over 0.20 g of Na_2CO_3 was treated with 1.359 g of nitrosomethylurethane,[6] and the resulting mixture was stirred overnight at room temperature. Work-up followed by distillation gave 0.569 g of colorless oil, bp 60–70° (20 mm), which showed four major peaks on glpc analysis. Isolation and analysis identified these as *N*-methylurethane (30%), starting material (62%), and two ring-expanded products in yields of 2 and 14%. Pure materials were isolated by preparative glpc on a 10-ft SE-30 column. The minor product, **9**, showed λ_{max} 5.84 μ and nmr signals at τ 8.87 (3 H, d, J = 7 Hz), 8.64 (2 H, m), 7.2–8.0 (5 H), and 7.47 (2 H, s). The high-resolution mass spectrum showed a molecular ion at m/e 124 ($C_8H_{12}O$), the base peak at m/e 67 (C_5H_7), and major oxygen-containing fragments at m/e 69 (C_4H_5O) (68% of base peak) and 83 (C_5H_7O), corresponding to the two modes of the fragmentation pattern observed for **7**.

The major product, **8**, showed λ_{max} 5.80 μ and nmr signals at τ 8.95 (3 H, d, J = 6.5 Hz), 8.42 (2 H, m), 7.3–8.1 (6 H), and 7.20 (1 H, m). The high-resolution mass spectrum showed a strong molecular ion at m/e 124 ($C_8H_{12}O$), the base peak at m/e 68 (C_5H_8), and the major oxygen-containing fragment at m/e 70 (C_4H_6O) (44% of base peak).

The *p*-toluenesulfonylhydrazone had mp 162–164°.

Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.63; H, 6.90; N, 9.58. Found: C, 61.59; H, 6.85; N, 9.62.

Ring Expansion of 3.—A solution of 0.284 g of **3** in methanol over 0.20 g of Na_2CO_3 was treated with 0.821 g of nitrosomethylurethane,[6] and stirred overnight at room temperature. Distillation gave a mixture which contained 26% of recovered starting material and two ring-expansion products in 2 and 10% yields, both of which were isolated by preparative glpc.

The minor product, **11**, showed λ_{max} 5.80 μ and nmr signals at τ 8.92 (3 H, s), 8.58 (2 H, dd, J = 8 and 2 Hz), 8.08 (2 H, m), 7.73 (2 H, s), 7.63 (2 H, s), and 7.6 (1 H, m). The high-resolution mass spectrum showed a molecular ion at m/e 124 ($C_8H_{12}O$), the base peak at m/e 55 (C_4H_7), and major oxygen-containing fragments at m/e 83 (C_5H_7O) (99% of base peak) and 69 (C_4H_5O) (83% of base peak) resulting from the two possible modes of fragmentation of **11** corresponding to that of **7**.

The major product, **10**, showed λ_{max} 5.82 μ and nmr signals at τ 8.93 (3 H, s), 8.29 (2 H, dd, J = 7.0 and 2.5 Hz), 7.96 (4 H, m), 7.52 (2 H, t, J = 7 Hz), and 7.5 (1 H, m). The high-resolution mass spectrum showed a molecular ion at m/e 124 ($C_8H_{12}O$), the base peak at m/e 81 (C_6H_9), and the major oxygen-containing fragment at m/e 69 (C_4H_5O) (94% of base peak), establishing the presence of the carbonyl group at the 2 position.

The *p*-toluenesulfonylhydrazone had mp 159–161°.

Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.63; H, 6.90; N, 9.58. Found: C, 61.64; H, 6.86; N, 9.60.

Ring Expansion of 4 and 5.—A solution of 0.250 g of a 3:1 endo:exo mixture of **4** and **5** in methanol over 0.20 g of Na_2CO_3 was treated with 0.692 g of nitrosomethylurethane,[6] and the mixture was stirred overnight at room temperature. Work-up followed by distillation gave 0.222 g of colorless oil, bp 60–80° (20 mm), which showed the presence of starting material (42%; 3:1), and two product peaks in yields of 1 and 9%. The minor product was identified as **14** on the basis of λ_{max} 5.82 μ, nmr signals at τ 8.72 (3 H, d, J = 6.8 Hz), 8.26 (1 H, br d, J = 7 Hz), 7.86 (2 H, m), 7.42 (4 H, s), and *ca.* 7.4 (2 H). The high-resolution mass spectrum showed a molecular ion at m/e 124 ($C_8H_{12}O$), the base peak at m/e 67 (C_5H_7), and the major oxygen-containing fragments in nearly equal intensity at m/e 83 (C_5H_7O) and 69 (C_4H_5O).

