84. The Reaction of Phenyl(trichloromethyl)mercury with Substituted Norbornenes

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(13. I. 72)

Summary. The addition of phenyl(trichloromethyl)mercury to five substituted norbornenes is described, and the results compared with those obtained with bicyclo[2.2.2]oct-2-ene and 3,3,5,5-tetramethylcyclopentene. The reaction proves to be useful for synthetic purposes, in that it leads usually to ring expansion. However, a possible disadvantage is that the addition step is sensitive to steric hindrance and depends on the reactivity of the double bond.

Introduction. The addition of dihalocarbenes to cyclo-olefins is a versatile reaction in which direct incorporation of single carbon atoms leads in principle to homologous cyclic products amenable to further synthetic elaboration [1]. The method possesses considerable preparative utility in the case of bridged bicyclic olefins such as norbornene, since its availability ensures ready access to derivatives of bicyclo[3.2.1]octane which have proved to be useful substrates for mechanistic and structural studies [2].

The chief methods used for these reactions so far have depended on reagents which furnish trihalomethanide anion as the carbene precursor. The employment of phenyl(trichloromethyl)mercury presents a possible advantage in that dihalocarbene arises by a non-ionic mechanism [3]. In the present study the behaviour of the mercurial towards a series of substituted norbornenes and structurally related compounds is examined in order to explore the scope of the overall reaction and to prepare new compounds for future study.

Results and Discussion. Five substituted norbornenes were studied together with bicyclo[2.2.2]oct-2-ene and 3,3,5,5-tetramethylcyclopentene by way of comparison. With one notable exception the reaction proceeded smoothly to give products resulting from the 1:1 adducts in yields ranging from 9 to 92% (Table). The products were those expected from the rearrangement of the *gem*-dihalocyclopropane intermediates.

Norbornene **1** constitutes the classic test model. It is a fact that nearly all additions take place on the *exo* face of the double bond, and this particularity has been diversely rationalized in terms of a stereoelectronic effect, steric hindrance and torsional interactions [4] [5]. True to form, the mercurial gave *exo*-3,4-dichlorobicyclo[3.2.1]oct-2-ene **3** in yields usually better, but not significantly so, than those obtained by other methods (Table) [6]. As has been discussed elsewhere, addition occurred

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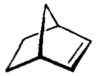
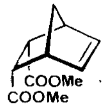
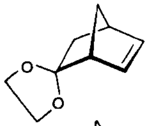
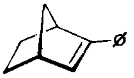
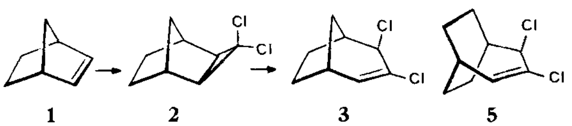
Yield of 1:1 Adducts obtained on Reaction of Phenyl(trichloromethyl)mercury with some Bridge Bicyclic Olefins

Olefin		(mmoles)	$\varnothing \mathrm{HgCCl_3}$ (mmoles)	Reflux time in h	Yield %
1		42.5	25.2	24	45
4		17.7	19.0	48	37
6		15.4 30.1	15.2 20.8	120	0
9		22.5	27.8	72	9
12		12.6	13.3	68	27
14		45.4	25.2	24	77
23		11.9	13.3	48	92

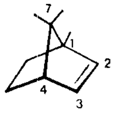
exclusively on the *exo* face to yield the cyclopropane adduct **2** which spontaneously and stereospecifically rearranged to the ring-enlarged product **3**.



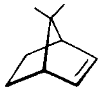
1 **2** **3** **5**

Bicyclo[2.2.2]oct-2-ene **4** behaved similarly to norbornene; 3,4-dichlorobicyclo[3.2.2]non-2-ene **5** was formed.

Substitution at C(7) on the norbornene skeleton brought about a dramatic change. Bornylene **6** was found to be completely unreactive. It has been suggested that the siting of a methly group in the *syn* C(7) position will block the *exo* face of the double bond with the result that *exo* and *endo* steric effects should be nullified [5]. Therefore, the residual torsional interactions would be expected to favour *exo* addition. In the present case, the failure of addition to occur probably means that repulsive *van der Waal's* interaction between the *syn* oriented chlorine of the incoming carbene and the *syn* C(7) methyl are so severe in the transition state that little bonding develops with consequently little torsional change around the C(1), C(2) and C(3), C(4) atoms. In contrast, it is interesting to note, that contrary to prediction, the sterically less demanding epoxidation process is reported to give exclusively the *endo* epoxide **8** with apobornylene **7**, whereas norbornene forms the *exo* epoxide to the extent of 94% [7].



