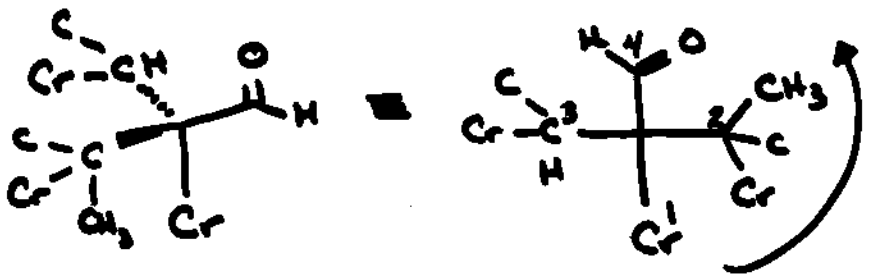
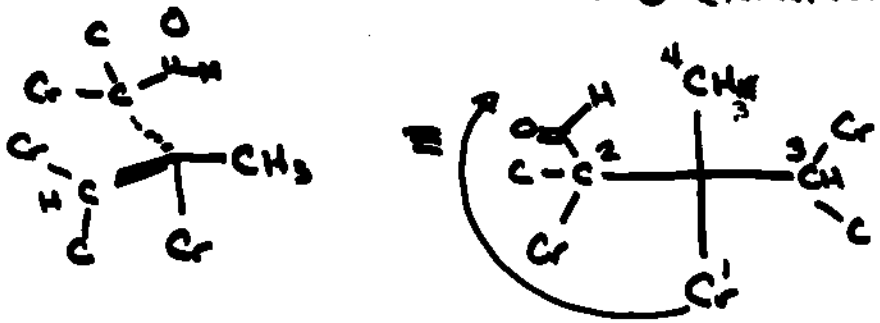
- AT POSITION 1 WE HAVE



∴ S ENANTIOMER.

- AT POSITION 2.

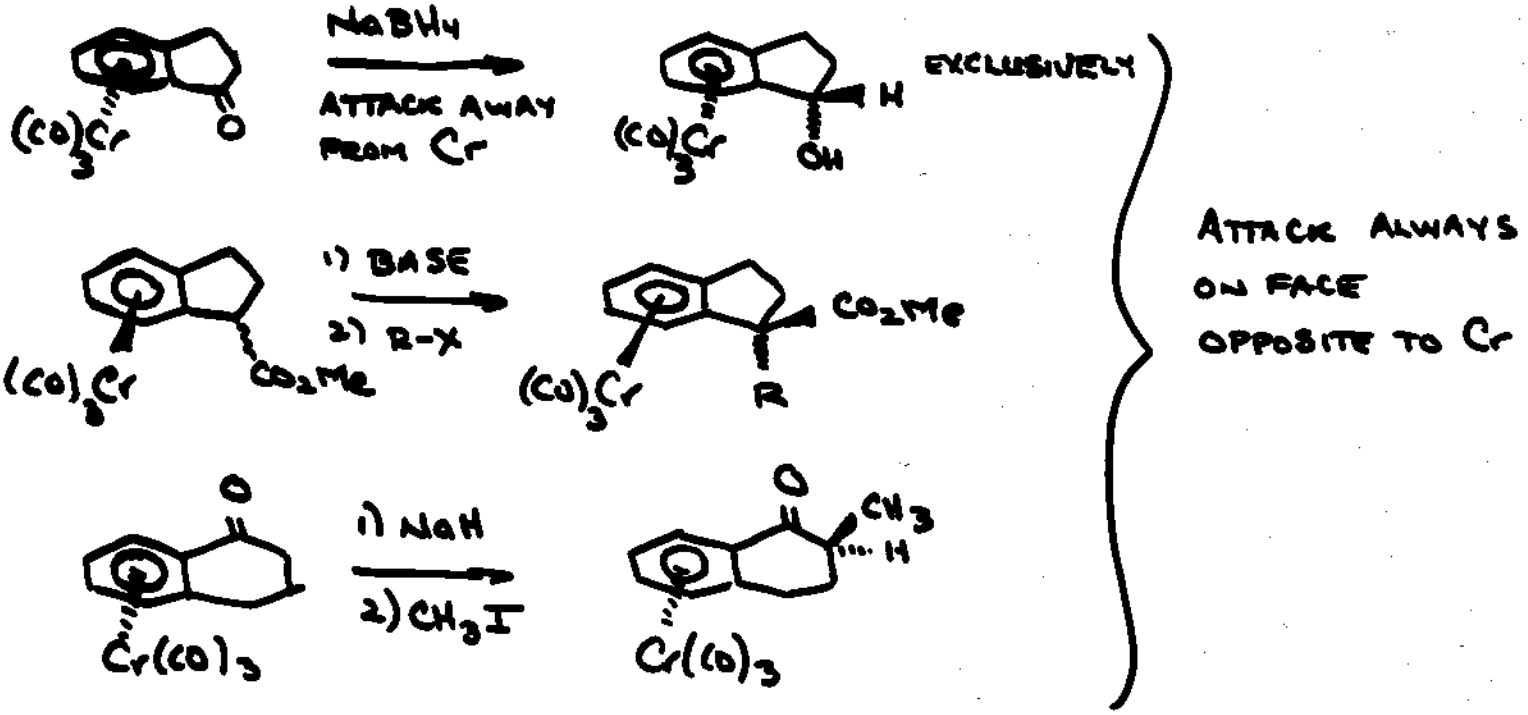


R-ENANTIOMER

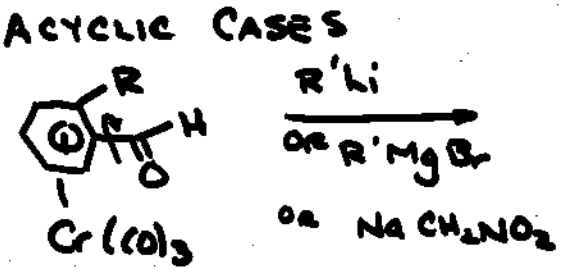
∴ THIS IS (1S,2R)-2-METHYLBENZALDEHYDE CHROMIUM TRICARBONYL

- NOTE - DAVIES JUST USES LABEL AT POSITION 1, AS 2-POSITION IS THEN DEFINED AUTOMATICALLY.

