peaks at 2950 (s), 2870 (s), 2870 (s), 1425, 1375, 1218 (w), 1190 (w), 1118, 1040 (w), 1015 (w), 948 (w), 909, and 750 cm^{-1}.

1,1-Dichloro-2-(chloromethyl)cyclopropane (**2c**) was prepared in 25.1% overall yield from allyl chloride (freshly distilled, dry) *via* a method similar to the preparation of compound **2a**. The crude reaction mixture was washed and dried ($MgSO_4$) and the solvent removed. 1,1-Dichloro-2-(chloromethyl)cyclopropane was separated from the other components by preparative vpc (Aerograph Autoprep Model A-700, 15% Carbowax 20M). The observed boiling point was 162° [lit.[15] bp 56° (17 mm)].

The nmr spectrum shows a perturbed doublet with the smaller peak at τ 6.3, the larger at 6.42 (2 H, $J = 8$ Hz, Cl-CH_2) and also a multiplet from 7.6 to 8.8 (3 H, cyclopropyl). The ir spectrum (CS_2) contains peaks at 2950 (w), 1425, 1370, 1265, 1220 and 1201 (doublet), 1113 and 1096 (doublet), 1043, 1025, 965 (w), 948, 918, 871 (w), 809 (w), 775 (s, sh), 755 (s), and 714 cm^{-1} (s).

Methyl 2,2-dichlorocyclopropylcarbinyl ether (**2b**) was prepared from methyl allyl ether in 7.45% yield by the procedure described for compound **2a**. The crude reaction mixture was washed and the solvent removed. The residue was stirred and kept at reflux for 3 hr with sodium hydroxide solution (a volume excess, 20% by weight). The basic solution was extracted with pentane; the pentane layer was washed and dried ($MgSO_4$); and the pentane was removed. The residual liquid was distilled to give colorless product, bp 155°, 73° (37 mm).

The nmr spectrum displays a doublet centered at τ 6.5 (2 H, $J = 6$ Hz, OCH_2CH), a singlet at 6.66 (3 H, CH_3O–), and a multiplet from 7.82 to 8.98 (3 H, cyclopropyl). The ir spectrum contains peaks at 2990 (w), 2920, 2880, 2820, 1430, 1400, 1220 (w), 1195, 1142, 1100 (s), 1052 (w), 1032 (w), 1009 (w), 985 (w), 915 (w), and 747 cm^{-1} (s).

Anal. Calcd for $C_5H_8OCl_2$: C, 38.74; H, 5.20. Found: C, 38.61; H, 4.96.

4,4-Dichloro-3-methoxy-1-butene is apparently formed as a minor (*ca.* 5%) product resulting from dichlorocarbene insertion into an allylic carbon–hydrogen bond during the formation of methyl 2,2-dichlorocyclopropylcarbinyl ether. A few drops of this insertion product were obtained by preparative vpc (F & M Model 700, 15% QF-1). The nmr spectrum shows a doublet centered at τ 4.4 ($J = 5$ Hz, –CCl_2H) superimposed upon a multiplet absorbing from 3.82 to 4.9 (total area 4 H) which resembles an ABC splitting pattern (–CH=CH_2). Additionally the spectrum contains a poorly resolved triplet at 6.16 (1 H, $J = 6$ Hz, –OCHCH=CH_2) and a sharp singlet at 6.6 (3 H, CH_3O–). The ir spectrum (CS_2) has peaks at 1180 (w), 1100, 980 (w), and 932 in common with those of methyl allyl ether, as well as a major peak at 778 cm^{-1} (CCl_2), some 35 cm^{-1} removed from the corresponding peak in the spectrum of the expected carbene addition product **2b**.

1,1-Dichloro-2-(2-phenylethyl)cyclopropane (**2d**), bp 69° (0.15 mm) [lit.[16] bp 96° (4 mm)], was obtained in 10% yield from 4-phenyl-1-butene (freshly distilled, Aldrich) *via* the process described for compound **2a**. The nmr spectrum contains a singlet at τ 2.82 (5 H, aryl), a triplet centered at 7.2 (2 H, $J = 8$ Hz, benzyl), and a multiplet from 8.0 to 9.1 (5 H, CH_2–cyclopropyl). The ir spectrum coincides with that reported.[16]