6



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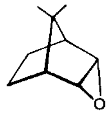
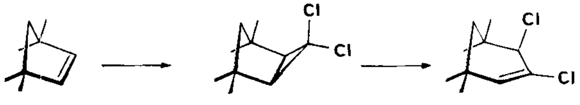


8

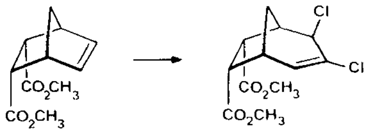
Unlike norbornene and its 1-methyl derivative which react smoothly with both dibromo- and dichloro-carbene, the structurally related 3,3,5,5-tetramethylcyclopentene **9** proved repeatedly unreactive towards the former carbene, but on reaction with phenyl(trichloromethyl)mercury gave 2,3-dichloro-4,4,6,6-tetramethylcyclohexene **11** in low yield.



9 **10** **11**

Although no evidence was forthcoming for the presence of the cyclopropane adduct **10**, there is no doubt of its intermediacy in the formation of **11**. Steric hindrance best accounts for the greater reactivity of dichlorocarbene. Models indicate that both faces of the double bond of **9** are equally hindered by the two sets of geminal methyl groups. Accordingly, simple differences in bulk between the carbenes best account for the relative reactivities. Similar arguments have previously been invoked to explain the sluggishness of the addition of dibromocarbene to a number of substituted endocyclic olefins [8].

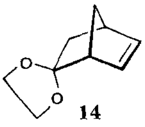
Reaction of phenyl(trichloromethyl)mercury with *endo-cis*-5,6-dimethoxycarbonyl-norborn-2-ene **12** proceeded smoothly with the formation of the rearranged *exo* product **13**. No product was detected which could have arisen by participation of the ester group in the rearrangement process [9].



12 **13**

The addition of dichlorocarbene to the unsymmetrical olefins, the ethylene acetal of norborn-5-ene-2-one **14** and 2-phenylnorbornene **23**, gave results which bear on the nature of the rearrangement of the initial adducts.

Addition of dichlorocarbene to **14** resulted in a roughly 50:50 mixture of the two *exo* isomers (**15** and **16**). It was obvious that these were the kinetic products, as heating or standing for several hours displaced the equilibrium so that **16** was converted nearly exclusively to **15**. It was not possible to obtain **16** in a pure state, as it isomerized readily to **15** in the isolation process [10]. Consequently, in order to study the isomeric equilibria and to unequivocally identify the structures of the isomers, the dibromo analogues (**17** and **18**) were prepared and separated. The application of the *von Auwers-Allinger* rule and NMR. spectral analysis permitted the assignment of the structures [11]. The difference in free energy between **17** and **18** is 0.8 kcal/mole. The stability difference can be attributed to the unfavourable non-bonded interaction between the *endo* allylic hydrogen atom and the contiguous oxygen atom found in **16** and **18**, but absent in **15** and **17**.



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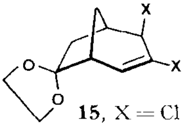
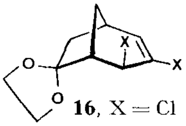
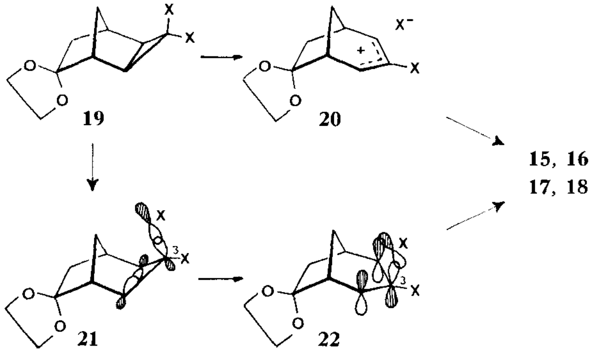