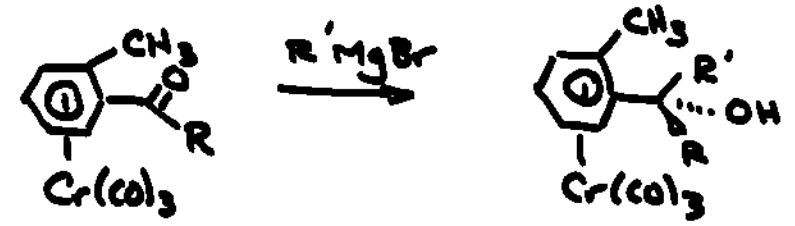
- CHIRAL CENTRE - ∴ SHOULD BE ABLE TO DO ASYMMETRIC RXNS
- WILL GIVE A SAMPLING, AS THIS IS A NEW η⁶-ACTIVE AREA



ACYCLIC CASES

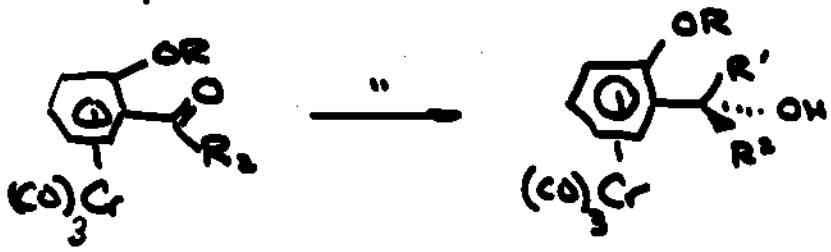


DISFAVOURED ROTAMER

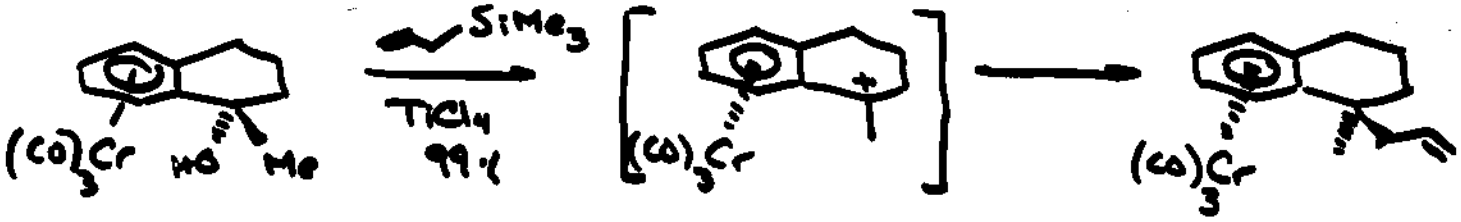


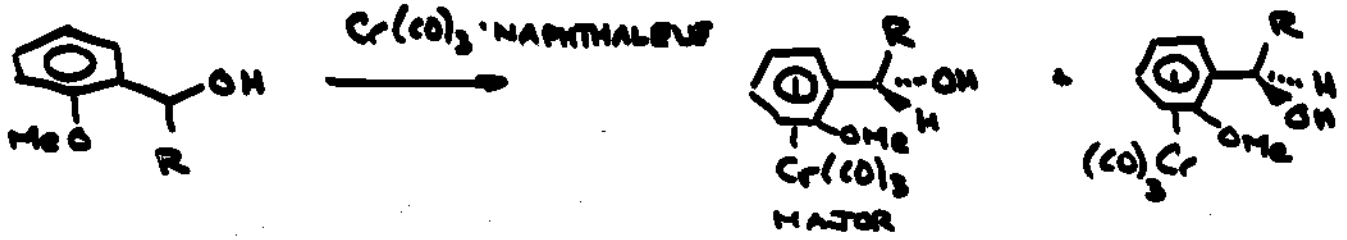
NOW DISFAVOURED

R = Me, Et

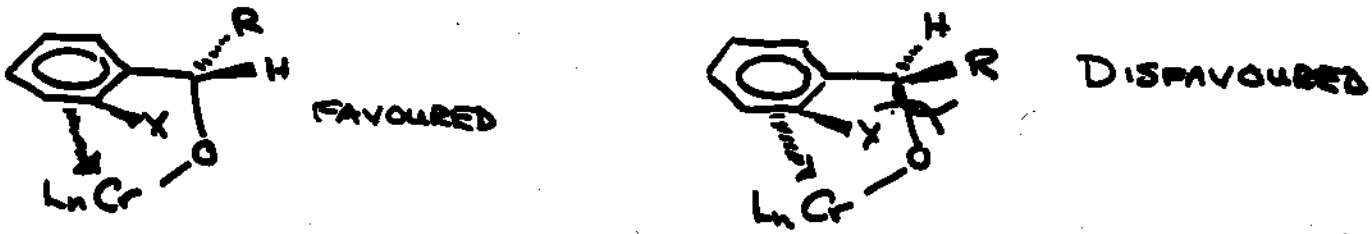


ALMOST EXCLUSIVE

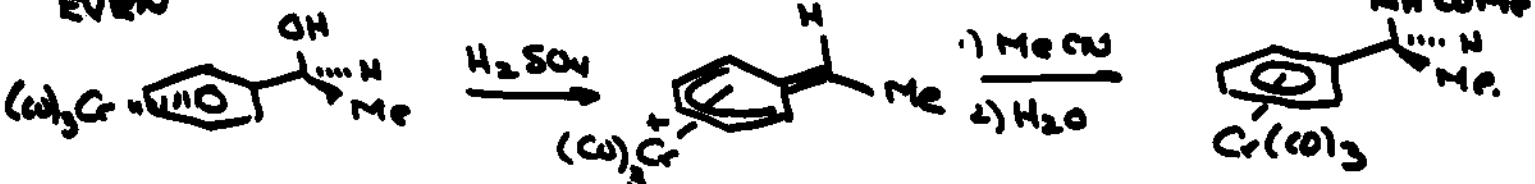




BECAUSE



EVEN



REVIEWS:

