TABLE II

	Anhydride	Lactone	Carbonate	Carbamate	Lactam	Ureide	Imide
5-membered	Succinic 4.22[a]	Butyro 4.09[b]	Ethylene 4.80[c]	Ethylene 5.07[d]	Butyro 3.55[f]	Ethylene 3.94[h]	Succinic 1.47[i]
6-membered	Glutaric 5.31[e]	Valero 4.22[b]	Trimethylene 5.21[c]	Trimethylene 5.10[d]	Valero 3.83[f]	Trimethylene 4.22[h]	Glutaric 2.58[i]
6-membered	Cyclohexane-1,3 4.97[e]	Cyclohexane-1,3 4.37	Cyclohexane-1,3 6.14	Cyclohexane-1,3 5.64[d]	Cyclohexane-1,3 3.73[g]	Cyclohexane-1,3 3.69	Cyclohexane-1,3 2.89[i]
		Cyclohexane-1,4 4.50		Cyclohexane-1,4 5.60[d]	Cyclohexane-1,4 4.24[g]		

[a] G. Rau and N. Ansatanarayanan, *Proc. Indian Acad. Sci.*, **5A**, 185 (1937). [b] Benzene, 25°; R, Huisgen and H. Ott, *Tetrahedron*, **6** 253 (1959). [c] Benzene, 25°; R. P. Steward and E. C. Vierira, *J. Chem. Phys.*, **62,** 127 (1958). [d] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83,** 4596 (1961). [e] C. M. Lee and W. D. Kumler, *J. Org. Chem.*, **27,** 2055 (1962). [f] Benzene, 25°; R. Huisgen and H. Walz, *Chem. Ber.*, **89,** 2616 (1956). [g] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83,** 4593 (1961). [h] Unpublished data; Brian Loader, L. E. Sutton, and W. D. Kumler. [i] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83,** 4586 (1961).

Anhydrides have higher moments than imides and here the same factors will be operating.

Compounds with nitrogen in the ring, namely, the imides, ureides, and lactams occupy the seventh, sixth, and fifth positions.

Five membered:
carbamate > carbonate > anhydride > lactone > ureide > lactam > imide

Six membered:
anhydride > carbonate > carbamate > lactone > ureide > lactam > imide

Six membered, 1,3-bridge:
carbonate > carbamate > anhydride > lactone > lactam > ureide > imide

Lactones are always in the fourth position with anhydrides third or first and carbonate second or first. Thus, in general, the compounds with oxygen in the ring have higher moments than those with nitrogen. The carbamate with both oxygen and nitrogen in the ring might be expected to be intermediate, but actually is near the front of the order being first, second, and third. The reason for this probably is that most of the plus charge in the forms with a separation of charge is confined to the nitrogen which augments the resultant of the ether and the carbonyl dipoles, giving rise to a high moment.

Experimental

All dipole moments were measured in dioxane at 30° and calculations were made using the equation and method of Halverstadt and Kumler.[6]

Acknowledgment.—We wish to thank Dr. H. K. Hall, Jr., of DuPont for providing the compounds.[7] We also wish to thank Mr. M. K. Hrenoff of the Spectrographic Laboratory for all spectrographic measurements. Infrared spectra were run on Perkin-Elmer, Model 21.

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(6) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64,** 2988 (1942).

(7) H. K. Hall, Jr., M. K. Brandt, and R. M. Mason, *ibid.*, **80,** 6412 (1958).

Diels–Alder Adducts of Hexachlorocyclopentadiene with Mono- and Divinyl Substituted Benzenes

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During the course of investigations aimed at developing a relationship between the structure and fire retardancy of halogen-containing compounds in polymeric systems, it was necessary to prepare several examples of the products derived from hexachlorocyclopentadiene by the Diels–Alder reactions with mono- and divinyl derivatives of substituted benzenes. This report describes the preparation of some of these compounds[1,2]; their use in polymeric systems is described in a previous publication.[3]

The Diels–Alder reaction proceeded with considerable ease in each of the cases studied; it was found that the styrene adduct previously described[4,5] is dimorphic. The reaction of commercial divinylbenzene with hexachlorocyclopentadiene gave rise to the two bis-adducts expected from the analysis of the starting isomeric divinylbenzenes. In addition, the commercial material contained isomeric ethylstyrenes, and from the bis-adduct reaction mixtures it was also possible to isolate the mixture of isomeric adducts of the ethylstyrenes. The pure bis-adduct from 1,2-divinylbenzene was prepared to determine the steric requirements imposed by the presence of two "norbornenyl" groups *ortho* to each other on the benzene ring. The yield of product indicates that the formation of the *ortho* product is not severely hindered.