15, X = Cl
17, X = Br

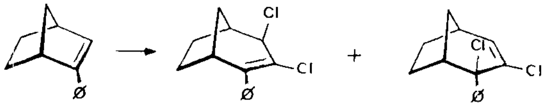


16, X = Cl
18, X = Br

The fact that the composition of rearrangement products is 50:50 may afford a clue to the nature of the rearrangement. Two distinct processes can be envisaged. The first is the disrotatory rupture of the cyclopropane derivative **19** to the intimate ion pair **20** which subsequently collapses to products (*e.g.* **15** and **16**) by random attachment of halide to the allylic termini. A second possibility is that rearrangement occurs by a non-ionic mechanism. In other words, cyclopropyl halide transfers to the adjacent carbon atom in a suprafacial process (**21** → **22**) [12]. The geometric constraint in the *exo*-tricyclo[3.2.1.0^{2,4}]octane skeleton permits both of these processes to be concerted [13]; the sole distinction between them being the separation of charge. Such a fine distinction is hard to detect [14]. Moreover, the product composition can be compatible with either process, if the two transition states for the collapse of the intimate ion pair are assumed to be identical. However, participatory or field electronic effects (by the acetal substituent) would be expected to be more important in the ionic than in the non-ionic process, even though they may be concerted [15].



2-Phenylnorbornene **23** on treatment with phenyl(trichloromethyl)mercury gave only one product, *exo*-2-phenyl-3,4-dichlorobicyclo[3.2.1]oct-2-ene **24**. Evidently the non-conjugated isomer **25** had rearranged under the reaction conditions. However, it could be obtained under the cooler conditions of the method of *Hoffmann* & *Doering* (50 min. at room temperature), when the ratio of stable **24** to unstable **25** isomer was found to be 3:1.



23 **24** **25**

Conclusion. The phenyl-trichloromethyl-mercury reagent provides an excellent procedure for ring expansion of bridged bicyclic olefins by means of carbene addition to the double bond. When the latter is activated as in 2-phenylnorbornene, the yield is nearly quantitative. Furthermore the outcome of the reaction on the norborn-5-ene-2-one ethylene acetal **14**, provides interesting insights concerning the mechanism of the cyclopropyl-allyl rearrangement.

We acknowledge Temple University for the provision of facilities for the carrying out of this research and awarding a visiting professorship to *B. W.* We are indebted to the *National Science Foundation* for the award of a fellowship (to *D. T. H.*). Acknowledgment is also made to the donors of the *Petroleum Research Fund* administered by the *American Chemical Society* for support of this research.

Experimental Part

Melting points were determined on a *Thomas-Hoover* capillary melting point apparatus. All melting points and boiling points are uncorrected. – Elemental analyses were performed by Dr. *G. Robertson*, Florham Park, N.J. and by *Micro-Analysis, Inc.*, Wilmington, Del.

Spectral Measurements. IR. spectra were obtained on a *Beckman* IR-5 A (NaCl optics) spectrophotometer. The spectra of liquids were taken as films on NaCl plates. Solids were examined as nujol mulls or in KBr pellets. Spectra were calibrated with polystyrene film by superpositioning the band at 1603 cm^{-1} (6.238 μ) on the spectra. – UV. spectra were determined on a *Carey* Model 14 spectrophotometer using cyclohexane as solvent. – NMR. spectra were determined at 60 MHz on a Model A-60A spectrometer (*Varian Associates*, Palo Alto, California). Spectral solutions were made up to 10 to 20% concentration in reagent grade carbon tetrachloride or deuteriochloroform as indicated. Tetramethylsilane (TMS) was used as an internal reference. The NMR. signals are expressed in ppm and are designated as singlets (*s*), doublets (*d*), triplets (*t*), etc.; their relative intensities are indicated in proton units, 1 H, 2 H, etc. as well as their attribution, *e.g.* vinyl.

2,2,4,4-Tetramethylcyclopentanone tosylhydrazone. 2,2,4,4-Tetramethylcyclopentanone[5]) (20.6 g, 0.15 mol) and *p*-toluenesulfonylhydrazide (30.0 g, 0.16 mol) were dissolved in methanol (150 ml) containing aqueous conc. hydrochloric acid (1 ml). The mixture was heated under reflux for 3 h then poured into ice-water (450 ml), and the resulting precipitate filtered, washed with water, pressed dry and recrystallized from absolute ethanol. A yield of 33.1 g (73%) of product as white needles (m.p. 130–132°) was obtained.