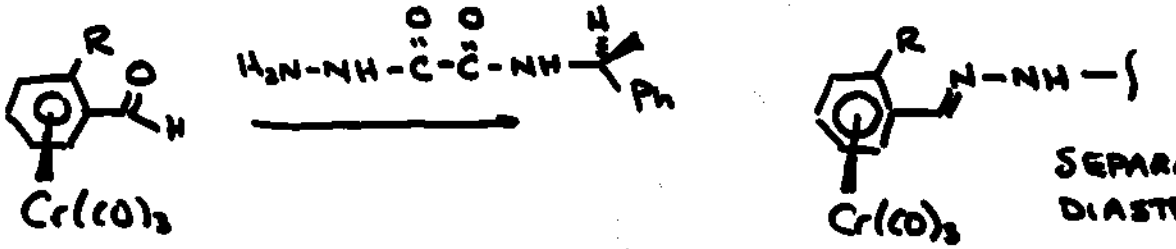
SOLLADIÉ-CAVALLO, A. ADV. MET. ORG. CHEM. 1989, 1, 99. (E)

UEMURA, M. " " " " 1991, 2, 195. (E)

DAVIES, S. ET AL. " " " " 1991, 3, 1. (E)

MANY OF THESE DONE ON RACEMIC MATERIAL

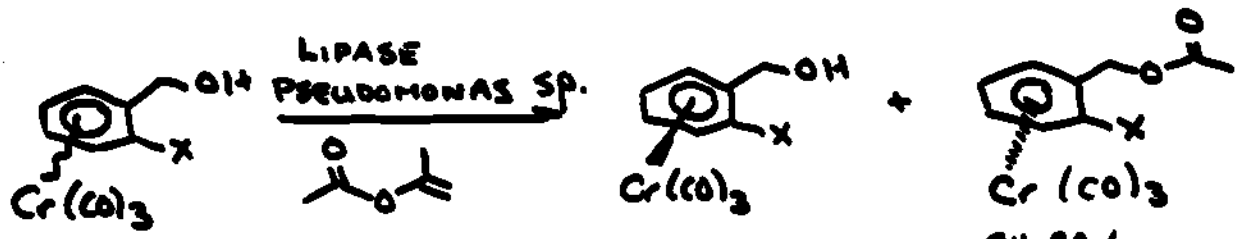
- HOW DO YOU GET ENANTIOMERICALLY PURE MATERIAL?

1) 

CLASSICAL RESOLUTION

- SEE ALSO DAVIES, S.G. ET AL J.C.S. PERKIN TRANS. I 1989, 192.

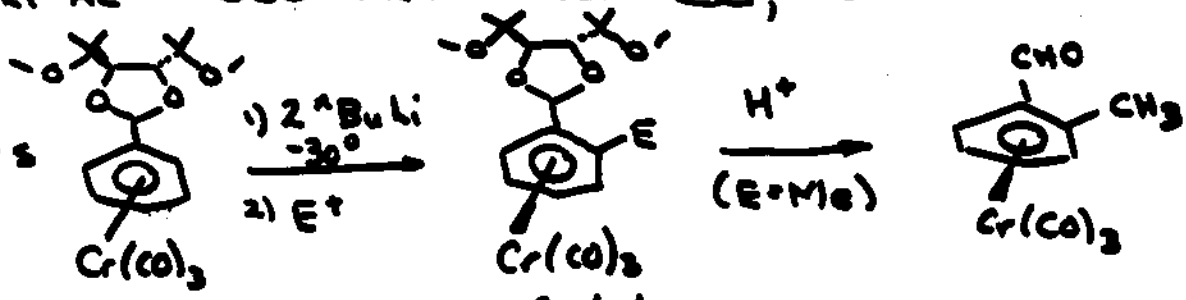
2) KINETIC RESOLUTION



UEMURA, M. ET AL TETRAHEDRON LETT. 1990, 31, 3603.

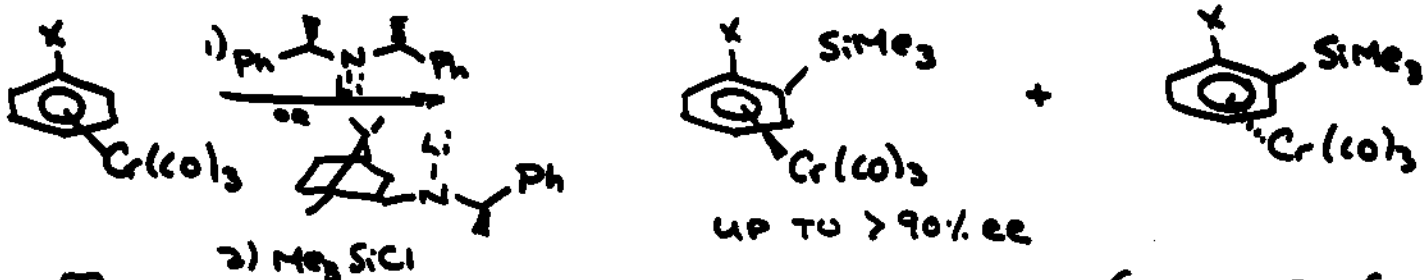
JAOUEN, G. ET AL JCS CHEM COMMUN 1984, 1284 ✓

3) CHIRAL AUXILIARIES



KONDO, Y.; GREEN, J.R.; HO, J. J. ORG. CHEM. 1993, 58, 6182.

4) ENANTIOSELECTNE FUNCTIONALIZATION



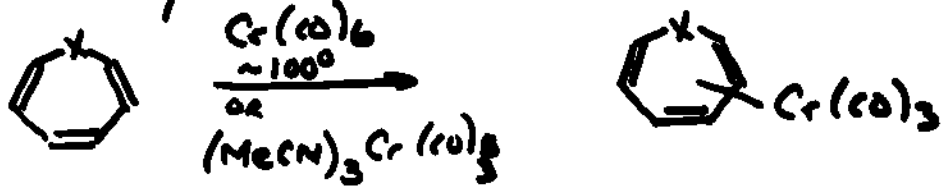
X =  , -OMe , $-CON^iPr_2$

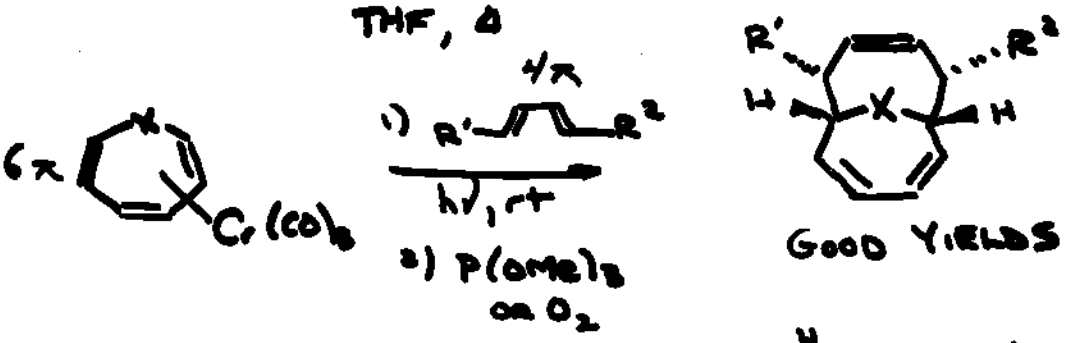
KÜNDIG, E.P. ETAL TETRAHEDRON LETT. 1994, 35, 3497

SIMPKINS, N.S. ET AL. J. ORG. CHEM. 1994, 59, 1961.

