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PHASE TRANSFER CATALYZED DIBROMOCARBENE INSERTION INTO DIENE-IRON TRICARBONYL COMPLEXES

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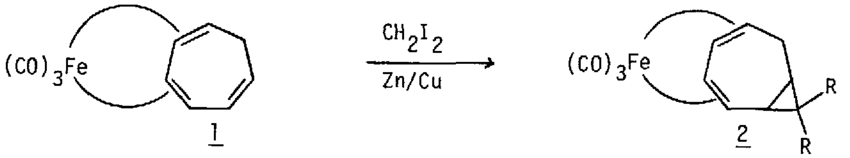
Summary The insertion of dibromocarbene into a saturated carbon-hydrogen bond of a diene-iron tricarbonyl complex can be effected in reasonable yields, and under gentle conditions, by phase transfer catalysis.

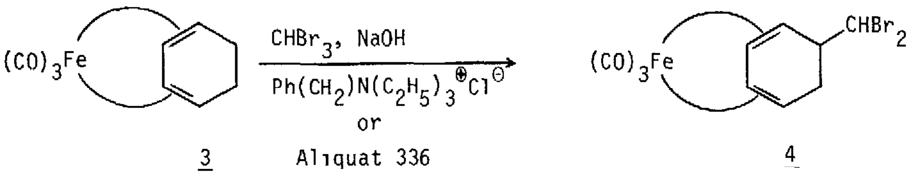
A number of publications have appeared in the last few years indicating the considerable potential of phase transfer catalysis in stoichiometric and catalytic organometallic chemistry. Applications to catalytic processes include the carbonylation[2] and hydrogenation[3] of dienes, and the carbonylation of halides[4,5] Phase transfer catalysis has proven to be of use in the synthesis of ferrocenes[6], *ortho*-metalated[7], ligand substitution[8], and π-allyl complexes[9,10], as well as in the preparation of fulvenes[11] and aromatic amines[12]

The formal addition of carbene to an uncoordinated double bond of a polyolefin transition metal complex [e g 1 → 2, R=H], using the Simmons-Smith reagent, was described in 1975 by Reger and Gabrielli[13]. More recently, Taylor[14] has examined the addition of dichlorocarbene [from chloroform and potassium t-butoxide] to 1 (to give 2, R=Cl) and to other polyene complexes There has been, to our knowledge, no reports on the insertion of dihalocarbene into a saturated carbon-hydrogen bond of a transition metal organometallic complex Diene-iron tricarbonyl complexes are an important class of compounds, particularly in terms of synthetic applications[15].



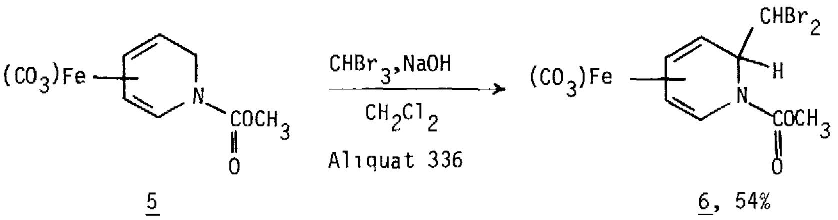
One of the most valuable phase transfer processes developed in organic chemistry is that involving dihalocarbene generation, and its subsequent addition and insertion reactions[16] This communication describes the simple, mild, and convenient phase transfer catalyzed insertion of dibromocarbene into a C-H bond of a diene-iron tricarbonyl complex