$C_{16}H_{24}N_2O_2S$	Calc.	C 62.30	H 7.84	N 9.08	S 10.40%
	Found	,, 62.58	,, 7.63	,, 9.33	,, 10.49%

3,3,5,5-Tetramethylcyclopentene (**9**)[6]). To a rapidly stirred mixture of 2,2,4,4-tetramethylcyclopentanone tosylhydrazone (30.8 g, 0.10 mol) in anhydrous ethyl ether (200 ml) at room temperature, under nitrogen, *n*-butyllithium in hexane (96 ml of 2.16 M soln., 0.21 mol) was added dropwise over 50 min; stirring was continued for 10 min. after all the reagent was added [17]. During the addition, nitrogen began to evolve. Another portion of *n*-butyllithium in hexane

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[5]) Purchased from the *Chemical Samples Co.* (Columbus, Ohio 43221).

[6]) The conventional preparation of **9** starting from isophorone is too long and gives only fair yields [16]. For procedure used here, see [17].

(0.04 mol in 20 ml) was added over 10 min and the solution was then stirred (30 min). The resulting mixture was cooled in an ice-salt bath and water (100 ml) was carefully added dropwise (the reaction is initially violent). The aqueous phase was separated and extracted with two 30 ml portions of ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered and the ether removed by distillation on a steam bath. The residue was fractionally distilled to give 9.3 g (75%) of product: b.p. 107–109° (lit.: 107.03°). NMR. (CCl_4): 5.20 (*s*, 2H, vinyl), 1.53 (*s*, 2H, CH_2), 1.03 (*s*, 12H, CH_3).

Reaction of Dichloro- and Dibromocarbene with the olefins. Dichlorocarbene adducts were prepared following the method of *Seyferth* [3]. *Doering & Hoffmann*'s method was used for the preparation of dibromocarbene adducts [18].

2,3-Dichlorobicyclo[3.2.2]non-2-ene (**5**). Bicyclo[2.2.2]oct-2-ene [19] (1.92 g, 17.7 mmol) was added in a single portion to benzene (25 ml) containing phenyl(trichloromethyl)mercury (7.54 g, 19.0 mmol). The mixture was heated under reflux for 48 h under a nitrogen atmosphere. After cooling to 5°, phenylmercuric chloride (5.24 g, 16.7 mmol) was removed by filtration and the resulting solution was distilled to remove the solvent. The residual oil was distilled *in vacuo* to yield 1.26 g of product (37% based on olefin): b.p. 84–90° (1.0–1.3 mmol); $n_D^{26} = 1.5414$. IR. (neat): 1642 cm^{-1} (C=C); NMR. ($CDCl_3$): 6.37 (*d*, 1H, $J = 9.5$ Hz, vinyl), 4.80 (*d*, 1H, $J = 1.0$ Hz, allylic), 1.90 (*m*, 10H, $-CH_2-$ and $-CH=$).

exo-*3,4-Dichlorobicyclo[3.2.1]oct-2-ene* (**3**). A mixture of norbornene (4.0 g, 42.5 mmol), phenyl-trichloromethyl-mercury (10.0 g, 25.2 mmol) in benzene (35 ml) was heated under the above conditions for 24 h. The usual work-up gave phenylmercuric chloride (5.8 g, 18.5 mmol) and a dark oil. Distillation of the latter gave 2.0 g (45% based on mercurial) of product: b.p. 74–76° (2 mmol). Comparison of the IR. and NMR. spectra with those of authentic material confirmed its identity as *exo*-3,4-dichlorobicyclo[3.2.1]oct-2-ene [6].

Reaction of Bornylene (**6**) [20]. Phenyl(trichloromethyl)mercury (8.22 g, 20.8 mmol), bornylene (4.10 g, 30.1 mmol) and benzene were heated for 5 days. – Initially the mixture is heterogenous, but on heating the mercurial goes into solution. After 1 to 2 h the solution turns pale yellow and finally deposits (after 2 to 3 h) phenylmercuric chloride. – After working-up, the orange oil, examined by NMR., gave the spectrum of bornylene. Bornylene was next removed by distillation and the residual black, viscous oil was again scrutinized by NMR. Only polymeric materials were detected, even at high amplitude.

Repetition of the reaction using 6.0 g (15.2 mmol) of mercurial and 2.1 g (15.4 mmol) of bornylene in 15 ml of benzene gave 3.6 g (11.5 mmol, 75.9%) of phenylmercuric chloride, again with no evidence of a carbon adduct.