SIWEK, M.J.; GREEN, JR JCS CHEM. COMMUN. 1996, 2359.

OTHER η^6-CYCLOALKATRIENE-$Cr(CO)_3$ COMPLEXES



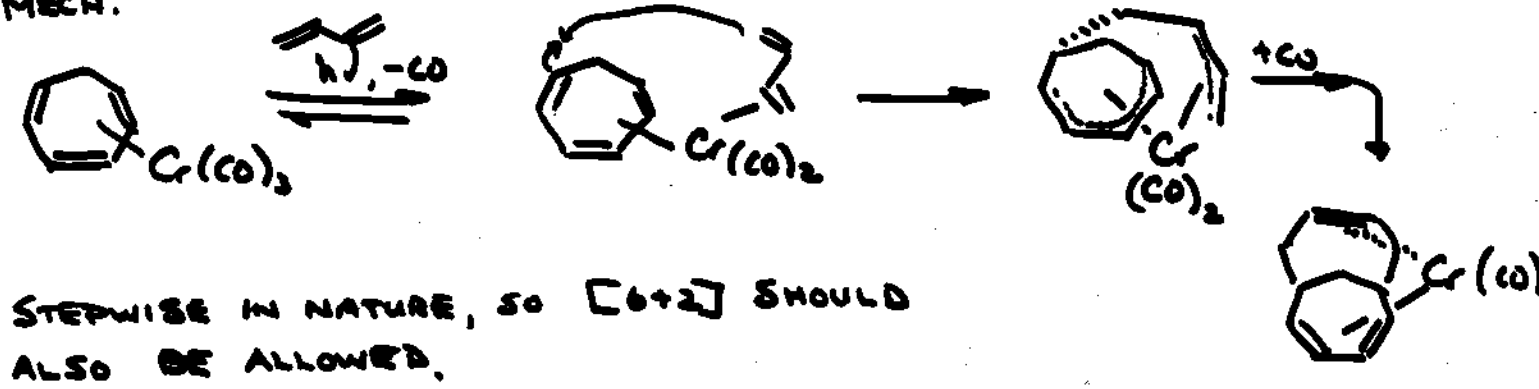


X = N-CO_2Me, C=O, SO_2, $C(H)CH_3$, CH_2

NOTES: RATES UNCHANGED IF R'S = EWG OR EDG

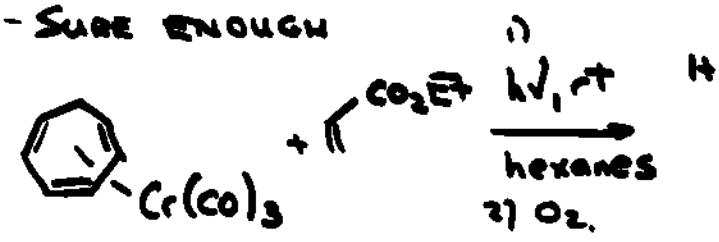
IF PUT SUBSTITUENT ON REMOTE SITES, OF TRIENE, REGIOCHEMISTRY IS ~1:1

MECH?

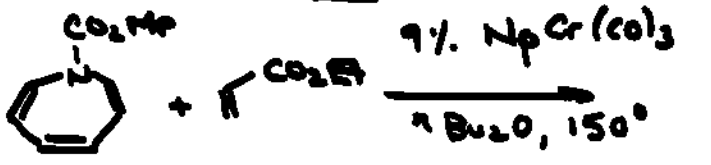


STEPWISE IN NATURE, SO [6+2] SHOULD ALSO BE ALLOWED.

- SURE ENOUGH



BOTH OF THE CAN BE CATALYTIC IN Cr. - USUALLY IN PRESENCE OF Mn°



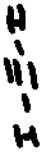
RIGBY, J.H. ET AL ADV. MET. ORG. CHEM 1995, 4, 89.

* RIGBY, J.H. TETRAHEDRON 1999 55 4251

RIGBY J.H. ORG. REACT. 1997 49 331.

MULTISTEP REACTIONS.

- BASED ON THE [2+2+2] MANIFOLD OF REACTIONS.

i.e. 3x  ⟶ 

FEASIBLE RXN
- REQUIRES 400°C
- MANY SIDE PRODUCTS
- NOT SYNTHETICALLY USEFUL.

- THERE ARE SEVERAL TRANSITION METAL FRAGMENTS WHICH ALLOW THIS TYPE OF REACTION TO OCCUR AT MUCH LOWER TEMPS. INCLUDING.

"  "

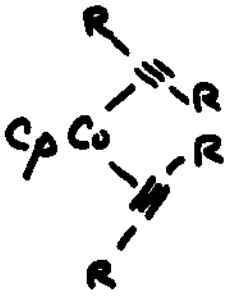
$(Ph_3P)_3RhCl$; R. GRIGG. JCS PERKIN I 1988, 1357 + 1365.

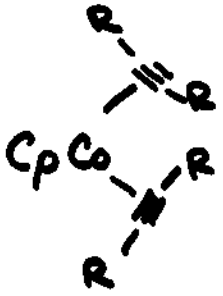
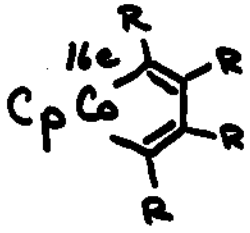
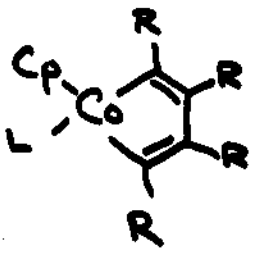
$CpCo(CO)_2$

+ 

$CpCo(II)_2$

How does this Go ? - EXAMPLE FOR $CpCo(CO)_2$

$CpCo(CO)_2 + R\text{-}C{\equiv}C\text{-}R \xrightarrow[-CO]{h\nu \text{ or } \Delta}$  $\xrightarrow[-CO]{h\nu \text{ or } \Delta,\ RC{\equiv}CR}$ 

 $\xrightarrow{\text{OXIDATIVE COUPLING}}$  $\xrightarrow{L}$ 

L = SOLVENT IN MANY CASES

L = PPh_3 ISOLATED IN MANY CASES BY YAMAZAKI GROUP.