Reaction of 1,3-cyclohexadiene-iron tricarbonyl(3)[15] with

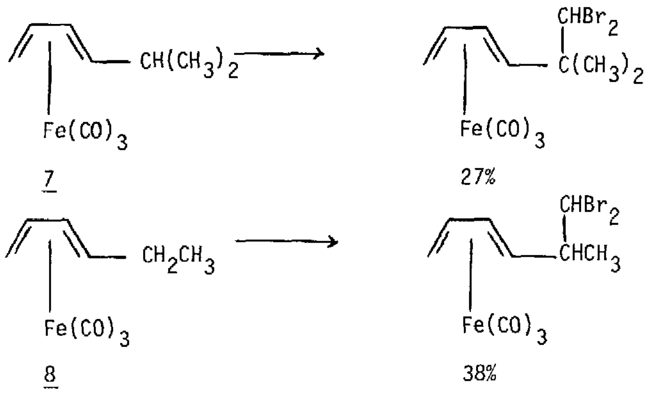


bromoform (as reactant and solvent), sodium hydroxide, and benzyltriethylammonium chloride as the phase transfer catalyst afforded the dibromomethyl complex(4) as a bright yellow oil in 14% yield A significant improvement in yield (to 31%) was realized by the use of Aliquat 336 [tricaprylmethylammonium chloride] as the phase transfer catalyst and methylene chloride as the organic phase. The structure of 4, and the products of the other insertion reactions, is supported by analytical and spectral data [Anal found C,30.4, H,2 0, Br,40.9, Calcd for $C_{10}H_8Br_2FeO_3$ C,30 6, H,2 0, Br,40.7, IR, ν_{CO} ($CHCl_3$) 2048w, 2038s, 2015sh, 1990vs cm^{-1}, ^1H NMR($CDCl_3$) δ1.60-2.30(m,3H, protons on saturated ring carbons), 3.00(m,2H, protons on terminal carbons of diene unit), 5 50(m,2H, protons on internal carbons of diene unit), *6.05(m,1H, $CHBr_2$)*; ^{13}C NMR($CDCl_3$) δ29 11, 29 50 (methylene carbons), 51 05($CHBr_2$), 57 61, 59.33, 85 33, 85.37 (unsaturated carbons), MS(m/e) 392, 364, 336, 308]

Dibromocarbene insertion was also attained with the dihydropyridine complex 5[15], resulting in the isolation of 6 in 54% yield. Acyclic diene-iron



carbonyl complexes(7,8) containing a secondary or tertiary C-H bond also



7

27%

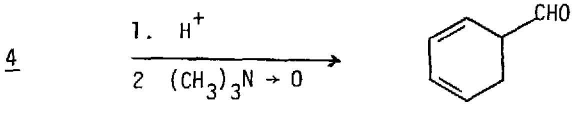
8

38%

experienced dibromocarbene insertion.

As anticipated, 1,4-diphenyl-1,3-butadiene-iron tricarbonyl, a compound devoid of saturated carbon atoms, failed to react with dibromocarbene. It should also be noted that insertion did not occur on attempted reaction of 3 with dichlorocarbene. The latter result is in accord with the excellent work of Dehmlow and co-workers[17], who demonstrated that CBr_2 is more reactive than CCl_2 under phase transfer conditions

The yields (27-54%) obtained in the dibromocarbene insertion reactions are good, particularly when compared with those reported for other insertion reactions into organic substrates[18] (except adamantane type systems)[19] Furthermore, this method provides a simple entry into organic and organometallic functionalized dienes since, for example, acid or base treatment will convert the dibromomethyl function to an aldehyde. The dienaldehyde (e.g. 9) formed on decomplexation[15] would be non-conjugated as far as the aldehyde and diene units are concerned



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The following general procedure was used A mixture of complex (7.5 mmol), bromoform (0 15 moles), Aliquat 336 (0.75 mmol), 50% NaOH (0.30 moles), methylene chloride (30 ml), and ethanol (1.5 ml) was vigorously stirred at room temperature for one hour, and then at 50°C (oil bath temperature) for five hours After cooling to room temperature, the reaction mixture was added to excess distilled water, and the organic phase was separated with the aid of additional CH_2Cl_2 The organic phase was dried ($MgSO_4$), and evaporated in vacuo. The product was purified by column chromatography on silica gel Elution with hexane gave recovered bromoform Pure dibromomethyl complex was then eluted with hexane, benzene, or a hexane/benzene mixture Preparative thin-layer chromatography could also be used for product purification

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