2,3-Dichloro-4,4,6,6-tetramethylcyclohexene (**11**). 3,3,5,5-Tetramethylcyclopentene (**9**) (2.8 g, 22.5 mmol) and phenyl(trichloromethyl)mercury (11.0 g, 27.8 mmol) in benzene (30 ml) were heated for 72 h. Work-up gave phenylmercuric chloride (6.6 g, 21.1 mmol, 76%) and a dark oil (1.4 g), distillation of which gave 0.41 g of colourless liquid (8.8% yield: b.p. 48–51° (0.6 mmol); n_D^{25} 1.4915. IR. (neat): 1648 cm^{-1} (C=C); NMR. ($CDCl_3$): 5.68 (*d*, 1H, $J = 1{,}0$ Hz, vinyl), 4,06 (*d*, 1H, $J = 1.5$ Hz, C(Cl)H), 1.53 (*dd*, 2H, $J = 14.3$ Hz, CH_2), 1.12 (*s*, 12H, CH_3).

$C_{10}H_{16}Cl_{22}$ Calc. C 57.98 H 7.79 Found C 58.12 H 7.74

No reaction occurred on treating the olefin with dibromocarbene generated by the interaction of bromoform and potassium *t*-butoxide [20].

exo-*3,4-Dichloro*-endo-cis-*6,7-dimethoxycarbonylbicyclo[3.2.1]oct-2-ene* (**13**). *endo-cis*-5,6-Dimethoxycarbonylnorborn-2-ene [21] (2.65 g, 12.6 mmol) was added in a single portion to 25 ml of benzene containing phenyl(trichloromethyl)mercury (5.26 g, 13.3 mmol) and the mixture was heated for 68 h. On work-up, the precipitated phenylmercuric chloride (3.10 g, 9.89 mmol) was separated together with 4.62 g of an oil. Addition of pentane to the latter induced crystallization. The solid (1.08 g) was filtered and recrystallized from ether to give 0.98 g (27% based on olefin) of small, white crystals, m.p. 125–127°. – The IR. (KBr) showed a strong, broad, poorly resolved doublet centred at 1725 cm^{-1} (ester C=O), 1639 cm^{-1} (C=C). NMR. ($CDCl_3$): *anti*-8-methylene proton centred at 1.60 (*d*, 1,H, $^2J = 10.7$ Hz), *syn*-8-methylene proton at 2.28 (*d*, 1H, $J = 10.7$ Hz), a broad bridgehead and protons α to methoxycarbonyl groups appeared at 3.18

(4H), methyl protons centred at 3.66 (*s*, 6H), allylic proton at 4.4 (*dd*, 1H, $^4J = 0.5$ Hz, $^3J = 2.4$ Hz) and a vinyl proton at 6.37 ppm (*dd*, 1H, $^4J = 1.0$, $^3J = 6.9$ Hz).

$C_{12}H_{14}Cl_2O_4$ Calc. C 49.16 H 4.81 Cl 24.19% Found C 49.02 H 4.72 Cl 24.13%

exo-*2,3-Dichlorobicyclo[3.2.1]oct-3-en-6-one ethylene acetal* (**15**) and exo-*3,4-dichlorobicyclo[3.2.1]-oct-2-en-6-one ethylene acetal* (**16**). Dehydronorcamphor ethylene acetal [22] (6.91 g, 45.4 mmol) and phenyl(trichloromethyl)mercury (10.0 g, 25.2 mmol) in benzene (35 ml) were heated for 24 h. After cooling, phenylmercuric chloride (5.78 g, 73%) was separated by filtration and volatile constituents evaporated under reduced pressure. The residual yellow oil (4.53 g, 77% yield based on mercurial) was examined by NMR. Two doublets appeared at 4.20 and 4.48 ppm, and two other doublets at 6.00 and 6.17 ppm corresponding to allylic and vinyl protons respectively. The ratio of the areas of the allylic signals was 1:1.

The two isomers (**15** and **16**) were separable in principle by thick-layer chromatography (using ether/pentane 3:7 as eluant, Rf 0.52 and 0.47). However, on extraction of the two bands with ether, it was found after evaporation that they gave identical NMR. spectra: The isomer **16**, responsible for the signals at 4.20 and 6.00 ppm, had disappeared to give solely the more stable isomer **15**. Recrystallization from pentane gave colourless crystals m.p. 68.5–70°.