WAKATSUKI, Y.; KURAMITSU, T.; YAMAZAKI, H. TETRAHEDRON LETT 1974, 4549.

YAMAZAKI, H.; WAKATSUKI, Y. J. ORGANOMET. CHEM. 1977, 139, 157.

WAKATSUKI, Y.; NOMURA, O.; KITAURA, K.; MOROKUMA, K.; YAMAZAKI, H. J. AM. CHEM. SOC. 1983, 105, 1907.

THEN - - - -

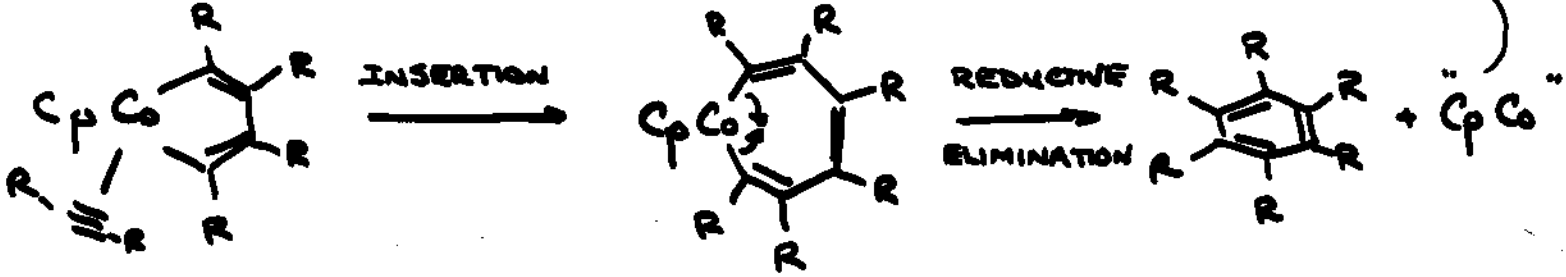
NOW COMES TROUBLE...

- THE NEXT STEPS ARE UNDECIDED BETWEEN 2 POSSIBILITIES.

POSSIBILITY #1 - CONCERTED CYCLOADDITION

"CpCo" REGENERATED ∴ POSSIBLE TO BE CATALYTIC IN Co

POSSIBILITY #2 - ALKYNE INSERTION / REDUCTNE ELIMINATION



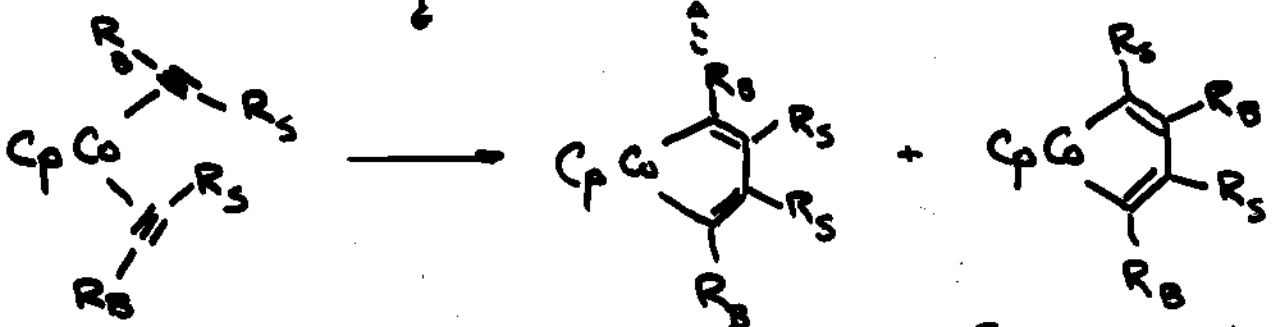
PERSONAL OPINION - THERE ARE CASES WHERE CONCERTED CYCLOADDN. IS OPERATING

- THERE ARE CASES WHERE INSERTION / ELIMINATION IS OPERATING

- MORE OFTEN, IT IS INSERTION / ELIMINATION.

REGIOCHEMISTRY.

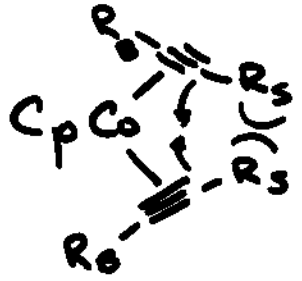
IF YOU HAVE  , WHAT HAPPENS ?



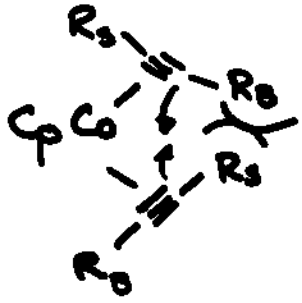
MAJOR PROD.

SOMETIMES MINOR AMOUNT OF THIS.

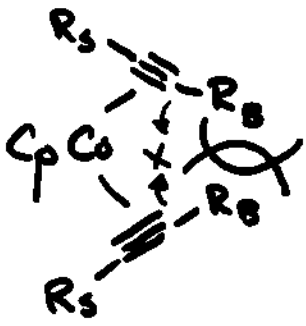
SIMPLY FROM STERICS



FAST

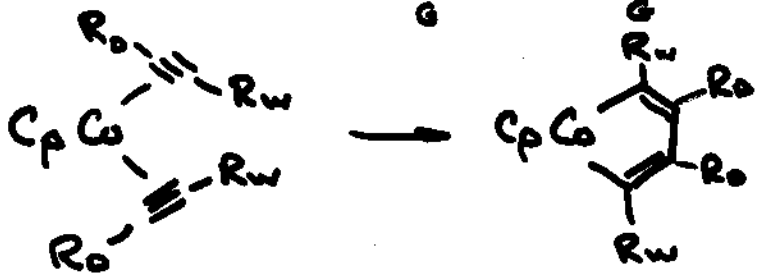


SLOWER

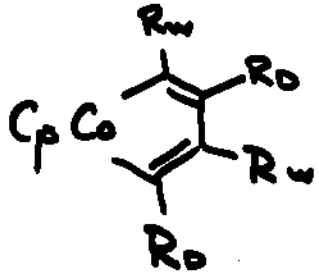


FORGET IT, BABY.