The nmr spectrum of the material corresponding to the major peak showed signals for two methyl groups at τ 9.15 (d, J = 6 Hz) and 8.67 (d, J = 6.8 Hz) in a ratio of 3:5. The high-resolution mass spectrum showed a molecular ion at m/e 124 ($C_8H_{12}O$) and a base peak at m/e 69 (C_4H_5O), while the ir spectrum showed a single carbonyl band at 5.82 μ. These data suggest the presence of a mixture of the two isomers **12** and **13** in a ratio of 5:3. The stereochemistry of the methyl groups in these compounds, as well as that of **14**, are assigned on the basis of their chemical shifts, in analogy with the chemical shift positions of methyl groups in other bicyclo[3.1.1]heptanes.[14]

Registry No.—**6**, 17159-87-4; **7**, 17159-75-0; **8**, 33122-17-7; **8** *p*-toluenesulfonylhydrazone, 33122-18-8; **9**, 33061-07-3; **10**, 33122-19-9; **10** *p*-toluenesulfonylhydrazone, 33122-20-2; **11**, 33061-08-4; **12**, 33066-01-2; **13**, 33066-02-3; **14**, 33061-09-5.

Acknowledgment.—The able technical assistance of R. L. Munyon, Sr., is gratefully acknowledged.

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The Crystal Structure of 1-(*p*-Bromophenyl)-1,2-epoxycyclohexane. Evidence for Three-Ring Phenyl Pseudoconjugation[1]

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1-(*p*-Bromophenyl)-1,2-epoxycyclohexane crystallizes in space group $P2_1/c$, with unit cell dimensions a = 9.91, b = 5.72, c = 19.41 Å; β = 102° 20 min. The structure was solved by single-crystal X-ray diffraction methods. Least-squares refinement led to a final agreement factor for the observed reflections, R = 0.072. In the molecular structure the cyclohexane ring has a half-chair conformation. The epoxydic ring (C–C bond length 1.48 Å with estimated standard deviation 0.02 Å, C–O bond lengths with mean value 1.47 Å, estimated standard deviation 0.02 Å) makes an angle of 83° with the phenyl ring, as the result of pseudoconjugative interaction. This interaction is also indirectly responsible for the particular conformation assumed by the cyclohexane ring.

The geometry of the variously substituted cyclohexane rings has been extensively studied by means of electron diffraction, X-ray, and microwave spectroscopy.[2] The structural determinations on 1,2-epoxycyclohexanes are largely limited[3,4] to the classical electron diffraction studies of Ottar[5] who measured the skeletal geometry and the various interatomic distances in this system. In particular, the 1,2-epoxycyclohexane

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[1] This work was supported by Consiglio Nazionale delle Ricerche, Roma.

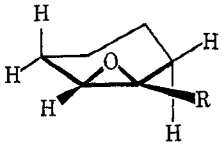
[2] (a) C. Altona and M. Sundaralingam, *Tetrahedron*, **26**, 925 (1970); (b) H. Booth, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5**, 231 (1969), and references cited therein.

[3] R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

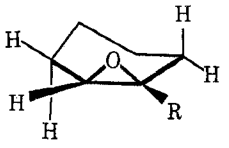
[4] A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part 1, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, p. 1.

[5] B. Ottar, *Acta Chem. Scand.*, **1**, 283 (1947).

molecule can exist in two enantiomeric "half-chair" conformations (I, II) which readily undergo chair inversion.



I



II

These two conformations are no longer equivalent when a substituent is present in the ring. It has been demonstrated by nmr spectrometry that, when the cyclohexane ring is incorporated into a rigid system, for example, steroids, or when there are bulky substituents such as a *tert*-butyl group present in the 4 position, the ring is constrained in one particular half-chair conformation.[6] However, this approach to the study of the ring conformations fails in assessing the subtle conformational effects arising when there are substituents at the 1 or 2 positions.