Phenyl 2,2-dichlorocyclopropylcarbinyl ether (**2e**) was synthesized from allyl phenyl ether in 12.1% yield according to the procedure described previously, bp 79° (0.28 mm). The nmr spectrum consisted of a complex multiplet from τ 2.55 to 3.3 (5 H, aryl), a doublet centered at 5.97 (2 H, $J = 6$ Hz, –OCH_2–), and a multiplet from 7.66 to 8.89 (3 H, cyclopropyl). The ir spectrum (CS_2) shows peaks at 3032 (w), 2934 (w), 2875 (w), 1592 (s), 1398, 1330 (w), 1298, 1237 (s), 1218 (s), 1168, 1112, 1077, 1041 (s), 884 (w), 800, 748 (s), and 687 cm^{-1} (s).

Anal. Calcd for $C_{10}H_{10}OCl_2$: C, 55.32; H, 4.64. Found: C, 55.59; H, 4.81.

Competitive Addition of Dichlorocarbene to Olefins.—To a magnetically stirred mixture of pentane (30 ml, dry, alkene free) and sodium methoxide (1.62 g, 0.03 mol, commercial) cooled in an ice bath were added, by syringe through a rubber septum, equimolar quantities (0.125 mol) of each olefin. The syringe cap was quickly replaced by a pressure compensated addition funnel containing ethyl trichloroacetate (4.78 g, 0.025 mol) and the system was held tightly closed by rubber bands. The ester was added dropwise (*ca.* 1.5 hr) and the reaction mixture left stirring an additional 1.5 hr. The reaction mixture was gravity filtered, the residual sodium methoxide rinsed with pentane (two 15-ml portions), and this washing combined with the filtrate. The solution was washed (four 30-ml portions) and dried ($MgSO_4$) and the solvent removed under vacuum at room temperature. Vpc analysis of the distillate indicated complete absence of any dichlorocyclopropyl product.

For olefins with an aryl substituent the reaction mixture was filtered, washed twice (two 20-ml portions), and dried ($MgSO_4$). The pentane was removed and the product mixture partially distilled under vacuum (50-cm wire spiral column). Methyl ethyl carbonate distilled from the mixture at room temperature (0.1 mm). Most of the excess olefin likewise distilled at a bath temperature of 75° (0.1 mm). The head temperature was not permitted to rise above 30° (0.1 mm). Vpc analysis of the distillate indicated complete absence of any dichlorocyclopropyl product.

Weighed portions (*ca.* 27 μl) of the product mixture were thoroughly mixed with weighed amounts (*ca.* 3 μl) of internal standard in small screw cap vials sealed with a square of polyethylene sheet. 7,7-Dichloronorcarane was used as the internal standard for all the olefin competitions except that of phenyl allyl ether *vs.* 4-phenyl-1-butene for which 1,1-dichloro-2-benzylcyclopropane was used. Several aliquots (*ca.* 1 μl) were withdrawn from each of the vials by a syringe (Hamilton, 10 μl) and injected directly into the vpc. Each column used was calibrated by injecting solutions containing internal standard in known and varied quantities of the carbene adduct products in order to provide an experimental correlation of peak area ratios with compound mole fractions. The observed peak area ratios were corrected to actual mole fractions by reference to this sensitivity calibration curve.

Registry No.—**2a**, 3722-08-5; **2b**, 33707-14-1; **2c**, 3722-05-2; **2d**, 20849-80-3; **2e**, 33666-40-9; dichlorocarbene, 1605-72-7; 4,4-dichloro-3-methoxy-1-butene, 33712-31-1.

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[15] W. M. Wagner, H. Kloosterziel, and S. Van der Ven, *Recl. Trav. Chim. Pays-Bas*, **80**, 740 (1961).

[16] V. S. Aksenov, I. A. Dyakonov, and R. R. Ksotokov, *Zh. Org. Khim.*, **4**, 1680 (1968).

Palladium-Catalyzed Reactions of Allene with Diolefins

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Several examples of transition metal catalyzed oligomerizations of allenes have been reported.[1] However, such reactions of allenes with other olefins are relatively rare.[2] In this regard we wish to report two novel examples of catalyzed reactions of allene with diolefins.

