(CN)_2en$ may be prepared by boiling benzene solutions of compounds (V) [unchanged compound (V) may crystallise from the mother-liquor] and recrystallising the insoluble product from boiling water, or even more conveniently by suspending the compound (V) in water and boiling the mixture. The compound is insoluble in organic solvents. It is extremely stable and its aqueous solution may be boiled for some time before decomposition is noticeable. In aqueous solution it yields a colourless precipitate with silver nitrate, and the apparent molecular weight in boiling water indicates that it is an electrolyte; its properties are in keeping with constitution (VIII).

The two compounds investigated are described as *monoethylenediaminodiethylgold aurocyanide* and *monoethylenediaminodi*-n-*propylgold aurocyanide.* On addition of the proper amount of hydrochloric acid to aqueous solutions of these compounds diethyldicyanodigold and di-*n*-propyldicyanodigold [compounds of type (VII)] respectively are obtained in a state of purity (see above).

The relationships between the various types of the cyano-compounds now described are illustrated diagrammatically:

$$\begin{tikzcd}
\text{(IV.)} & (R_2AuCN)_4 \arrow[r] \arrow[d, "-4R'"] & R_2Au(CN)\,.\,en\,.\,(CN)AuR_2 \arrow[d, "-2R'"] & \text{(V.)} \\
\text{(VII.)} & {[R_2Au_2(CN)_2]_2} \arrow[d, "-4R'"] & {[R_2Au\,.\,en]Au(CN)_2} \arrow[l] & \text{(VIII.)} \\
 & AuCN & &
\end{tikzcd}$$

and in all the new compounds, the gold atoms, whether tervalent or univalent, conform to the general rules enunciated.

There is reason to believe that the immediate volatile products from the decomposition of compounds of types (IV), (V) and (VII) are free radicals, although they have not yet been recognised as such by the classical methods. In the present investigation, the hydrocarbon formed by the combination of two identical radicals produced in the decomposition has been quantitatively identified. Indirectly, this is a means of identifying the particular radical, especially when, as in the present work, no other product but the saturated hydrocarbon appears to be formed. Two types of apparatus were used, (i) and (ii).

(i) A Victor Meyer's apparatus for vapour-density determinations, supplied with an automatic release for introducing the weighed amount of compound. This was used chiefly in those cases where the decomposition did not proceed explosively and the ultimate volatile product was evolved regularly and in reasonable time. It was used even when the decomposition was slow and when the ultimate volatile product was gaseous under atmospheric conditions. Although it was the most suitable for investigating the decomposition of the *n*-propyl compounds, it could not be used with di-*n*-propylmonocyanogold (IV, $R = Pr^a$), since, when it began, the decomposition proceeded too violently. This method is subject to errors inherent in Victor Meyer's method for determining vapour densities.

(ii) An apparatus for measuring accurately over mercury the volume of a gas evolved during the reaction, the vessel being sealed to the rest of the apparatus and of such a type that, unless the reaction proceeded explosively, the change in weight of the gold compound could be determined. This apparatus was used for investigating the decomposition of the ethyl compounds, from which the ultimate volatile product (butane) is a gas under ordinary atmospheric conditions.

The following are typical experiments. *Apparatus ii*: (a) Diethylmonocyanogold (IV, R = Et), heated at 80° (hot water), suffered explosive decomposition indicating reaction (a) above. Mol. wt. of gaseous product (based on calc. loss in wt.), 58·6; mol. wt. of butane = 58·1. (b) Monoethylenediaminotetraethyldicyanodigold (V, R = Et) was heated in boiling water. The gaseous product was evolved rapidly and the non-volatile product solidified after previous melting; loss, 9·0% [calc. for reaction (c) above, loss, 9·3%]. Mol. wt. of gaseous product (based on actual loss in wt.) 59·7 and (in another experiment) 59·0.

Apparatus i: (a) Diethyldicyanodigold (VII, R = Et) was heated at 120° for 1 hour. The decomposition was slow and incomplete; loss, 8·6% [calc. for reaction (b) above, loss, 11·5%]. Mol. wt. of volatile product (calc. from actual loss in wt.) 57·4. (b) Monoethylenediaminotetra-*n*-propyldicyanodigold (V, R = Pr^{α}) lost 12·6, 12·0% [calc. for reaction (c) above, loss, 12·7%]. Mol. wt. of volatile product (calc. from loss in wt.) 83·4, 87·3; mol. wt. of hexane = 86·1. (c) Di-*n*-propyldicyanodigold (VII, R = Pr^{α}) lost 6·2%, the decomposition being incomplete [calc. for reaction (b) above, loss, 16·2%]. Mol. wt. of volatile product (calc. on actual loss in wt.) 86·6.