While the geometry of a molecule in the solid state does not necessarily reflect its conformations in solution, we have considered it worthwhile, in relation to the behavior of 1-phenyl-1,2-epoxycyclohexanes,[7] to investigate the geometry of the 1-(*p*-bromophenyl)-1,2-epoxycyclohexane by X-ray diffraction. This investigation should allow, at least in the solid state, to establish the exact conformational situation of the phenyl ring, with regard to its possible conjugation with the epoxide ring.[8-10] This problem is of some importance since it can be very useful in connection with the physical and chemical properties of these epoxides and, more generally, can be of significance in connection with the electronic structure of the epoxide ring which at the present time is still a subject of much discussion.[3,4]

Experimental Section

Preparation of the Compound. 1-(*p*-Bromophenyl)cyclohexene.—A solution of 1-(*p*-bromophenyl)cyclohexanol[11] (10.0 g) in acetic acid (10 ml) was treated with sulfuric acid (2 ml). The resulting mixture was swirled for 30 sec and then poured into water. After cooling the precipitate was collected, washed with water, and crystallized from ethanol to give the pure product (7.60 g), mp (Kofler hot stage) 72–73° (lit.[12] mp 73.5–74°).

1-(*p*-Bromophenyl)-1,2-epoxycyclohexane.—A solution of 1-(*p*-bromophenyl)cyclohexene (5.0 g, 0.021 mol) in 75% aqueous dioxane (100 ml) was treated with *N*-bromoacetamide (3.30 g, 0.024 mol) in 50% aqueous dioxane (50 ml). This suspension was warmed on a steam bath for 10 min, cooled, treated with potassium hydroxide (10.0 g) in water (50 ml), stirred for 15 min, poured in water, and extracted with ether. The ether layer was washed with water, dried ($MgSO_4$), and evaporated to yield a residue (5.10 g) which was dissolved in petroleum ether and chromatographed through a 1.5 × 25 cm column of neutral alumina (grade II) collecting 10-ml fractions. Elution with petroleum ether (bp 30–50°) yielded in succession small quantities of unreacted starting material and pure 1-(*p*-bromophenyl)-1,2-epoxycyclohexane (3.20 g), which crystallized from petroleum ether (bp 30–50°), mp 57–57.5° (lit.[13] mp 48.5°).

X-Ray Data.—The crystal data were determined by means of rotation and Weissenberg photographs obtained with Cu Kα radiation and precession spectra taken with Mo Kα radiation. 1-(*p*-Bromophenyl)-1,2-epoxycyclohexane: mol wt 253.1; monoclinic space group $P2_1/c$, from systematic absences ($h0l$ absent for $l = 2n + 1$, $0k0$ absent for $k = 2n + 1$); $a = 9.91 \pm 0.02$ Å, $b = 5.72 \pm 0.01$ Å, $c = 19.41 \pm 0.03$ Å; $\beta = 102°\ 20 \pm 10$ min; unit cell volume $U = 1075.4$ Å^3; $D_c = 1.57$ g cm^{-3} with $Z = 4$; F(000) = 512; μ (Cu Kα) = 50 cm^{-1}.

The intensity data were recorded with Ni-filtered Cu Kα radiation (λ 1.5418 Å), by means of Weissenberg photographs, with the multiple films technique and integration process. A crystal elongated in the b direction was reduced to cylindrical shape with a diameter of 0.017 cm ($\mu R = 0.425$ for Cu Kα radiation). Four layers with b as rotation axis ($k = 0$–3) were taken. A total of 753 independent reflexions were observed. The intensities, measured with a Nonius microdensitometer, have been corrected for Lorentz and polarization factors and for the absorption factor using the three-constants formula proposed by Palm[14] for cylindrical crystals.

Determination and Refinement of the Structure.—The structure determination was carried out by means of a three-dimensional Patterson synthesis. The bromine position was determined and a successive three-dimensional Fourier synthesis, calculated with the signs determined by the bromine atom, revealed all the heavy atoms of the structure; the agreement index $R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$ calculated at this stage resulted in 0.27.

Three cycles of full-matrix least-squares refinement were computed; positional coordinates, isotropic temperature factors, and the scale factors were introduced among the refined parameters. Unit weights were given to all the reflections. The R_1 value was calculated as 0.14.

At this point anisotropic temperature factor for the bromine atom was introduced and the following weighting scheme was used: $\sqrt{w} = 0$ for unobserved reflexions; $\sqrt{w} = 1$ for observed reflexions with $|F_o| \leq 8$; $\sqrt{w} = 1/(0.06\ |F_o| + 0.5)$ for observed reflexions with $|F_o| > 8$. Two further refinement cycles reduced R_1 to 0.082.

