at 3400 cm^{-1}. The nmr spectrum revealed a singlet at τ 6.63 (two hydrogens) and ten ring hydrogens at 8.50.

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.78. Found: C, 43.63; H, 6.78.

The above bromination was carried out in pyridine yielding similar results.

Treatment of methylenecyclohexane epoxide (0.6 mol) (K & K Chemical Co.) with 48% aqueous hydrogen bromide according to the procedure of Traynham[3] produced a solid which, when recrystallized from petroleum ether, melted at 82–83° (60%). The product was shown to be identical with **1** (n = 5) (from the bromination of **3**), mixture melting point and infrared and nmr spectra identical (CCl_4). After removal of the petroleum ether vacuum distillation of the residue, bp 50–51° (0.15 mm), yielded a colorless oil: nmr spectrum (CCl_4), singlet τ 6.30 (80%), singlet, 6.63 (20%). Two redistillations, bp 41–42° (0.08 mm), yielded a viscous oil: nmr spectrum (CCl_4), singlets, τ 6.30 and 6.63 in equal amounts. The oil was treated with a few crystals of **1** (n = 5) and petroleum ether, cooled, and filtered. The petroleum ether was then removed under vacuum. The nmr spectrum (CCl_4) of the residual oil now revealed singlets at τ 6.30 (90–95%) and 6.63 (5–10%): ir, ν^{film} 3400 cm^{-1} broad).

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.78. Found: C, 43.80; H, 6.93.

Treatment of the oil with excess alcoholic silver nitrate at room temperature for 2 hr followed by dilution with water and extraction with ether yielded, after drying and removal of the ether, cyclohexanecarboxaldehyde which was characterized as the 2,4-dinitrophenylhydrazone, mp 170–171° (ethanol) (lit.[8] mp 172–173°).

Reduction of Methyl 1-Bromocyclohexanecarboxylate.—Into a flask was placed 100 ml of anhydrous ether and 2.5 g (0.066 mole) of pulverized lithium aluminum hydride. The mixture was cooled to 0° and the dropwise addition of 20 g (0.09 mol) of methyl 1-bromocyclohexanecarboxylate[9] dissolved in 25 ml of ether was commenced. The reaction mixture was stirred for an additional hour at 0°. Decomposition was effected with water followed by the addition of a 10% solution of sulfuric acid. The ether layer was separated, washed with water, and dried over magnesium sulfate. Removal of the ether followed by distillation of the residue yielded 5 g of a colorless oil, bp 55° (0.55 mm), and a large amount of nondistillable material. The nmr spectrum (CCl_4) of the oil showed a singlet at τ 6.30 due to two hydroxymethyl hydrogens (2) and a doublet at τ 6.58–6.65 (4). Treatment of the oil with alcoholic silver nitrate produced an instantaneous precipitate of silver bromide. Dilution of the reaction mixture with water was followed by extraction with ether. After drying the ether with magnesium sulfate, the removal of the ether left an oil which was converted into its 2,4-dinitrophenylhydrazone, mp 170–171° (ethanol) (lit.[8] mp 172–173°) for cyclohexanecarboxaldehyde.

The Reaction of 1 (n = 5) with Isopropylmagnesium Bromide.—To 21 g (0.11 mol) of **1** (n = 5) dissolved in 300 ml of anhydrous benzene was added, dropwise, an equivalent of isopropylmagnesium bromide (prepared from 16 g (0.13 mol) of isopropyl bromide, 75 ml of ether, and 3.2 g of magnesium) at room temperature. The reaction mixture was refluxed for 8 hr. It was then poured into a saturated solution of ammonium chloride, and the organic layer was separated and washed with water, a 10% sodium carbonate solution, and water, and finally the organic layer was dried over magnesium sulfate. The solvent was subsequently removed under vacuum. Examination of the residue by vpc revealed no cycloheptanone. Distillation afforded 5 g (0.045 mol, 40%) of cyclohexanecarboxaldehyde, bp 49–50° (30 mm) [lit.[8] bp 50–53° (20 mm)]. The 2,4-dinitrophenylhydrazone melted at 172–173° (lit.[8] mp 172–173°). A large amount of decomposition resulted during distillation with the production of polymeric material.

Registry No.—**1** (n = 5), 17299-10-4; **2**, 17299-11-5; **3**, 17299-12-6; **4**, 100-49-2; reduction product of **3**, 590-67-0.

Acknowledgment.—I am grateful to Mr. B. Waxman for helpful discussions during this project and to Mr. T. Kolesar for the nmr spectra.

[8] M. Stiles and A. J. Sisti, *J. Org. Chem.*, **25**, 1691 (1960).