These preliminary investigations on the production of free radicals by decomposition of suitable organo-gold compounds and on their products of interaction have two points of interest. (i) In reactions in which the ethyl radical may be expected to be evolved, for the first time, substantially pure butane has been isolated. Frankland (*Annalen*, 1849, **71**, 171, 189; compare, however, "Experimental Researches," p. 238), by the action of zinc on ethyl iodide at 150°, obtained a mixture consisting of 50% of butane ("ethyl"), 26% of ethane ("methyl"), and 22% of ethylene ("elayl"). Later workers (for references, see Paneth and Lautsch, *Ber.*, 1931, **64**, 2702, 2708) found that a similar mixture of gases was obtained when the ethyl radical was expected, or known to be the immediate volatile product of the reaction studied; and from the thermal decomposition of ethylsodium (which, from its physical properties, must be a complex substance) a mixture of ethylene and ethane was obtained. (ii) Substantially pure hexane has been obtained for the first time in experiments in which *n*-propyl radicals would appear to be the immediate volatile product of the particular reaction. From the thermal decomposition of tetra-*n*-propyl-lead, Paneth and Lautsch (see also this vol., p. 380) obtained little, if any, hexane and, apparently, only ethane and ethylene. The differences between the results now obtained and those obtained by other workers may be due to the unusually low temperatures, in no case higher than 120° and frequently below 100°, at which the decompositions take place. Gold compounds of the types now described may prove to be convenient sources not only of ethyl and *n*-propyl but also of higher alkyl radicals.

EXPERIMENTAL.

Diethylmonocyanogold (IV, R = Et) is prepared by shaking a dry ethereal solution of diethylmonobromogold (1 part) with silver cyanide (2 parts, five times the theoretical quantity) for about 3 hours. After filtration, the solution is evaporated under diminished pressure in a dry atmosphere and the resulting long colourless needles are washed with alcohol or ligroin. The substance may be further purified by the addition of alcohol to its ethereal solution. It is soluble in ether, benzene, chloroform, and carbon tetrachloride, very sparingly soluble in ligroin and in alcohol, and insoluble in water [Found: Au, 70·0, 70·0; *M* in freezing bromoform, 1084, 1092, 1125. $(C_5H_{10}NAu)_4$ requires Au, 70·1%; *M*, 1124].

In a melting-point tube, diethylmonocyanogold melts at 103—105° (slight variation according to crystal size) to a clear liquid, gas being evolved; at 110—120° a colourless solid is formed, which decomposes above this temperature, sometimes slowly and sometimes with explosion. In bulk, the compound decomposes explosively when rubbed, or when heated above 80°, or when treated with a drop of concentrated sulphuric acid, leaving substantially pure aurous cyanide as a flocculent, greenish-yellow, electrified powder (Found: Au, 88·6. Calc.: Au, 88·3%); the volatile product may be collected quantitatively as butane.

A solution of diethylmonocyanogold in chloroform was boiled until cloudiness just developed (2 minutes). The slightly impure *diethyldicyanodigold* which separated on cooling was washed with chloroform; it began to decompose without melting from 110—120° (Found: Au, 78·6;

loss at 120°, 10·4. $[Et_2(CN)_2Au_2]_2$ requires Au, 78·2; loss of 4Et, 11·5%), leaving substantially pure aurous cyanide (Found: Au, 87·8%).

Monoethylenediaminotetraethyldicyanodigold (V, R = Et) is prepared by shaking a benzene solution of diethylmonocyanogold with a few drops of an aqueous solution of ethylenediamine and washing the colourless precipitate with water. It is purified by precipitating in the cold a chloroform solution with ligroin or an alcoholic solution with water (Found: N, 9·3; Au, 63·3, 63·4; *M* in freezing nitrobenzene, 599, 625. $C_{12}H_{28}N_4Au_2$ requires N, 9·0; Au, 63·3%; *M*, 622·6).

The compound is soluble in ether, chloroform, ethyl alcohol, and in dilute aqueous solutions of ammonia, ethylenediamine, and pyridine, sparingly soluble in cold benzene, and insoluble in ligroin and in water. It melts at 96—98° to a colourless liquid, gas being evolved. At about 110°, when gas has ceased to be evolved, a colourless solid forms, and this has m. p. 161—162°, again with evolution of gas, followed by complete decomposition. The volatile product evolved at about 100° has been obtained as butane.