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(1) C. W. Roberts, U. S. Patent 2,952,711 (September 13, 1960).

(2) C. W. Roberts and D. H. Haigh, U. S. Patent 2,952,712 (September 13, 1960).

(3) C. W. Roberts, U. S. Patent 2,976,842 (January 10, 1961).

(4) P. B. Polen, M. Kleiman, and H. G. Fechter, U. S. Patent 2,673,172 (March 23, 1954).

(5) S. H. Herzfeld, R. E. Lidov, and H. Bluestone, U. S. Patent 2,606,910 (August 12, 1952).

TABLE I

DIELS-ALDER ADDUCTS OF HEXACHLOROCYCLOPENTADIENE WITH MONO- AND DIVINYL SUBSTITUTED BENZENES

Substituent R	Starting compound	Yield, %	M.p., °C.	Composition, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
H	Styrene[a]	80	58–59 71.5–72.5[b]	...	...	..	..	...	...
ar-CH_3—	Vinyltoluenes[c]	94	163.5 (0.8[d] mm.)	43.01	43.29	2.58	2.65	54.41	54.25
ar-C_2H_5—	Ethylstyrenes[e]	75	194 (2.2[f] mm.)	44.48	44.62	2.99	2.90	52.53	52.42
4-*t*-C_4H_9—	4-*t*-Butylstyrene[g]	93	103.5–104	47.15	47.10	3.72	3.83	49.13	48.87
2,4-Cl_2—	2,4-Cl_2-styrene[h]	35	127–128	35.02	35.05	1.36	1.46	63.62	63.13
2-($C_7H_3Cl_6$)[i]	1,2-Divinylbenzene[j]	82	121–121.5	35.54	35.64	1.49	1.54	62.96	62.45
3-($C_7H_3Cl_6$)[i]	1,3-Divinylbenzene[k]	90	213–215	35.54	35.35	1.49	1.54	62.96	62.45
4-($C_7H_3Cl_6$)[i]	1,4-Divinylbenzene[k]	85	291	35.54	35.72	1.49	1.51	62.96	62.20

[a] The Dow Chemical Co. [b] Ref. 4, reported m.p. 73.7–74.5°. The compound isolated here was shown to be dimorphic; the compound recrystallized from heptane showed the indicated melting points. After melting at the lower temperature the compound resoldified and melted again at the higher temperature. [c] The Dow Chemical Co., an isomeric mixture containing 35% *meta* and 65% *para* compounds. [d] B.p., $n^{25}D$ 1.5828. [e] Mixed ethylstyrenes contained to 30% in the isomeric mixture of divinylbenzene (see footnote *k*); 30% *meta* and 70% *para* isomer distribution. Yields based upon original available ethylstyrenes. [f] B.p., $n^{25}D$ 1.5750. [g] Prepared by dehydration of 1-(4-*t*-butylphenyl)ethanol; b.p. 65–70° (6 mm.), $n^{25}D$ 1.5245. D. T. Mowry, M. Renoll, and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946), reported b.p. 77–100° (14 mm.), $n^{22}D$ 1.5245. [h] From a mixture of isomeric dichlorostyrenes; yield based upon available 2,4-dichlorostyrene (45% in original mixture). [i] $C_7H_3Cl_6$ represents the substituent (1,4,5,6,7,7-hexachloro-5-norbornen-2-yl). [j] Prepared according to the published procedure, J. O. Halford and B. Weissmann, *J. Org. Chem.*, **17**, 1646 (1952), b.p. 78–79° (16 mm.). [k] The Dow Chemical Co. divinylbenzene; contains 55% divinyl compounds of which 65% is the 1,3-isomer. Yields in the 1,3- and 1,4-divinylbenzene reaction are based on potential available isomer.

Experimental[6]

Most of the preparations were run in a similar fashion; typical syntheses are described for the reaction of commercial divinylbenzene with hexachlorocyclopentadiene and 4-*t*-butylstyrene with hexachlorocyclopentadiene. Where isomeric mixtures of products were obtained or when a pure isomer was produced, infrared analysis was used for analysis of isomeric purity.