When a mixture of allene, butadiene, and a catalytic amount of bis(triphenylphosphine)(maleic anhydride)palladium[3] was heated to 120°, a 39% yield of a 3:1 mixture of *trans*- and *cis*-2-methyl-3-methylene-1,5,7-octatriene (**1**), respectively, was obtained. Hydrogenation of **1** over 5% Pd on charcoal yielded 2,3-dimethyloctane.

During the preparation of **1**, concurrent dimerizations of the butadiene to a mixture of 4-vinylcyclo-

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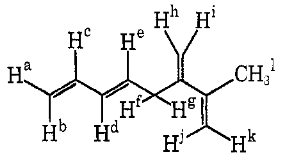
[1] (a) F. N. Jones and R. V. Lindsey, Jr., *J. Org. Chem.*, **33**, 3838 (1968); (b) R. E. Benson and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **81**, 4247 (1959); (c) G. Shier, *J. Organometal. Chem.*, **10**, 15 (1967); (d) E. L. Jenner and R. V. Lindsey, Jr., U. S. Patent 2,876,254 (1959); (e) S. Otsuka, *et al.*, *Chem. Commun.*, 191 (1969); (f) T. Susuki and J. Tsuji, *Bull. Chem. Soc. Jap.*, **41**, 1954 (1968).

[2] A. Greco, A. Carbonaro, and G. Dall'Asta, *Tetrahedron Lett.*, **No. 57**, 5009 (1969); *J. Org. Chem.*, **35**, 271 (1969).

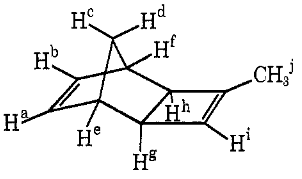
[3] S. Takahashi, T. Sibano, and N. Hagihara, *Bull. Chem. Soc. Jap.*, **41**, 454 (1968).

hexene and 1,3,7-octatriene[4] were also observed. These competing reactions consumed almost all the excess butadiene. When isoprene or 1,3-pentadiene was used in this reaction, only the corresponding dimers could be isolated.



1

A similar study of the reaction of allene with bicyclo[2.2.1]hepta-2,5-diene was made. Under conditions similar to those applied to butadiene, a *ca.* 25% yield of *exo*-3-methyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**2**) was obtained.



2

The preparation appeared to yield a single isomer and differentiation between the two possible ring junction isomers was made possible by an analysis of the nmr spectrum. Spin decoupling of the pairs H^a, H^e and H^b, H^f verified the assignments of H^e and H^f. Computer simulation[5] of the region containing the H^{e-h} protons gave a closest fit with $J_{g,h} \cong 4$; $J_{e,g} = J_{f,h} \leqslant 2$ and $J_{g,i} \cong 0.5$ Hz. The second coupling constant, in the cases of *endo*- and *exo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene, has been reported[6] to be 3.5 and $\leqslant 1$ Hz, respectively. Also, the proton chemical shifts reported for the latter isomer closely resembled comparable shifts found with **2**. Hence, we have assigned the exo configuration to the reaction product. Catalytic hydrogenation of **2** gave a single, saturated hydrocarbon following an uptake of 2.04 equiv of hydrogen.

Substantial amounts of an impure, higher boiling material [bp 53–54° (0.12 mm)] were also isolated from the reaction. Although elemental analysis suggested a 2:1 allene–bicyclo[2.2.1]hepta-2,5-diene adduct, a complete structural assignment was thwarted by the lack of sufficiently pure material.

It may be noted that **2** could conceivably arise from a cycloaddition of methylacetylene, formed *in situ* from allene, to bicyclo[2.2.1]hepta-2,5-diene.[7] However, no evidence for the formation of **2** was found upon substitution of methylacetylene for allene in the reaction.

Experimental Section

Boiling points are uncorrected. The relative proton intensities, determined by nmr, may be assumed to be within ±3% where not noted otherwise.