- IF YOU HAVE $R_{EDG}-\equiv-R_{EWG}$, WHAT HAPPENS?



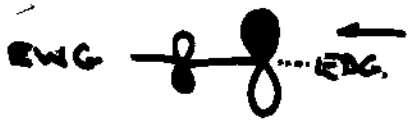
MAJOR



SOMETIMES MINOR AMOUNT.

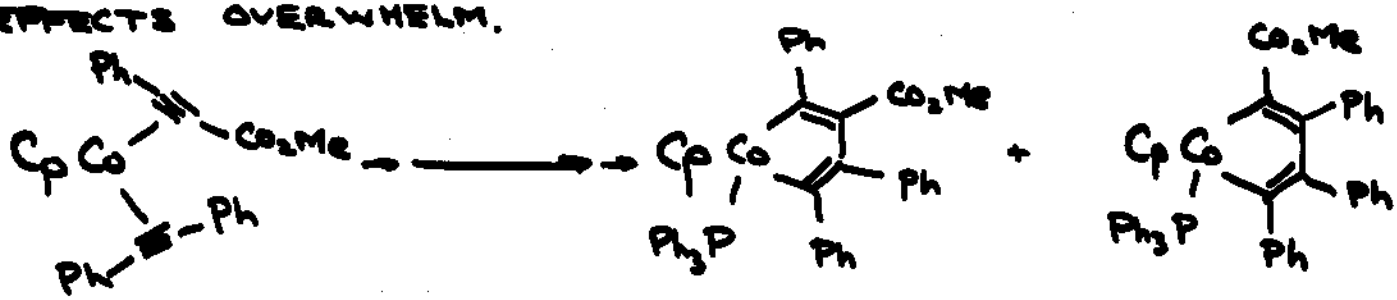
REASON - RVN. PROPOSED TO OPERATE UNDER ORBITAL CONTROL.

- HOMO OF COMPLEX, WHICH IS DOMINATED BY π^* OF ALKENE



← C-C BOND FORMATION TO METALLACYCLE OCCURS AT CARBON β- TO EWG.

- IF STERIC AND ELECTRONIC EFFECTS COMPETE, THE <u>STERIC</u> EFFECTS OVERWHELM.



43%

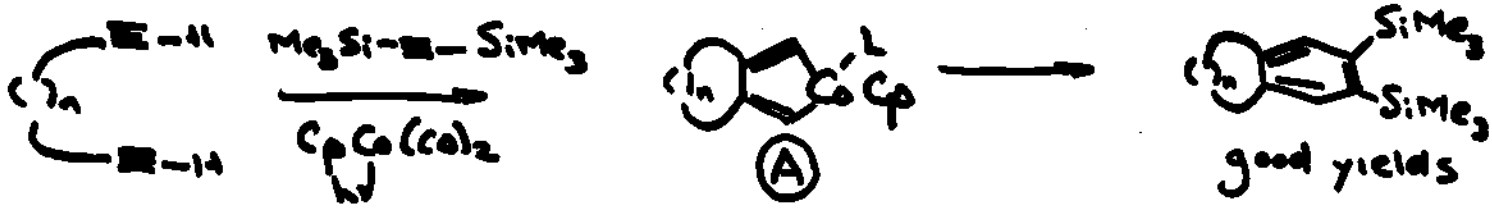
5%

- STILL IS THIRD ALKYNE TO PARTICIPATE IN REACTION, SO OFTEN ONE GETS FURTHER REGIOCHEMICAL MIXTURES.

- RVN BECOMES SYNTHETICALLY USEFUL WHEN $Me_3Si-\equiv-SiMe_3$ (BTMSA) IS USED AS THIRD ALKYNE (IT ONLY ADDS TO ITSELF V. SLOWLY)

- PARTICULARLY USEFUL RXN WHEN TWO OTHER ALKYNES ARE CONNECTED.

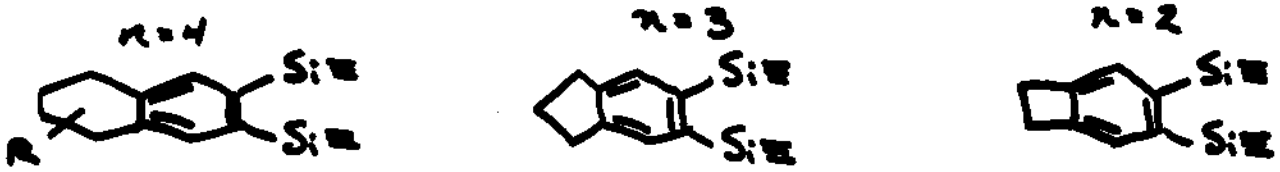
I.E.



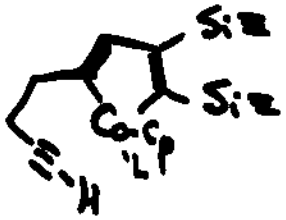
A

n = 2, 3, 4.

I.E. CAN FORM.

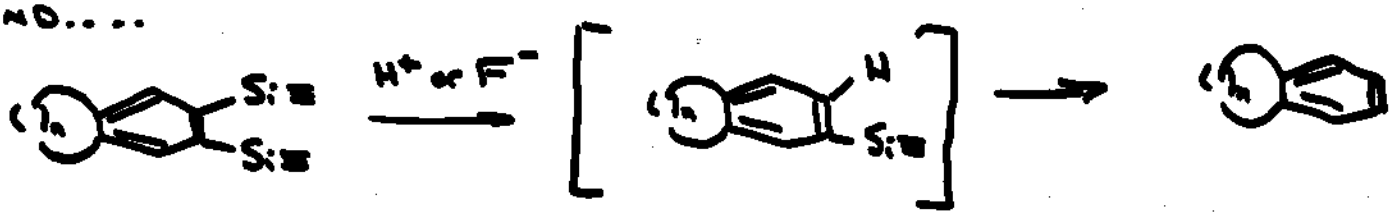


NOTE: IN n=2 CASE, RXN GOES THROUGH



INSTEAD OF (A)

AND....