Preparation of 5-(4-*t*-Butylphenyl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene.—A solution of 273 g. (1 mole) of hexachlorocyclopentadiene (Hooker) in 500 ml. of *n*-heptane was heated to reflux and 160 g. (1 mole; purity 90–95%) of 4-*t*-butylstyrene was added dropwise during 1 hr. The resulting mixture was heated under reflux for 70 hr. and then chilled. The resulting precipitate was removed by filtration and recrystallized from *n*-hexane to give 333 g. of product, m.p. 103.5–104°. The combined filtrates, on evaporation, gave additional product which, when recrystallized from *n*-hexane, gave 73.5 g., m.p. 103.5–104°, a 93% yield based on 100% 4-*t*-butylstyrene or nearly a quantitative yield based on estimated purity of the 4-*t*-butylstyrene used.

Preparation of 1,4-Bis(1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-hept-2-en-6-yl)benzene and 1,3-Bis(1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-en-6-yl)benzene (Fractional Crystallization and Method I).—A mixture of 900 g. (3.3 moles) of hexachlorocyclopentadiene, 264 g. (55% divinylbenzene, 45% ethylstyrene—70% *para*, 30% *meta;* approximately 3.3 moles of vinyl groups) and 1 l. of anhydrous toluene was allowed to stand at room temperature for 72 hr.; the mixture then was warmed and heated under reflux for 4 hr. and allowed to cool to room temperature and stand overnight. The precipitated solid was removed by filtration and the mother liquor partially evaporated at room temperature under vacuum; additional crops of crystalline products were obtained in this fashion. A total yield of solid product was obtained representing an 85% yield of bis-adducts of the isomeric divinylbenzenes. From this mixture was isolated a pure sample of each of the pure *para* and pure *meta* isomers (see Table I) by fractional crystallizations from mixtures of toluene and heptane; the pure isomers which resulted were recrystallized from 1,2-dibromoethane. The infrared spectra[6] of these pure isomeric compounds established the identity of the *para* and *meta* isomers, "using the well known correlation of the summation bands in the 1650–2000-cm.$^{-1}$ region.[7] The spectra were obtained as Nujol mulls. The isomer, m.p. 291°, showed weak absorption at 1910 cm.$^{-1}$, a very weak absorption at 1790 cm.$^{-1}$, and no other absorption in the 1700–200-cm.$^{-1}$ region; this is very typical of the *para*-disubstituted phenyl structure. The isomer, m.p. 213–215°, showed three weak absorptions at 1940 cm.$^{-1}$, 1870 cm.$^{-1}$, and 1790 cm.$^{-1}$, and no other significant absorption in the 1700–200-cm.$^{-1}$ region; this is very typical of the *meta*-substituted phenyl structure or the 1,3,5-trisubstituted phenyl structure; in these examples the latter structure is ruled out."

The mother liquors from several preparations of the bis-adducts were combined and evaporated to dryness under reduced pressure. The oily residue was distilled under reduced pressure to give the adducts of the isomeric *meta*- and *para*-ethylstyrenes (see Table I).

The experimental procedure for the preparation of the other adducts listed in Table I varied primarily in the duration of reflux. In most instances the best yields of product are obtained after a 24- to 48-hr. reflux time.

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[6] Analytical data kindly supplied by S. Shrader. Infrared spectra and interpretations by W. J. Potts.

[7] C. W. Young, R. B. DuVall, and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

Condensation Derivatives in Corticosteroid Side Chains. IV. Aldosterone 20,21-Cyclic Acetals[1,2]

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In order to account for the low intensity of the 20-ketone band in the infrared spectrum of aldosterone, Ham, *et al.*,[3] suggested at automeric 20,21-dihydroxy-11,18;18,20-bisepoxide form (I) in equilibrium with the ketol–aldehyde and ketol–hemiacetal forms. Others[4] proposed a hydrogen bond between the 18-hydroxyl and the 20-ketone.

Now we wish to report the preparation of aldosterone acetals doubtless recognized as derivatives of form I. Interchange reaction between aldosterone and acetone diethyl acetal, carried out in a suitable solvent in the

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(1) Previous paper in this series, III, *Gazz. chim. ital.*, in press.

(2) This paper represents a part of the Round Table contribution by R. Gardi at the International Congress on Hormonal Steroids, Milan, May 14–19, 1962 (Excerpta Medica, International Congress Series No. 51, p. 57).

(3) E. A. Ham, R. E. Harmon, N. G. Brink, and L. H. Sarett, *J. Am. Chem. Soc.*, **77**, 1637 (1955).

(4) S. A. Simpson, J. F. Tait, A. Wettstein, R. Neher, J. Van Euw, O. Schindler, and T. Reichstein, *Helv. Chim. Acta*, **37**, 1163 (1954).