[9] W. J. Bailey and R. Baylouny, *ibid.*, **81**, 2126 (1959).

The Reaction of Phenyl Derivatives of Transition Metals with Acetylene

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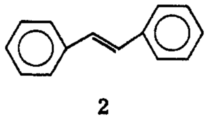
Numerous examples of the reaction of acetylenes with transition metal carbonyls and their derivatives are known,[1] but there appear to be only a few examples of the reaction of alkyl (or aryl) transition metal complexes with acetylenes. Tsutsui, Herwig, Metlesics, and Zeiss have investigated the reaction of various aryl- and alkylchromium compounds and other transition metal alkyls with disubstituted acetylenes.[2] In some reactions they found the formation of compounds containing two acetylene units and an alkyl or aryl group from the metal, as well as the cyclotrimerization product of the acetylenes, hexasubstituted benzene. For example, triphenyl- and triethylchromium reacted smoothly with diphenylacetylene in tetrahydrofuran (THF) to give 1,2,3,4-tetraphenylnaphthalene and -benzene, respectively, in addition to hexaphenylbenzene. Diethylnickel and diphenylacetylene gave tetraphenylcyclohexadiene and hexaphenylbenzene. However, for the reaction of triphenylchromium with a monosubstituted acetylene or acetylene itself, they reported that the triarylchromium was rapidly decomposed by acetylenic hydrogen and the acetylene was polymerized under the conditions they used. The fate of the phenyl group was not determined.[2b] This type of sensitivity toward acidic hydrogen of acetylene seems to be general in other alkyl or acyl transition metal compounds,[3,4] and only a few examples were reported about the reaction of acylmetal carbonyls with acetylene or monosubstituted acetylenes.[5]

In this paper we wish to report the formation of all-*trans*-1,6-diphenyl-1,3,5-hexatriene by the reaction of triphenylchromium with acetylene in THF at low temperature. A large excess of acetylene was bubbled into a THF solution containing triphenylchromium as its tetrahydrofuranate at −70°, and the reaction mixture was slowly warmed with stirring. After the ordinary treatment, the following products were obtained: all-*trans*-1,6-diphenyl-1,3,5-hexatriene (**4**), *trans*,*trans*-1,4-diphenyl-1,3-butadiene (**3**), biphenyl



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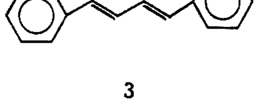

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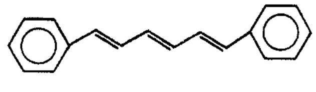

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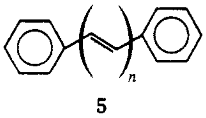

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[1] M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

[2] (a) M. Tsutsui and H. Zeiss, *J. Amer. Chem. Soc.*, **81**, 6090 (1959); (b) W. Herwig, W. Metlesics, and H. Zeiss, *ibid.*, **81**, 6203 (1959).

[3] R. F. Heck, *ibid.*, **86**, 2819 (1964).

[4] A. Nakamura, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **19**, 81 (1962); *Chem. Abstr.*, **59**, 8786 (1963).

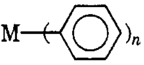
[5] Y. Sawa, I. Hashimoto, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **33**, 2159 (1968).

(1), and a large amount of greenish black polymer. The polymer was slowly oxidized by exposing to air for about a month which changed the color from black to dark brown. On the basis of the ir spectrum, this material was assumed to be a conjugated *trans*-polyene depicted as **5**.

According to Zeiss, *et al.*,[2] triphenylchromium reacts with disubstituted acetylenes to give 1,2,3,4-tetrasubstituted naphthalene. In this reaction, however, the expected naphthalene was not detected, but **4** in a moderate yield and **3** in a small amount were isolated. It is interesting to note that the reaction of the organotransition metal compound with acetylene led to the linear trimerization of acetylene.

The results of the reaction of acetylene with some other phenyl derivatives of transition metals are summarized in Table I. As may be seen in Table I, the yields of **1**–**4** are closely related to the thermal stability of the phenyl–metal bond. In the reaction of acetylene with diphenylmanganese, which is more stable than triphenylchromium and does not react with 2-butyne in THF,[6] a small amount of *trans*-stilbene (**2**) was also detected. These low yields, especially that of **1**, indicate that the phenyl–metal compound is too stable to react with acetylene and affords benzene by the subsequent hydrolysis. On the other hand, diphenylcobalt[7] and -nickel[8] are known to be more unstable than triphenylchromium, and also in this reaction the immediate decomposition of these compounds took place to give mainly the coupling product, **1**.

