resulting solid was extracted with 225 ml. of boiling water in six portions. Chilling in ice and filtering left a brown crystalline solid. This was extracted with boiling 90–100° ligroin, decanting from the insoluble dark oil. Cooling and filtering yielded 0.8 g. of white crystals, m.p. 110.5–111.5°. The reported melting point for *m*-toluic acid is 111–112°. This product was converted,[14] *via* the acid chloride, to the amide, m.p. 93–94° (lit.[14] 94°).

3-Methyl-2-nitro-1,2,3,6-tetrahydrobenzotrichloride (IIIc) *and/or 6-methyl-2-nitro-1,2,3,6-tetrahydrobenzotrichloride* (IVc). A mixture of 15 g. (0.22 mol.) of pentadiene-1,3 and 39 g. (0.22 mol.) of I was allowed to stand in a stoppered flask for 14 days. Fractionation afforded 26 g. (65%) of pale yellow liquid, b.p. 110–111.5°/1 mm., d^{20}_{20} 1.3626, n^{20}_{D} 1.5232.

Anal. Calcd. for $C_8H_{10}Cl_3NO_2$: N, 5.42; Cl, 41.14. Found: N, 5.32; Cl, 41.34.

4,5-Dimethyl-2-nitro-1,2,3,6-tetrahydrobenzotrichloride (IIId). A mixture of 18 g. (0.22 mol.) of 2,3-dimethylbutadiene-1,3 and 39 g. (0.22 mol.) of I was allowed to stand in a stoppered flask at room temperature for 14 days. Fractionation gave 41 g. (69%) of pale yellow liquid, b.p. 118–119°/1 mm., d^{20}_{20} 1.4225, n^{20}_{D} 1.5253.

Anal. Calcd. for $C_9H_{12}Cl_3NO_2$: N, 5.14; Cl, 39.05. Found: N, 5.17; Cl, 39.21.

3,6-Endomethylene-2-nitro-1,2,3,6-tetrahydrobenzotrichloride (IIIe). To 78 g. (0.44 mol.) of cold I was added 31 g. (0.44 mol.) of cold freshly-prepared cyclopentadiene in 3-ml. portions with swirling and cooling in an ice bath so that the temperature was maintained at 35–50°. When the mixture was no longer exothermic, the container was stoppered and allowed to stand at room temperature. Fractionation yielded 98 g. (87.5%) of pale yellow liquid, b.p. 113.5–115°/1 mm., d^{20}_{20} 1.4831, n^{20}_{D} 1.5334.

Anal. Calcd. for $C_8H_8Cl_3NO_2$: N, 5.50; Cl, 41.45. Found: N, 5.40; Cl, 41.04.

DEPARTMENT OF CHEMISTRY
DEPAUW UNIVERSITY
GREENCASTLE, INDIANA

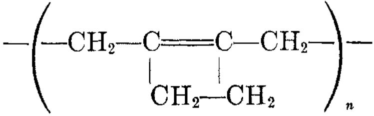
Reactions of Allene. I. Diels-Alder Adducts

H. PLEDGER, JR.

Received September 2, 1959

The Diels-Alder reaction between simple olefins and dienes is known[1] The same reaction between dienes and activated double bonds has received much attention.[2] However, the Diels-Alder reaction between dienes and compounds possessing cumulated double bonds has received very limited study.[3]

In this laboratory the Diels-Alder reactions between allene, which contains cumulated double bonds, and several conjugated dienes were studied. These Diels-Alder adducts were sought as intermediates for other studies now in progress in this laboratory. We wish to report at this time some results on cyclopentadiene and hexachlorocyclopentadiene.

Cyclopentadiene reacted with allene yielding four isolable products (II and III were not previously known): 5-methylenebicyclo[2.2.1]-2-heptene (I);[4] 1,2,3,4,4a,5,8,8a-octahydro-2-methylene-1,4,5,8-dimethanonaphthalene (II); 1,2,3,4,4a,5,5a,6,9,9a,10,10a-dodecahydro-2-methylene-1,4,5,10,6,9-trimethanoanthracene (III); and a polymer (IV). The structures of the cuts corresponding to compounds II and III have not been proved but are probably as named. The characterization of IV has not been made, but collected data does not refute Lebedev and Merezhkovskii's[5] presumption that the polymerization of allene in metallic vessels yields a polymer of the structure  . Average molecular weight coupled with percent unsaturation would indicate that the average value of n is 11.5 in the particular sample of polymer reported here. Three different elemental analyses gave total carbon and hydrogen of about 95–97%. Mass spectroscopy analyses showed water present in the polymer. The infrared absorption at 11.45 μ is indicative of terminal unsaturation at the polymer chain end. While higher adducts such as four or five diene molecules to one of allene may have been formed in this reaction, they were in such low concentration that they were not isolated by distillation of the reaction mixture.