Then hydrogen atoms were introduced in calculated positions with isotropic temperature factors of 5.0 Å^2. One further least-squares cycle in which the hydrogen parameters were not varied led the agreement index to $R_1 = 0.072$.

The scattering factors used in the structure factor calculations were taken from International Tables for X-ray Crystallography[15] for all atoms.

The observed and the calculated factors and the final positional and thermal parameters with their standard deviations appear in the microfilm edition of this journal.[16]

Description and Discussion of the Structure.—Interatomic distances and bond angles (Table I and II) have been calculated by means of the ORFFE program of Busing, Martin, and Levy and the least-squares plane by means of the program LSQPL, incorporated in the Crystal Structures Calculations System X-RAY 63.[17]

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(14) J. H. Palm, *Acta Crystallogr.*, **17**, 1326 (1964).

(15) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(16) Listing of structure factors, coordinates, and anisotropic temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(17) J. M. Stewart, "Crystal Structure Calculations System for the IBM 709/7090/7094," Technical Report TR-64-6, Computer Science Center, University of Maryland, and Research Computer Laboratory, University of Washington, 1964.

Table I

Bond Lengths and Their Standard Deviations

Atoms	Distances, Å	Esd, Å
C(1)-O	1.45	0.02
C(2)-O	1.48	0.02
C(1)-C(2)	1.48	0.02
C(2)-C(3)	1.51	0.02
C(3)-C(4)	1.51	0.03
C(4)-C(5)	1.55	0.02
C(5)-C(6)	1.51	0.02
C(6)-C(1)	1.51	0.02
C(1)-C(7)	1.49	0.02
C(7)-C(8)	1.36	0.02
C(8)-C(9)	1.40	0.02
C(9)-C(10)	1.35	0.02
C(10)-C(11)	1.43	0.02
C(11)-C(12)	1.40	0.02
C(12)-C(7)	1.39	0.02
Br-C(10)	1.926	0.015

Table II

Bond Angles and Their Standard Deviations

	Angle, deg	Esd, deg
C(1)-O-C(2)	60.7	1.0
C(1)-C(2)-O	58.9	1.0
C(2)-C(1)-O	60.5	1.0
C(3)-C(2)-O	113.4	1.3
C(6)-C(1)-O	111.5	1.3
C(7)-C(1)-O	113.7	1.4
C(7)-C(1)-C(2)	119.2	1.3
C(6)-C(1)-C(2)	117.9	1.3
C(1)-C(2)-C(3)	122.4	1.4
C(2)-C(3)-C(4)	114.7	1.3
C(3)-C(4)-C(5)	108.3	1.7
C(4)-C(5)-C(6)	110.4	1.4
C(5)-C(6)-C(1)	112.4	1.4
C(6)-C(1)-C(7)	119.0	1.3
C(1)-C(7)-C(8)	122.8	1.5
C(1)-C(7)-C(12)	119.4	1.3
C(12)-C(7)-C(8)	117.7	1.4
C(7)-C(8)-C(9)	123.4	1.6
C(8)-C(9)-C(10)	117.7	1.5
C(9)-C(10)-C(11)	122.8	1.4
C(10)-C(11)-C(12)	116.0	1.6
C(11)-C(12)-C(7)	122.3	1.5
C(9)-C(10)-Br	120.6	1.2
C(11)-C(10)-Br	116.5	1.3