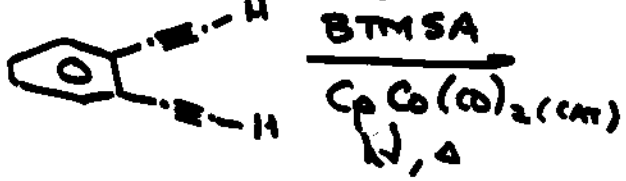
REACTIONS TOLERATE A PRETTY GOOD RANGE OF SUBSTITUENTS

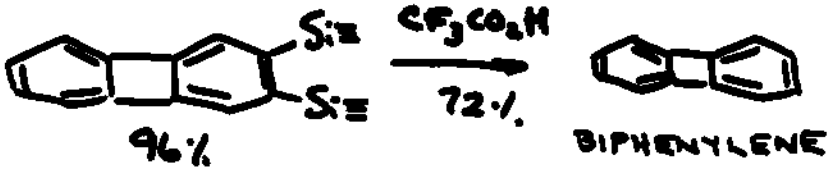
$-CO_2R'$, $-CH_2OH$, $-CH_2OR'$, $-\overset{O}{\overset{\|}{C}}-R'$, $-\underset{H}{\overset{N-OR'}{\overset{\|}{C}}}$, NR_2', SR'

- REACTION CARRIED OUT THERMALLY OR PHOTOCHEMICALLY

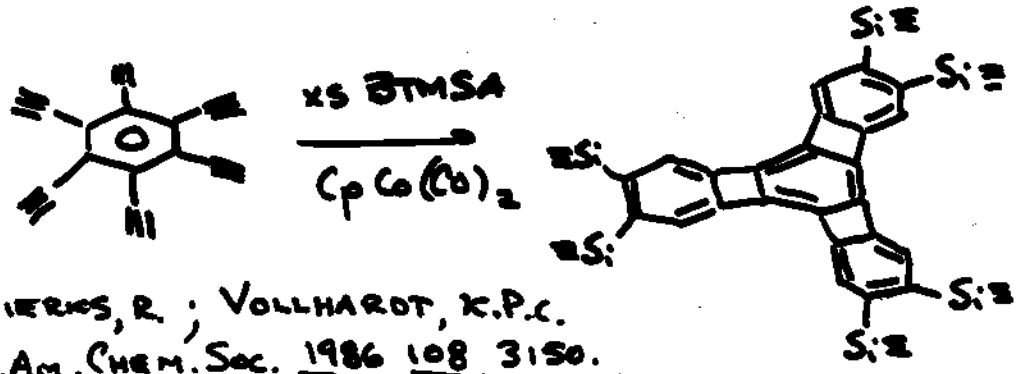
- REACTION IS OFTEN (NOT ALWAYS) CATALYTIC IN COBALT.

EXAMPLES:

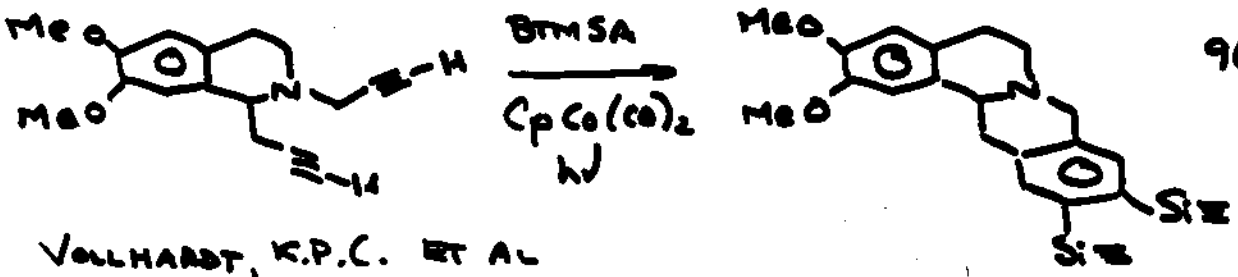




BERRIS, B.C.; LAI, Y.-H. VOLLHARDT, K.P.C. J.C.S. CHEM. COMMUN. 1982, 953.



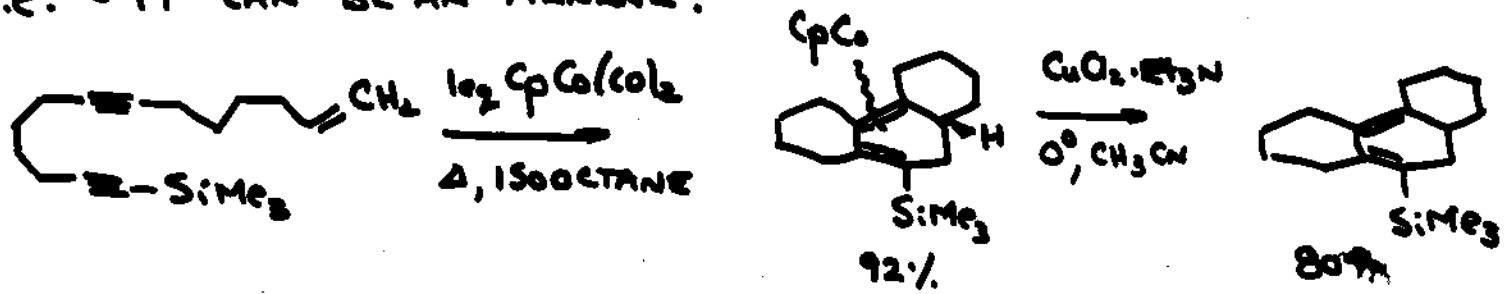
DIERKS, R.; VOLLHARDT, K.P.C.
J. AM. CHEM. SOC. 1986, 108, 3150.