$C_{10}H_{12}Cl_2O_2$ Calc. C 51.08 H 5.15 Cl 30.16% Found C 50.99 H 4.98 Cl 30.04%

The NMR. spectrum showed five kinds of protons: a methylene region centred at 1.93 (4H), bridgehead at 2.33 (2H), allylic at 4.53 (1H), and vinylic at 6.21 ppm (1H).

exo-*2,3-Dibromobicyclo[3.2.1]oct-3-en-6-one ethylene acetal* (**17**) and exo-*3,4-dibromobicyclo-[3.2.1]oct-2-en-6-one ethylene acetal* (**18**). Bromoform (114 g, 0.44 mol) was added dropwise (1.5 h) to a stirred mixture of potassium *t*-butoxide, (0.46 mol) and dehydronorcamphor ethylene acetal (10.0 g, 0.066 mol) in pentane (220 ml). The layers were separated, the aqueous layer extracted with petroleum ether (b.p. 30–80°, 4 × 100 ml) and the combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated at reduced pressure. The resultant yellow oil (containing bromoform, unreacted acetal and product) was examined by NMR. spectroscopy. Two isomers were present as indicated by two sets of allylic signals at 4.38 and 4.79 ppm, corresponding to **17** and **18** in a ratio of 52:48 (by integration). – Excess bromoform and acetal were removed by vacuum distillation and the crude product was kept for an additional hour at 98° and 1 Torr to ensure removal of all volatile material. The resultant oil (6.2 g, 29% based on acetal) was again checked by NMR. when the signal at 4.38 ppm was found to have increase in height, whereas the 4.79 ppm signal had diminished by an equivalent amount. Integration showed that the ratio of the two signals was now 63:37.

Separation of the two isomers was effected by column chromatography over florisil[7]) which had been activated by heating *in vacuo* overnight at 150°. On elution with ether/pentane 2:98 the first isomer to be eluted was isomer **18** (as verified by NMR.), followed by a mixture of **18** and **17** and then by pure **17**. Recrystallisation from pentane afforded the pure isomers: **18** had m.p. 101.5–103.5° and isomer **17** had m.p. 79–81°. Both isomers were white and crystalline.

$C_{10}H_{12}Br_2O_2$ Calc. C 37.06 H 3.73 Br 49.33% **17** Found C 37.04 H 3.72 Br 48.75%
18 Found ,, 37.15 ,, 3.65 ,, 49.01%

The above column chromatography procedure using florisil was only successful on two occasions. With a new batch of florisil, separation could not be achieved on the column. Therefore the following procedure was instituted. The crude oil was taken up in pentane and passed through a column containing a top layer of sea-sand and a lower layer of florisil. In this way most of the polymeric material was removed. Subsequent separation was by thin-layer chromatography (tlc), employing ether-pentane 3:7 as eluent. Rf values on analytical tlc plates are 0.39 for isomer **17** and 0.55 for isomer **18**. Rf values determined from preparative thick-layer plates are: isomer **17** 0.49; isomer **18** 0.62.

IR. spectra (KBr) showed maxima at 1618 (isomer **18**) and 1623 cm^{-1} (isomer **19**). For both isomers NMR. showed five kinds of protons: methylene, bridgehead, dioxolane, allylic and vinylic. The chemical shifts are as follows: isomer **18**, methylene at 2.09 (4H), bridgehead 2.43 and 2.80

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[7]) We thank Dr. *E. S. Rothman* of the U.S. Dept. of Agriculture, Eastern Utilization Laboratory, Mermaid Lane, Philadelphia, for a generous gift of this material.

(1 H each), dioxolane at 3.90 (4H), allylic at 4.57 (1H), and vinyl at 6.27 ppm (1 H). Isomer **19**, methylene at 2.08 (4H), bridgehead at 2.73 (2H), dioxolane at 3.96 (4H), allylic at 4.85 (1H), and vinyl at 6.43 ppm (1 H).