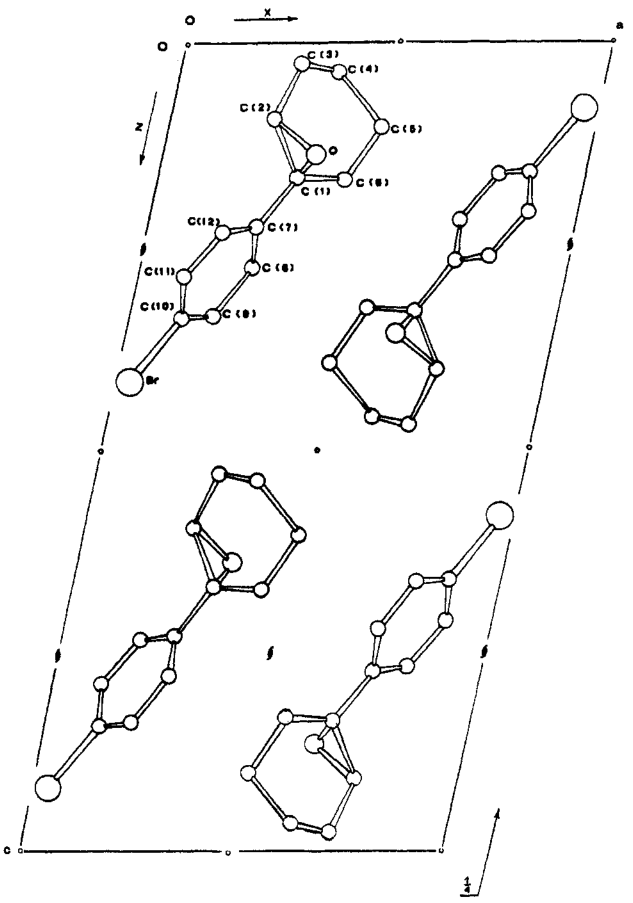

Figure 1.—The molecular structure of 1-(*p*-bromophenyl)-1,2-epoxycyclohexane, viewed along the direction normal to the epoxydic ring.

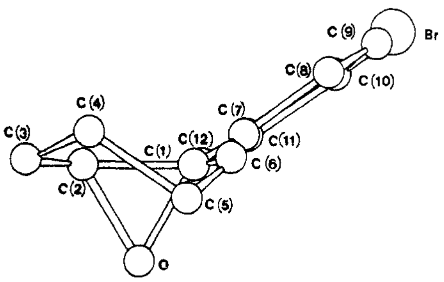

Figure 2.—Crystal structure as viewed along the *b* axis.

In what follows we shall examine the different aspects of the molecular structure: (a) bond lengths and angles in the system 1,2-epoxycyclohexane, (b) the geometry of the bromophenyl group, (c) the stereochemistry of the system made up by the epoxydic and phenyl rings, and (d) the conformation of the epoxycyclohexane ring.

(a) The structure of the 1,2-epoxycyclohexane group is very similar to that determined by an electron diffraction study[5] for 1,2-epoxycyclohexane, with the four carbon atoms C(1)-C(2)-C(3)-C(6) almost in a plane (the least-squares plane and the deviations from planarity are given in Table III); the angle between this plane and the plane of epoxydic ring is 80°. As regards bond lengths in the epoxydic ring, Ottar[5] determined a distance equal to 1.42 Å for the C-O bond; the values found in this work (1.48 Å for C-C bond and the mean value 1.47 Å for C-O bond) agree with the values determined by Erlandsson[18] in a microwave spectroscopic investigation of 1,2-epoxycyclopentane (1.52 Å for C-C and 1.47 Å for C-O bond lengths).

(b) In Table III we report two least-squares planes relative to the phenyl ring and the deviations from the calculated plane. The C-C bond lengths (mean value 1.39 Å) and the bond angles are normal.

(c) The conjugative properties of the three-membered rings have been amply documented and are clearly explained by the bent bond model developed for cyclopropane. The theory[10] shows that the geometry for maximum pseudoconjugative interaction between a three-membered ring and an adjacent π system is that where the plane of the ring and the axis of the π-orbital's system are parallel. This situation is satisfied in the molecular structure of 1-(*p*-bromophenyl)-1,2-epoxycyclohexane (Figure 1) where the dihedral angle between the epoxy ring and the phenyl ring is of 83°. This point is also relevant for the conformation assumed by the epoxycyclohexane group.

(d) In fact, once the pseudoconjugative interaction induces the phenyl ring to dispose its plane normal to the three-membered ring, the conformation I is preferred over II, because of more

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[18] G. Erlandsson, *Ark. Fys.*, **9**, 341 (1955); *Chem. Abstr.*, **49**, 11421 (1955).

TABLE III

LEAST-SQUARES PLANES[a]

	Atoms defining the plane	*A*	*B*	*C*	*D*
Plane I	C(7), C(8), C(9), C(10), C(11), C(12)	7.1773	2.4574	7.2735	3.4945
Plane II	Br, C(7), C(8), C(9), C(10), C(11), C(12), C(1)	7.2141	2.4532	7.1623	3.4674
Plane III	C(1), C(2), C(3), C(6)	6.7074	4.2102	−2.5713	1.6003

	Deviations from the plane (in Å)		
Atoms	Plane I	Plane II	Plane III
Br		0.002	
C(1)		0.016	−0.003
C(2)			0.003
C(3)			0.001
C(6)			−0.003
C(7)	−0.004	−0.016	
C(8)	0.005	−0.002	
C(9)	−0.006	−0.005	
C(10)	0.005	0.011	
C(11)	−0.003	−0.002	
C(12)	0.003	−0.005	

[a] The equations, in the form $Ax + By + Cz = D$, where x, y, and z are fractional coordinates, were calculated [V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12,** 600 (1959)] with all weights equal to 1.