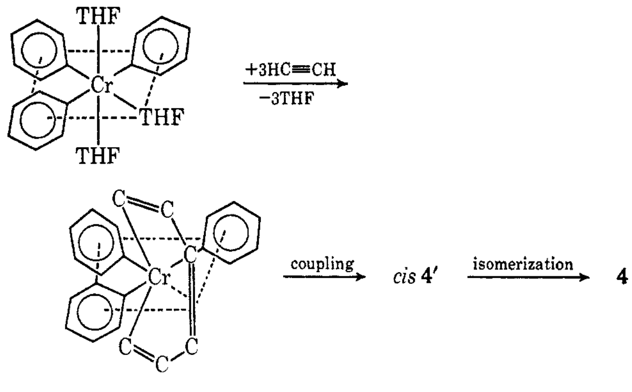
TABLE I

THE REACTION OF $(THF)_mM-($  $)_n$ WITH $HC\equiv CH$ IN THF

M	Temp, °C[a]	Products, %: 1[b]	2[b]	3[b]	4[b]	5[c]
Cr^{III}	−70	20[d]		<1[d]	18[d]	4.3
Mn^{II}	−50 to −30	6.5[e]	<1[e]	Trace	4[d]	0.64
Co^{II}	−50 to −40	35[e]	Trace	2.5[e]	<1[d]	2.0
	−55 to −45	51[e]	2.2[e]	<1[e]	Trace	0.77
Ni^{II}	−45 to −25	37[e,f]				3.2

[a] See Experimental Section. [b] Theoretical yields are based on the metal compounds. [c] Moles of acetylene converted into this product per mole of the metal compounds. [d] Isolated. [e] Estimated by glpc. [f] *p*-Terphenyl (2.3%) was also detected.

We cannot make a definite decision about the reaction course for the formation of the triene **4** owing to the low yields and lack of other data. An acetylene polymerization process, whose initiation and termination steps are caused by free phenyl radicals, is less probable from the above-mentioned experimental results; *i.e.*, in the reaction of diphenylcobalt and -nickel with acetylene which would form phenyl radicals[9] more favorably than triphenylchromium the yields of the triene are very low. Hence, as for the reaction of triphenylchromium with acetylene which gave the triene as a main product, the following course seems to be plausible,[10] although the alternative mechanism which involves stepwise insertion of acetylene into the metal–phenyl bond cannot be fully denied.



Experimental Section

General.—Acetylene was passed through aqueous $NaHSO_3$ and dried with H_2SO_4. Tetrahydrofuran (THF) was refluxed with sodium wire in the presence of benzophenone for 2 hr. The mixture was then fractionally distilled. All reactions were carried out under a dry argon atmosphere. Gas–liquid partition chromatographic analyses were performed on a Yanagimoto GCG-5DH instrument using 2.5 m × 3 mm columns packed with 5% SE-30 (column temperature, 230–280°, 4° per min; carrier gas, He, 50 cc per min). Infrared spectra were run on a Shimazu IR-27 in KBr disks.

Treatment of Triphenylchromium with Acetylene.—Triphenylchromium was prepared by the reported method[11] from 0.100 mol of phenylmagnesium bromide and 5.3 g (0.033 mol) of anhydrous $CrCl_3$ in 280 ml of THF in a four-necked flask. To the stirred solution containing *ca.* 0.033 mol of triphenylchromium was introduced slowly (40 ml per min) a large excess of acetylene (*ca.* 6 l.) at −70°. The reaction mixture was gradually warmed up to room temperature during 28 hr with efficient stirring. In this period the color of the solution changed from red-brown to dark violet, and the formation of a large amount of greenish black polymer was observed. The reaction mixture was hydrolyzed by 100 ml of 4 *N* HCl and the solvent was removed. The resulting mixture was divided into a hot, benzene-soluble part and an insoluble black polymer. The red-brown benzene extract was washed with aqueous $NaHCO_3$ and water, dried over anhydrous $MgSO_4$, and evaporated. The residual oil was distilled under reduced pressure to give the following fractions: (1) bp 76–83° (10 mm), 1.7 g of unidentified colorless oil; (2) bp 108–135° (10 mm), 1.0 g (20%) of biphenyl, melting point and mixture melting point with an authentic sample, 70–71° (purified by sublimation two times at 110°); and (3) bp 135–150° (0.35 mm), 1.9 g of green-yellow crystals. Fraction 3 was recrystallized from ethanol–dioxane to give 1.4 g of pale yellow leaflets, mp 200–201.5°. A sample of all-*trans*-1,6-diphenyl-1,3,5-hexatriene, prepared by another method,[12] showed the same behavior and the melting point was undepressed when mixed with the above sample. Their ir spectra were also identical in all respects (yield 18% based on $CrCl_3$). Concentration of the mother liquor and recrystallization from ethanol afforded 40 mg of *trans,trans*-1,4-diphenyl-1,3-butadiene, which was characterized by comparison of its melting point and ir spectrum with those of an authentic sample,[12] mp 149–150°. The black polymer was powdered, treated with boiling 4 *N* HCl in order to remove inorganic material, washed with water, and dried *in vacuo*. The polymer was scarcely soluble in ordinary organic solvents. The ir spectrum exhibited a strong absorption at 1010 cm^{-1} owing to a C–H bending mode with the hydrogen