trans- **and** *cis*-**2-Methyl-3-methylene-1,5,7-octatriene** (**1**).—A solution of bis(triphenylphosphine)(maleic anhydride)palladium (1.47 g, 0.002 mol) in 25 ml of tetrahydrofuran was charged to a 400-cc stainless steel lined autoclave. To this solution was added allene (20 g, 0.50 mol) and butadiene (162 g, 3.0 mol). The mixture was heated to 120° for 5 hr with stirring. The resulting liquid was directly distilled giving a fraction of bp 45–100° (16 mm). Redistillation of this crude fraction through a 24-in. spinning-band column gave **1** (14.8 g, >90% purity, 39% yield). A pure sample was prepared by glc collection: bp 67.5–69° (16 mm); ir (neat) 1595, 1630, and 1650 cm^{-1} (C═C); uv (ethanol) λ_{max} 225 mμ (ϵ 35,600); nmr (220 MHz, CCl_4) δ 1.88 (H^l, s), 2.97 (H^f, H^g, d, J = 7 Hz, trans), 3.08 (H^f, H^g, d, J = 7 Hz, cis), 4.82–5.20 (H^a, H^b, H^h, H^i, H^j, H^k, m), 5.40–6.65 (H^c, H^d, H^e, m, $J_{c,d,cis}$ = 9 Hz, $J_{c,d,trans}$ = 14 Hz).

Anal. Calcd for $C_{10}H_{14}$: C, 89.50; H, 10.51. Found: C, 89.60; H, 10.60.

Hydrogenation of *trans*- **and** *cis*-**2-Methyl-3-methylene-1,5,7-octatriene** (**1**).—A sample of **1** (1.34 g, 0.0097 mol, >97% purity) and 5% palladium on charcoal (0.1 g) were mixed with 10 ml of absolute ethanol and exposed to hydrogen with stirring. The mixture absorbed 944 ml of hydrogen. The mixture was filtered to remove catalyst and the solvent was evaporated from the filtrate to give 1.2 g of colorless liquid. Glc purification of this material gave a liquid which had an infrared spectrum and a glc retention time identical with that of an authentic sample of 2,3-dimethyloctane.

exo-**3-Methyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene** (**2**).—A solution of bicyclo[2.2.1]hepta-2,5-diene (660 ml, 6.57 mol) and bis(triphenylphosphine)(maleic anhydride)palladium (8.75 g, 0.01 mol) was charged to a 1000-ml stainless steel lined autoclave. The system was then charged with allene (57.5 g, 1.40 mol) and heated to 145° for 5 hr. The resulting solution was distilled through a 24-in. spinning-band column, giving **2** (45.6 g, 25% yield): bp 49–50.5° (16 mm); ir (neat) 1630, 1590, and 1561 cm^{-1} (C═C); nmr (220 MHz, CCl_4) δ 1.31 (H^c, H^d, AB pattern, $J_{c,d}$ = 8 Hz), 1.67 (H^j, s), 2.18 and 2.15 (H^g and H^h, s), 2.32 (H^e, H^f, m), 5.85 (H^i, s), 6.00 (H^a, H^b, s).

Anal. Calcd for $C_{10}H_{12}$: C, 90.8; H, 9.20. Found: C, 90.67; H, 9.26.

Hydrogenation of *exo*-**3-Methyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene** (**2**).—A mixture of **2** (0.661 g, 0.005 mol) and 0.05 g of 5% palladium on charcoal in 5 ml of ethanol was exposed to 1 atm of hydrogen with stirring. A total of 252.2 ml of hydrogen was absorbed. Filtration and evaporation of the ethanol gave an oil which appeared to be a single compound by glc analysis (retention time 17 min, on 20% silicone gum nitrile, 4 ft × 1/4 in., 78°). Glc collection afforded a pure sample: nmr (60 MHz, CCl_4) δ 1.6–3.3 (m, 7 protons), 0.8–1.6 (m, 9 protons).

Anal. Calcd for $C_{10}H_{16}$: C, 88.25; H, 11.85. Found: C, 88.64; H, 12.22.

Registry No.—*trans*-**1,** 33885-13-1; *cis*-**1,** 33885-14-2; **2,** 33885-15-3; hydrogenation product of **2,** 33885-16-4; palladium, 7440-05-3; allene, 463-49-0; bicyclo[2.2.1]-hepta-2,5-diene, 121-46-0; butadiene, 106-99-0.

Acknowledgment.—I thank Dr. Raymond C. Ferguson for the nmr simulation studies.

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[5] A five-spin approximation using a modified LAOCOON-type program developed by C. W. Haigh, University College, Swansea, Wales.

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Photochemical Conversion of Primary and Secondary Amines to Carbonyl Compounds

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The occurrence of the Norrish type II elimination as the major process[1] in the photolysis of α-phenacylamines prompted an investigation of the utility of this reaction in effecting the conversion of amines to car-

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