TABLE IV

SHORTEST INTERMOLECULAR DISTANCES[a]

Br···Br^{v}	3.52
Br···C(3^{iii})	3.90
Br···C(2^{iv})	3.79
C(7)···C(6^{ii})	3.66
C(11)···C(8^{i})	3.75
C(11)···C(8^{iv})	3.73
C(11)···C(9^{i})	3.70
C(11)···C(9^{iv})	3.60
C(11)···C(10^{iv})	3.59
C(11)···C(11^{iv})	3.78
C(12)···Br^{iv}	3.98
C(12)···C(8^{i})	3.76
C(12)···C(10^{iv})	3.68
O···C(4^{iii})	3.74
O···C(5^{iii})	3.78
O···C(6^{iii})	3.54

[a] C···C and C···O contacts are below 3.80 Å; C···Br and Br···Br contacts are below 4.00 Å.

favorable steric interaction between the hydrogen atom linked to C(8) atom at one hand and the two hydrogen atoms linked to C(6) at the other hand; the distances between H(8) and H(6a) (pseudoequatorial) and between H(8) and H(6b) (pseudoaxial) are 2.6 and 2.2 Å, respectively.

Crystal Packing.—The packing of the molecules in the crystal is described by Figure 2. In Table IV we report the short intermolecular distances. In this table the atoms of the different asymmetric units are related to the atoms of the fundamental unit as follows: i, atom at x, $1 + y$, and z; ii, atom at $1 - x$, $^1/_2 + y$, and $^1/_2 - z$; iii, atom at x, $^1/_2 - y$, and $^1/_2 + z$; iv, atom at $-x$, $^1/_2 + y$, and $^1/_2 - z$; v, atom at $-x$, $-y$, and $1 - z$.

As the values reported in Table IV clearly show, the intermolecular interactions are exclusively of the van der Waals type.

All the calculations were performed on the IBM 7090 computer of Centro Nazionale Universitario di Calcolo Elettronico (CNUCE), Pisa.

Registry No.—1-(*p*-Bromophenyl)-1,2-epoxycyclohexane, 1605-15-8.

Photochemical Rearrangements of Bicyclic 6/5-Fused Cross-Conjugated Cyclohexadienones and Related Compounds[1a]

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The ring A unsubstituted bicyclic 6/5-fused cross-conjugated cyclohexadienone **7a** and its 4-methyl (**7b**) and 6-methyl (**7c**) derivatives have been prepared and irradiated at 2537 Å in dry dioxane. The major product in each case was the corresponding bicyclo[3.1.0]hex-3-en-2-one (**8**); **7a** and **7b** also gave small amounts of linearly conjugated dienones (**9**). The bicyclo[3.1.0]hex-3-en-2-one **8b**, which has similar substitution to lumisantonin **12**, was irradiated with light of wavelength greater than 3000 Å in both dioxane and ethanol. In the former solvent it gave mainly the homoannular dienone **14**, while in the latter it afforded the 5/6-fused ethoxy ketone **19**. The photochemistry of these compounds is compared with that of related substances and possible mechanistic pathways are discussed.

It is well known that on irradiation at 2537 Å in inert solvents such as dioxane 6/6-fused bicyclic (**1**) and steroidal cross-conjugated cyclohexadienones, for example, **2**, undergo facile rearrangements into the corresponding bicyclo[3.1.0]hex-3-en-2-ones **3** and **4**, respectively, termed lumiproducts.[2] In contrast, Jeger, Schaffner, and coworkers[3] have reported that *B*-nor-1-dehydrotestosterone acetate (**5**), having a five-mem-

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[1] (a) This investigation was supported by Public Health Service Grant No. 15044 from the National Institute of General Medicine and by a NASA Institutional Grant (NsG-657). (b) National Science Foundation Undergraduate Research Participant, summer 1968.

[2] For reviews see (a) P. J. Kropp, *Org. Photo. Chem.*, **1,** 1 (1967); (b) K. Schaffner, *Advan. Photochem.*, **4,** 81 (1966).

[3] G. Bozzato, H. P. Throndsen, K. Schaffner, and O. Jeger, *J. Amer. Chem. Soc.*, **86,** 2073 (1964).