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[6] M. Tsutsui and H. Zeiss, *J. Amer. Chem. Soc.*, **83**, 825 (1961).

[7] M. Tsutsui, *Ann. N. Y. Acad. Sci.*, **93**, 133 (1961).

[8] (a) E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compound," John Wiley & Sons, Inc., New York, N. Y., 1957, p 251; (b) M. Ryang, K. Yoshida, H. Yokoo, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **38**, 636 (1965).

[9] The formation of phenyl radicals as a precursor of the coupling product, biphenyl, has not been fully established.

[10] This route seems to be supported by the following results; *e.g.*, the formation of tropone–iron tricarbonyl from the treatment of diiron nonacarbonyl with acetylene [W. Hübel and E. Weiss, *Chem. Ind.* (London), 703 (1959)] and the formation of tetrasubstituted ferracyclopentadiene–iron carbonyl from the reaction of polynuclear iron carbonyls with disubstituted acetylenes [E. H. Braye and W. Hübel, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959)], and also by the report by Hagihara [H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **7**, 22 (1967)].

[11] W. Herwig and H. Zeiss, *J. Amer. Chem. Soc.*, **81**, 4798 (1959).

[12] S. Misumi and M. Nakagawa, *Bull. Chem. Soc. Jap.*, **36**, 399 (1963).

atom out of plane of the double bond, which is known to occur only for a *trans* system.[13] In addition to this absorption, the ir spectrum showed two weak peaks at 695 and 740 cm^{-1} due to the monosubstituted phenyl group. Although this material was not purified satisfactorily for analytical purposes, it was assumed to be a conjugated *trans* polyene from acetylene whose ends are attached to a phenyl group (yield 3.7 g).

Treatment of Diphenylmanganese, -cobalt, or -nickel with Acetylene.—Diphenylmanganese was prepared by the reported method[6] from 0.12 mol of phenylmagnesium bromide and 6.3 g (0.060 mol) of anhydrous $MnCl_2$ in 300 ml of THF at −50 to −20°. Diphenylcobalt and -nickel were also prepared by a similar method at −40 and −50°, respectively. Stirring was continued for 1 hr at these temperatures. To the solutions prepared above was introduced slowly an excess of acetylene (*ca.* 6 l.) at the temperature given in Table I. The reaction mixture was slowly warmed to room temperature with stirring, followed by hydrolysis with 100 ml of 4 *N* HCl. After the same treatment as above, the organic layer was, in each case, distilled under reduced pressure. After the separation of **4** by recrystallization from ethanol, the mother liquor was concentrated and subjected to quantitative glpc analyses.

Registry No.—Biphenyl, 92-52-4; **2,** 103-30-0; **3,** 538-81-8; **4,** 17329-15-6; acetylene, 74-86-2.

(13) (a) M. Akhtar, T. A. Richards, and B. C. L. Weedon, *J. Chem. Soc.,* 933 (1959); (b) M. Hatano, *Kogyo Kagaku Zasshi,* **65**, 723 (1962).

The Addition of Nitrosyl Chloride to Cyclohexene[1]

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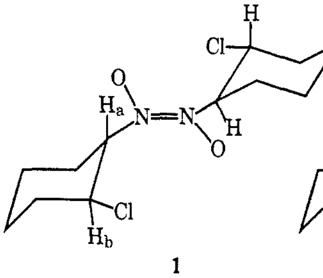
In connection with some of our recent synthetic work on the addition of nitrosyl chloride to olefins,[2] we became interested in the stereochemistry of the addition to cyclic olefins. We report here our results with cyclohexene whose reaction with nitrosyl chloride to yield a solid dimer has been reported many times.[3-7] Also formed in this reaction are several liquid products and these have more recently been identified.[8-11] These liquid products, however, can reasonably be assumed to have risen from a secondary reaction of the initially formed nitroso chloride, so we felt that an investigation of the stereochemistry of the solid dimeric nitroso chloride would serve to adequately define the stereochemical course of the addition reaction. One other study concerning the stereochemistry of this solid nitroso chloride dimer from cyclohexene has been reported by Nukada, *et al.*,[8] and we find significant differences between our work and theirs.