Monoethylenediaminodiethylgold aurocyanide (VIII, R = Et) is the product of heating the above compound at about 100° (just above the m. p.), the loss being equivalent to two ethyl groups (Found: loss, 9·2. $C_{12}H_{28}N_4Au_2$ requires loss, 9·3%). It is most conveniently prepared by boiling a suspension of monoethylenediaminotetraethyldicyanodigold in water for 30 minutes; this melts with evolution of gas and slowly dissolves and (VIII, R = Et) crystallises in long colourless needles from the filtered solution on cooling. The substance is soluble in water and alcohol and insoluble in ether, benzene, chloroform, and ligroin. It has m. p. 161—162° (decomp.), gas being evolved (Found: N, 10·3; Au, 69·9, 69·8; apparent *M* in boiling water 433, 427, 427. $C_8H_{18}N_4Au_2$ requires N, 9·9; Au, 69·9%; *M*, 564·6).

When a slight excess of hydrochloric acid is added to an aqueous solution of the compound, colourless crystalline diethyldicyanodigold (VII, R = Et) is precipitated. This is insoluble in water and almost insoluble in all the usual organic solvents. When heated slowly, it decomposes without melting above 100°; when heated rapidly, it decomposes explosively, leaving a greenish-yellow flocculent residue of aurous cyanide (Found: N, 6·1; Au, 77·9, 77·9. Calc. for $[C_6H_{10}N_2Au_2]_2$: N, 5·55; Au, 78·2%. Found: loss at 120°, 11·5. Calc. for loss of 4Et, 11·5%. Found in the residue: Au, 87·8. Calc. for AuCN: Au, 88·3%). The volatile product evolved slowly at 120° is butane.

Di-n-*propylmonocyanogold* (IV, R = Pr^a).—Monoethylenediaminotetra-*n*-propyldibromodigold (3 g.) (this vol., p. 219), suspended in water, is shaken with an excess of hydrobromic acid until it is converted into a colourless oil. This is extracted in ether, washed with water, dried with anhydrous sodium sulphate, and shaken with silver cyanide (6 g.) for some hours. After filtration, the ethereal solution is concentrated under diminished pressure in a dry atmosphere and treated carefully with alcohol; *di*-n-*propylmonocyanogold* crystallises in long colourless needles, soluble in ether, benzene, chloroform, and carbon tetrachloride, sparingly soluble in ligroin, and insoluble in alcohol and water. Its general behaviour is similar to that of the analogous ethyl compound. It melts at 94—95° to a colourless liquid, evolving gas and yielding a colourless solid at about 105°, above which gradual decomposition ensues. In spite of its decomposing explosively when heated in bulk, leaving a residue of flocculent aurous cyanide (Found: Au, 88·2. Calc.: Au, 88·3%), it is possible to carry out analyses [Found: Au, 63·6; loss at 100° (explosive decomp.), 27·9; *M* in freezing bromoform, 1202, 1233. $(C_7H_{14}NAu)_4$ requires Au, 63·7; loss of 8Et, 27·8%; *M*, 1237].

When a solution of di-*n*-propylmonocyanogold in chloroform is warmed on the water-bath, it behaves similarly to the analogous ethyl compound, almost colourless but slightly impure di-*n*-propyldicyanodigold being precipitated. This is purified through its compound with ethylenediamine (see below).

Monoethylenediaminotetra-n-*propyldicyanodigold* (V, R = Pr^a) is prepared from di-*n*-propylmonocyanogold similarly to the analogous ethyl compound. It usually separates as a colourless oil, which solidifies on stirring. By precipitation of its chloroform solution with ligroin, it is obtained in colourless needles. It melts at 84—85° with evolution of gas, followed by solidification at about 110°; this colourless product has m. p. 151—152°, again with evolution of gas, followed by complete decomposition (Found: Au, 58·2; loss at 100°, 12·7. $C_{16}H_{36}N_4Au_2$ requires Au, 58·1; loss of 2Pr, 12·7%). The volatile product obtained at 100° is hexane.

When monoethylenediaminotetra-*n*-propyldicyanodigold is boiled in water as described for the analogous ethyl compound, *monoethylenediaminodi*-n-*propylgold aurocyanide* (VIII, R = Pr^a) is obtained in colourless needles. This salt is soluble in water and behaves similarly in all respects to the analogous ethyl compound. It is the non-volatile product of heating the parent substance. It has m. p. 151—152° with evolution of gas, followed by complete decomposition. It is moderately stable in boiling aqueous solution (Found : Au, 66·7. $C_{10}H_{22}N_4Au_2$ requires Au, 66·6%).

When an aqueous solution of the above compound is acidified, pure *di*-n-*propyldicyanodigold* (VII, R = Pr^a) is obtained as a colourless crystalline precipitate. Like the analogous ethyl compound, it is insoluble in organic solvents and in water. It decomposes without melting from about 100°, yielding aurous cyanide. When heated rapidly, it decomposes explosively above 120° (Found : Au, 74·1; loss at 120°, 15·7. $C_8H_{14}N_2Au_2$ requires Au, 74·1; loss of 2Pr, 16·2%). The volatile product of the decomposition is hexane.

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