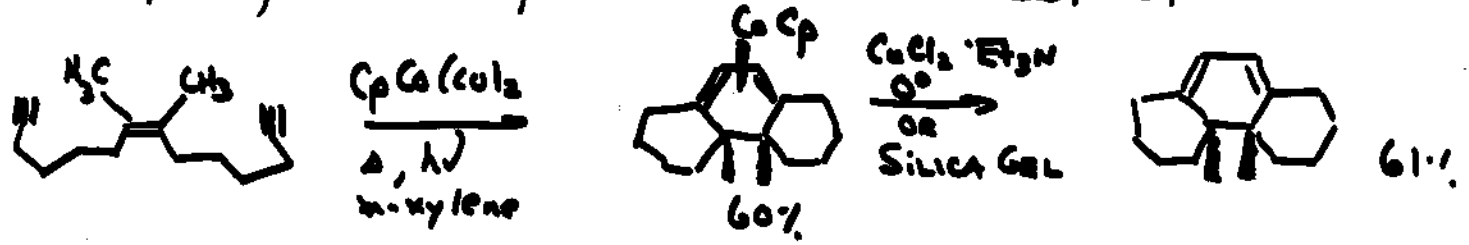
VOLLHARDT, K.P.C. ET AL
TETRAHEDRON 1983, 39, 905.

OTHER CYCLIZATION PARTNERS

- THE 'THIRD ALKYNE' DOESN'T HAVE TO BE AN ALKYNE PER SE
I.E. - IT CAN BE AN ALKENE.

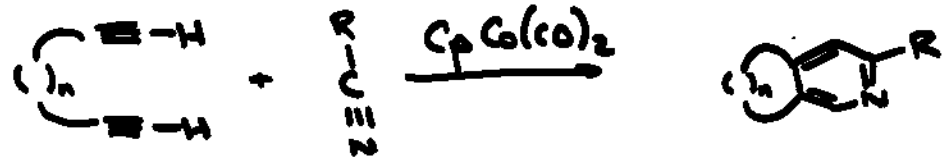


STERNBERG, E.D.; VOLLHARDT, K.P.C. J. ORG. CHEM. 1984, 49, 1564.



VOLLHARDT, K.P.C. ET AL J. ORG. CHEM. 1984, 49, 5010.
ANGEW. CHEM. INT. ED. ENGL. 1981, 20, 802.

- IN THESE CASES, THERE MUST BE AT LEAST ONE EQUIVALENT OF Co
- MUST SUBSEQUENTLY DECOMPLEX Co-DIENE COMPLEX.
- NORMALLY ALKENE IS THE 'THIRD' PARTNER.
- THIRD PARTNER CAN ALSO BE → NITRILE R-C≡N



n=3-5

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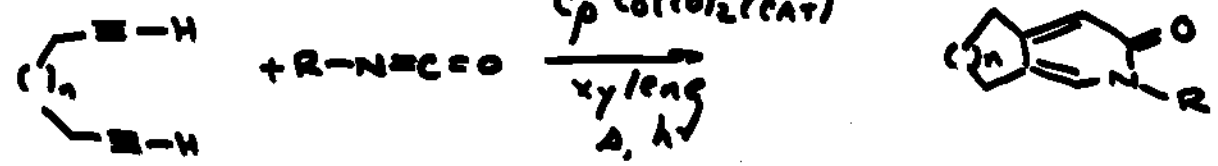
– AND ISOCYANATES.



n=1,2.

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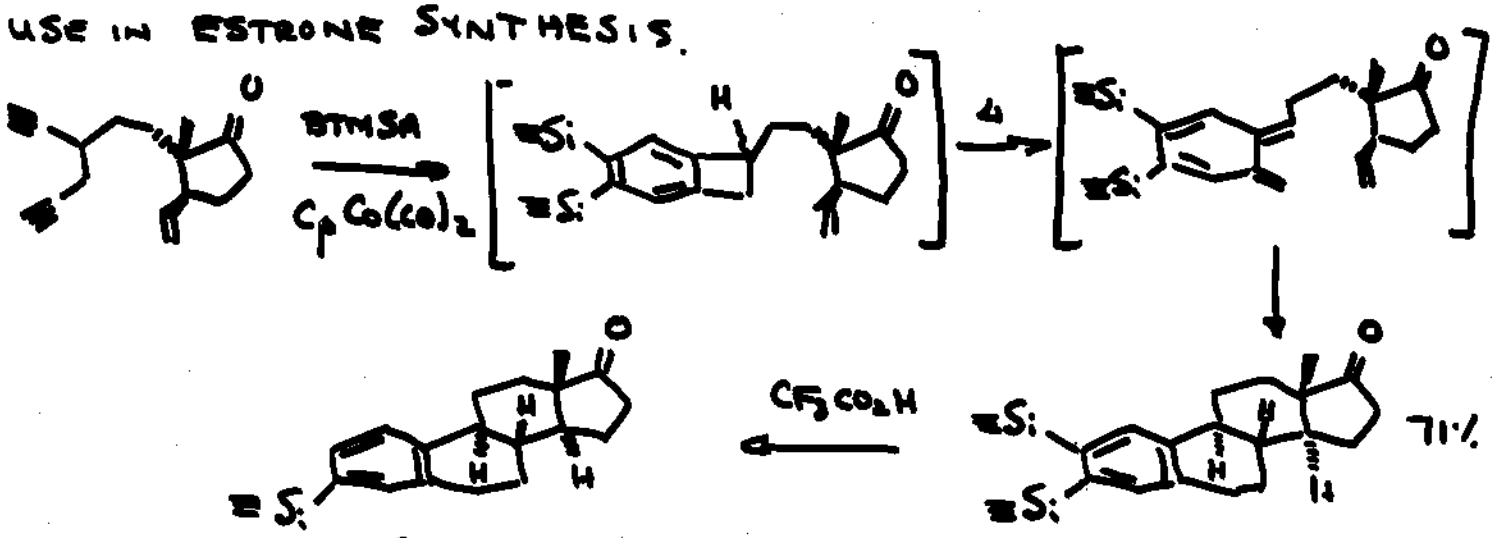
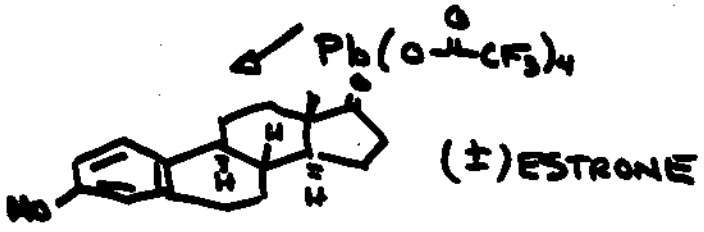
– AGAIN, THESE ARE THE 'THIRD' PARTNER.

I.E.

ETC.

USE IN ESTRONE SYNTHESIS.





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