Hexachlorocyclopentadiene (V) reacted with allene yielding only one isolable product which was previously unknown: 1,2,3,4,7,7-hexachloro-5-methylenebicyclo [2.2.1]-2-heptene (VI). As would be expected, V reacted with allene at a lower temperature than cyclopentadiene and the yield of VI was higher than for I. No higher molecular weight adducts or polymer was isolated or indicated.

EXPERIMENTAL[6]

Allene. Fractional distillation of Dow methylacetylene-propadiene mixture (30% allene and 70% methylacetylene) at atmospheric pressure through a 60-inch glass, helices packed column yielded allene, b.p. −34.8° to −33.9°, having 98+% purity which was stored in steel cylinders until used.

Cyclopentadiene was prepared as 99+% pure material, b.p. 41–43°, by pyrolysis of Enjay dicyclopentadiene. The

---

[1] L. M. Joshel and L. W. Butz, *J. Am. Chem. Soc.*, **63**, 3350 (1941).

[2] H. L. Holmes, "Organic Reactions," John Wiley and Sons, Inc., New York, 1948, Vol. IV, 60.

[3] von O. Diels and W. Friedrichsen, *Ann.*, **513**, 145 (1934); O. Wickterle and J. Rocek, *Chem. Listy*, **47**, 1768 (1953); *Coll. Czechoslov. Chem. Comm.*, **19**, 282 (1954).

[4] This compound was made by dehydrobromination of the Diels-Alder adduct between allyl bromide and cyclopentadiene and was presented by P. von R. Schleyer and R. E. O'Connor before the Division Organic Chemistry, American Chemical Society, Chicago, Ill., September, 1958, Paper No. 66.

[5] S. V. Lebedev and B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 1249.

[6] Boiling points are uncorrected. Elemental analyses were carried out by Galbraith Laboratory, Knoxville, Tennessee. Yields are calculated on charged reactant as noted.

material was stored at −20° for periods not longer than one month before use.

Hexachlorocyclopentadiene was received as a sample from Hooker Electrochemical Company (C-56) and was used as such.

5-Methylenebicyclo[2.2.1]-2-heptene (I). A 2960 ml. stainless steel autoclave was cooled to −78° while purging with dry nitrogen and was then charged with 330 g. (5.0 mol.) cyclopentadiene and 200 g. (5.0 mol.) allene (determined by passage through a calibrated flow meter). The autoclave was capped, placed in a rocker, and heated to 200° over a 1.25-hr. period. At 200° the autogeneous pressure reached 620 p.s.i. and began dropping. During the next 5 hr. the temperature was maintained between 200 and 230° with a subsequent drop in pressure to 280 p.s.i. (210°). When the autoclave had cooled to room temperature, it was vented (while warming) through a trap at −78° to collect 55.4 g. of unreacted allene. The straw yellow liquid (479.2 g.) in the autoclave was distilled rapidly through a 3-inch tube containing a side arm at a total take off yielding 200.9 g. liquid, b.p. 26–100°/160 mm. This crude product was redistilled through a 10-inch glass spiral column at atmospheric pressure yielding 186 g. (48.6% yield based on allene) I, b.p. 115–120°, n_D^{25} 1.4834–1.4840. A heart cut, b.p. 73.0°/172 mm., n_D^{25} 1.4838, n_D^{20} 1.4860, d_4^{20} 0.889, from the redistillation of combined I from several runs was used for analyses. The infrared spectrum showed principal bands at 5.72, 6.03, 6.38, 11.44, 13.8, and 14.6 μ. Mass spectroscopy analyses support the structure of I.

Anal. Calcd. for C_8H_{10}: C, 90.6; H, 9.4. Found: C, 90.5; H, 9.5.

Mol. refr. calcd.: 33.8. Found 34.1. Mol. wt. calcd.: 106.2. Found (ebulioscopic): 114.

A sample of I, b.p. 73.0/160 mm., absorbed 4 equivalents of hydrogen in 4 hr. at 175–185° and 1500 p.s.i. over Harshaw 0104 Ni/Kieselguhr catalyst. Distillation gave a 95% yield of 2-methylbicyclo[2.2.1]heptane,[7] b.p. 124.5–125.0°, n_D^{25} 1.4516, n_D^{20} 1.4541.

1,2,3,4,4a,5,8,8a-Octahydro-2-methylene-1,4,5,8-dimethanonaphthalene (II). The residues from the rapid distillation and from the redistillation above were combined and distilled through a 10-inch glass spiral column yielding 74.8 g. (12.1% yield based on allene) II, b.p. 92–98°/7.0 mm., n_D^{25} 1.5312–1.5330, d_4^{20} 1.020. A heart cut, b.p. 92.0°/6 mm., n_D^{25} 1.5319, n_D^{20} 1.5338, d_4^{20} 1.012, from redistillation of combined II from several runs was used for analyses. The infrared spectrum showed principal bands at 5.72, 6.03, 6.38, 11.44, 13.2, and 13.6 μ.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.6; H, 9.3. Found: C, 90.10; H, 9.88.

Mol. refr. calcd.: 52.5. Found: 52.8. Mol. wt. calcd.: 172. Found: 170.