The identity of each isomer was confirmed by analysis of their NMR. spectrum using proton decoupling [11b].

exo-2-Phenyl-3,4-dichlorobicyclo[3.2.1]oct-2-ene (**24**). – a) To a stirred mixture of 2-phenylnorbornene (10.1 g, 0.0593 mol) and *t*-butoxide (0.535 mol) in pentane (225 ml) in an ice-salt bath at 0 to –10°, chloroform (52.5 g, 0.44 mol) was added dropwise over a one hour period. The cold bath was removed and the stirred mixture was allowed to warm to room temperature. The mixture was poured into ice-water (200 ml), extracted with pentane (3 × 50 ml), the extracted solution was dried over anhydrous magnesium sulfate, filtered and the solvent removed on a steam bath. Vacuum distillation yielded, after removal of excess reagents, 8.2 g of liquid (55% based on olefin), b.p. 148–150°/0.25 Torr, which solidified on being scratched. Crystallization from pentane gave white platelets, m.p. 60–63°. IR. (nujol mull): 1637 cm^{-1} (C=C). The NMR. spectrum ($CDCl_3$) revealed only one *exo* isomer and showed five kinds of protons: a broad methylene region at 1.65 ppm (5H); *syn*-8-methylene at 2.32 ppm (1 H); bridgehead at 2.83 ppm (2H); allylic at 4.40 ppm (1H); and a sharp spike due to phenyl at 7.30 ppm (5H). UV. (cyclohexane) showed λ_{max} at 246 nm ($\varepsilon = 9670$). Sublimation (50°/0.2 Torr) gave an analytical sample.

$C_{14}H_{14}Cl_2$ Calc. C 66.42 H 5.57 Cl 28.01% Found C 66.59 H 5.78 Cl 27.64%

b) The reaction of 2-phenylnorbornene (2.02 g, 11.9 mmol), phenyl(trichloromethyl)mercury (5.24 g, 13.3 mmol) in benzene (25 ml) for 48 h gave, after crystallization from pentane, 2.76 g (92% yield based on olefin) of white crystals, m.p. 60–62°.

c) When the reaction described in a) above was worked up so that the temperature was kept below room temperature (25° for 50 min) the NMR. spectrum of the resultant oil revealed the presence of two *exo* isomers (**24** and **25**). The second isomer showed a doublet of doublets ($^3J = 8.0$ and $^4J = 1.0$ Hz) at 6.48 ppm, clearly due to a vinyl proton (2-phenylnorborn-2-ene shows a doublet of doublets ($^3J = 3.0$ and $^4J = 1.0$ Hz) at 6.20 ppm). Integration showed that the ratio of the stable to the unstable isomer was 3.3 and 2.7 to 1 (from two experiments).

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85. Catalytic Deoxygenation of Organic Compounds by Carbon Monoxide:

III[1]). The Reaction under Pressure of Aromatic Nitro Compounds in the Presence of *o*-Phthalaldehyde

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(14. I. 72)

Summary. The reaction of *o*-phthalaldehyde with several aromatic nitro compounds in the presence of carbon monoxide and catalytic quantities of hexarhodium-hexadecacarbonyl eventuated in the formation of the corresponding N-substituted isoindolinone as the major product. A reaction mechanism has been suggested incorporating deoxygenation of the nitro compound by carbon monoxide to a nitrene intermediate and the subsequent interception of the latter by *o*-phthalaldehyde.

Introduction. – Concurrent with the recent rapid growth of the chemistry of metal carbonyls, the application of carbon monoxide in the domain of organic syntheses has likewise gathered momentum. While such industrial processes as hydroformylation and hydrocarboxylation of olefins [2] conspicuously demonstrate the extensive exploitation of carbon monoxide as a carbonylating agent, its application as a reductant for organic compounds is confined to relatively few examples. For such studies, compounds containing the N–O linkage have constituted a fruitful substrate of frequent choice. The deoxygenating process here involved is accompanied by the oxidation of carbon monoxide to carbon dioxide.

The essentially stoichiometric reduction of nitrobenzene to aniline by alkaline solutions of iron carbonyl [3] is one of the earliest reports where deoxygenation by a carbon monoxide ligand is implied. Later [4] [5], iron pentacarbonyl was also found to effect the deoxygenation of amine oxides, azoxybenzenes, and nitrones, while nitro- and nitrosobenzenes were reduced, under the same conditions, to azo and/or amino compounds. The drastic conditions required for the reductive coupling of nitrobenzene to azobenzene by carbon monoxide alone [6] could be obviated by using catalytic quantities of iron pentacarbonyl [7]. Aryl isocyanates [8], or products derived therefrom [9] [10], were synthesized by the interaction between nitrobenzenes and carbon monoxide using selective catalyst systems. In the presence of a mixture

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[1]) For Part II, see reference [1].