The addition of nitrosyl chloride to cyclohexene in liquid sulfur dioxide gives in good yield, as has been reported, *trans*-2,2′-dichloro-*trans*-azodioxycyclohexane[9] (**1**), mp 152–153° (lit.[7] mp 152–153°). The *trans* configuration about the N–N bond of recrystallized **1** was established from the infrared spectrum which shows N–O stretching frequencies at 1193, 1227, and 1216 cm^{-1},[12] and from the observed uv absorption maximum of 294.5 mμ (ethanol, ε 8000).[13]



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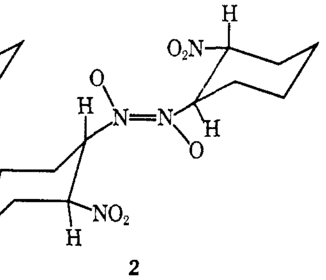

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When the addition reaction is carried out at room temperature in carbon tetrachloride solution, very little solid dimer is obtained, but instead, the liquid product mixture contains 1,2-dichloro-1-nitrosocyclohexane, 1-nitro-2-chlorocyclohexane, 2-chlorocyclohexanone, and 1,2-dichlorocyclohexane.[10,11] Lowering the reaction temperature to −30° in carbon tetrachloride solution allows one to obtain a 30% yield of solid dimer, mp 136–144° (mp 152–153°, after three recrystallizations from ethanol). The infrared spectrum of this crude adduct before recrystallization (but after washing with cold carbon tetrachloride) showed, in addition to the characteristic peaks for compound **1**, strong absorption at 1555 cm^{-1} which indicates the presence of a secondary nitro group.[14]

The yield of solid product in this addition reaction is strongly dependent upon the solvent and the reaction temperature. However, in most cases, the major product (**1**), is accompanied by a second solid product which shows characteristic nitro absorption in the infrared. This nitro containing product has now been separated from the crude reaction mixture by fractional crystallization and has been identified as *trans*-2,2′-dinitro-*trans*-azodioxycyclohexane (**2**), mp 168–169°. Its infrared spectrum, its elemental analyses, and its ready conversion into 2-nitrocyclohexanone by hydrolysis with levulinic acid[2] all support this assignment.

The *trans* arrangement of the tertiary hydrogens on the cyclohexane ring in both **1** and **2** has been established by analysis of their nmr spectra. The spectrum of **1** ($CDCl_3$, Figure 1) shows signals at δ 1.85 (broad, complex multiplet, 8 H), 4.27 (1 H), and 5.43 (1 H). The signals at δ 5.43 and 4.27 are assigned to the single hydrogens on carbon atoms 1 and 2, respectively. The observed spectrum compared favorably with that expected from a first-order analysis of an ABMX system.

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[1] Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1, 1967.

[2] B. W. Ponder and D. R. Walker, *J. Org. Chem.,* **32**, 4136 (1967).

[3] A. Baeyer, *Ann.,* **278**, 88 (1894).

[4] O. Wallach, *ibid.,* **343**, 40 (1905).

[5] R. Perrot, *C. R. Acad. Sci., Paris,* **202**, 494 (1936); **203**, 329 (1936).

[6] R. K. Allison, U. S. Patent 2,485,180 (1949).

[7] W. Pritzkow, H. Schafer, P. Pabst, A. Ebenroth, and J. Beyer, *J. Prakt. Chem.,* **29**, 123 (1965).

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[9] The nomenclature suggested by A. Mackor, *et al.* [*Tetrahedron Lett.,* 2757 (1967)], is used in this paper.

[10] T. E. Walton, M.S. Thesis, The University of Alabama, 1967.

[11] G. Doucet, *C. R. Acad. Sci., Paris,* **264**, 1868 (1967).

[12] B. G. Gowenlick and W. Luttke, *Quart. Rev.* (London), **12**, 321 (1958).

[13] It is well known[12] that the nitroso dimer formed initially has a *cis* configuration about the N–N multiple bond and that this linkage is rapidly and quantitatively transformed to the *trans* isomer upon recrystallization. This behavior was verified by the following spectral observations: before recrystallzation, uv max (EtOH) 280.5 mμ; after recrystallization, ir (KBr), 1193, 1227, and 1216 cm^{-1}; uv max (EtOH), 294.5 mμ.

[14] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 299.