1,2,3,4,4a,5,5a,6,9,9a,10,10a-Dodecahydro-2-methylene-1,4,5,10,6,9-trimethanoanthracene (III). Continued distillation of the above residues at reduced pressure yielded 10.9 g. (9.3% yield based on allene) III, b.p. 71–76°/0.07 mm., n_D^{25} 1.5444. A heart cut, b.p. 74.5°/0.07 mm., n_D^{25} 1.5442, n_D^{20} 1.5463, d_4^{20} 1.048, was used for analyses. The infrared spectrum of III showed principal bands at 5.72, 6.03, 6.38, 11.44, 13.29, and 13.4 μ.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.71; H, 9.33. Found: C, 90.0; H, 8.6. Mol. ref. calcd.: 71.6. Found: 71.9. Mol. wt. calcd.: 238.0. Found: 218.

Polymer. The 31.5 g. of residue from the above distillation cooled to a hard glass which was dissolved in 100 ml. boiling benzene. The cooled solution was slowly poured into 3 l. of methanol and the resulting brown precipitate was filtered, mixed with 300 ml. methanol, beaten 1 min. in a Waring blendor, filtered, and air dried 3 days yielding 30 g. (15.0% yield based on allene) of cream colored powder. This polymer softened at 81° and melted at 162–165°.

Anal. Calcd. for $(C_6H_8)_n$: C, 90.0; H, 10.0. Found: C, 86.5; H, 9.2. Mol. wt. calcd. for $n = 11.5$: 920. Found: 903 ± 1%. % Unsatn. calcd. for $(C_6H_8)_{11.5}$: 30. Found (Bromination): 29.

The infrared spectrum of a Nujol mull of this polymer has bands at 6.04, 11.45, and 12.57 μ.

1,2,3,4,7,7-Hexachloro-5-methylenebicyclo[2.2.1]-2-heptene (VI). A 2960 ml. stainless steel autoclave was charged as above with 1173.8 g. (4.3 mol.) hexachlorocyclopentadiene (V) and 208.7 g. (5.2 mol.) allene. After capping and placing in a rocker, the autoclave was heated to 150° while rocking. At 150° the autogeneous pressure reached 245 p.s.i. and remained constant during the next 6 min. while the temperature continued to rise to 176° without external heating. The heat of reaction produced a maximum rise in temperature to 200° while the pressure dropped to 190 p.s.i. over the next 23 min. The temperature then began dropping. Over a 2.25-hr. period the temperature had risen from 150° to a maximum 200° and dropped to 170° while the pressure dropped from 245 p.s.i. to a constant 150 p.s.i. After the autoclave had cooled to room temperature it was vented through a trap (−78°) yielding 7.8 g. allene. Gaseous hydrogen chloride was also liberated during venting. The black liquid (1347.1 g.) remaining in the autoclave was subjected to reduced pressure for 1 hr. to remove absorbed hydrogen chloride. Rapid distillation of the residual liquid through a 4-inch Vigreaux column yielded 1098.7 g. yellow liquid, b.p. 74 (0.5 mm.) −80° (0.08 mm.), and 185 g. black charred residue. Redistillation of the 1098.7 g. of distillate through a 24-inch glass helices packed column yielded 1021.9 g. (76% yield based on hexachlorocyclopentadiene charged) VI, b.p. 72° (0.08 mm.) −85° (0.25 mm.), n_D^{25} 1.5590. A heart cut, b.p. 90°/0.3 mm., n_D^{25} 1.5592, n_D^{20} 1.5611, d_4^{20} 1.605, was used for analyses. Infrared spectrum showed principal bands at 6.02, 6.23, 10.95, 13.5, 13.8, and 15.38 μ.

Anal. Calcd. for $C_7H_4Cl_6$: C, 30.73; H, 1.29; Cl, 68.0. Found: C, 30.44; H, 1.66; Cl, 67.97. Mol. refr. calcd.: 63.0. Found: 63.0. Mol. wt. calcd.: 312.9. Found: 326.

Acknowledgment. We wish to acknowledge the able assistance of Mr. W. D. Beck in carrying out several of the autoclave reactions and Mr. D. H. Wolfe for his help in hydrogenating one of the products.

ORGANIC PROCESS DEVELOPMENT LABORATORY
THE DOW CHEMICAL COMPANY
FREEPORT, TEXAS

---

(7) These properties agree with the values, b.p. 126.9–127.3° and n_D^{20} 1.4540, reported by G. Calingaert, H. Soross, and H. Shapiro, *Ind. Eng. Chem.*, **36**, 1055 (1944).

The Chemistry of β-Bromopropionyl Isocyanate. II. Use in Identification of Alcohols[1]

HARRY W. JOHNSON, JR., HENRY A. KREYSSLER, AND HOWARD L. NEEDLES

Received August 24, 1959

The reaction of β-bromopropionyl isocyanate (I) with alcohols has been examined to determine the utility of I in making solid urethanes for the

---

(1) Supported in part by grant G 7850 from the National Science Foundation under the Undergraduate Research Participation Program.