oxide mixture (64.4% *trans*, 27.8% *cis*, and 7.8% 4,5-dihydrooxepine) heated on a steam bath overnight resulted in the disappearance of *cis*-1,2-divinylethylene oxide. The composition after the heating period was 61.8% *trans* oxide and 38.2% 4,5-dihydrooxepine.

The thermal requirements for ring expansion of 1,2-divinylethylene oxide and 1,2-divinylcyclopropane[8] are apparently analogous. In both cases, ring expansion of the *cis* isomer requires about 200° less than the corresponding *trans* isomer. Extension of valence tautomerism to other small ring heterocycles is currently under investigation in our laboratories.

Experimental

3-Chloro-4-acetoxy-1,5-hexadiene.—The procedure used for the preparation of 3-chloro-4-acetoxy-1,5-hexadiene was an adaptation of Searles[9] technique for preparation of chloro esters from 1,3-diols.

Acetyl chloride, 190 g. (2.44 moles), was added to a stirred suspension of 41.6 g. (0.38 mole) of calcium chloride and 228 g. (2.0 moles) of 1,5-hexadiene-3,4-diol over a period of 45 min. During the addition, the temperature was maintained below 10°. The reaction mixture then was stirred for 40 hr. at room temperature and then 1 hr. at 50°. The dark brown viscous product was poured into ice, neutralized with cold aqueous sodium bicarbonate extracted with ether, and dried over anhydrous potassium carbonate. After filtration and removal of ether, there remained 269 g. of crude chloro ester.

The crude chloro ester was distilled through a spinning band column to give a water-white, sweet-smelling liquid, b.p. 88–93° (19 mm.).

Anal. Calcd. for $C_8H_{11}ClO_2$: C, 55.17; H, 6.32; Cl, 20.11. Found: C, 54.53; H, 6.26; Cl, 20.00.

1,2-Divinylethylene Oxide. High Temperature Ring Closure.—Crude 3-chloro-4-acetoxy-1,5-hexadiene, 257 g., was slowly added to a reactor containing 362 g. (9.05 moles) of sodium hydroxide 362 g. (6.46 moles) of potassium hydroxide, and 36.2 g. (2.01 moles) of water at 170°. The addition of the chloro ester caused a rapid rise in temperature. During the addition, the pressure in the reactor was decreased so that an overhead temperature of 90–100° was maintained. If the pressure were too low, the overhead temperature dropped and the caustic foamed up into the distillation head causing it to plug. Approximately 80 ml. of product–water mixture was collected in a receiver cooled to −78°. Separation of the crude product from water, drying over anhydrous magnesium sulfate, and atmospheric distillation yielded 40 g. of *trans*-1,2-divinylethylene oxide–4,5-dihydrooxepine mixture, b.p. 105–113° (760 mm.), in a ratio of 2:1.

The composition of this mixture was determined on a Perkin-Elmer g.c. 2-m. column (Dow-Corning silicone oil no. 200 on firebrick) at 75°. The relative retention times of *trans*-1,2-divinylethylene oxide to benzene was 1.83 and 2.81 for 4,5-dihydrooxepine. Separation of the epoxide–oxepine mixture was not effective by distillation through a 75-plate concentric tube column. Pure *trans*-1,2-divinylethylene oxide and 4,5-dihydrooxepine for structural determination and subsequent reactions were obtained with an Autochrome preparatory g.c. unit. A Carbowax–Chromosorb column operated at 175° was utilized.

trans-1,2-Divinylethylene oxide (93% pure by g.c.) gave the following physical constants: b.p. 108° (760 mm.)[10]; n^{25}_D 1.4470; d^{20}_4 0.870; infrared maxima (neat) 3.35 (m), 6.10 (m), 7.03 (m), 10.17 (s), 10.82 (vs), 11.38 (s), 11.50 (vs), and 14.79 (s)μ. 4,5-Dihydrooxepine (93% pure by g.c.) had b.p. 113° (760 mm.)[10]; n^{25}_D 1.4735; d^{20}_4 0.978; infrared maxima (neat) 3.45 (m), 6.05 (s), 6.10 (s), 7.46 (m), 7.70 (vs), 8.99 (vs), and 13.35 (s) μ.

Anal. Calcd. for C_6H_8O (*trans* epoxide): C, 75.01; H, 8.33. Found: C, 74.68; H, 8.46.

Low Temperature Ring Closure.—The apparatus and quantities used in this procedure were identical with that used in the high temperature ring closure except that 700 ml. of ethylene glycol was used in addition to the caustic and water. The reactor temperature was maintained at 40–50° and the pressure at 10–15 mm. during the addition of the chloro ester. In this way, 241 g. of crude chloro ester yielded 101 ml. of *cis–trans* 1,2-divinylethylene oxide in ratio of 1:2 (composition determined by g.c.). This product showed only trace quantities (1–2%) of 4,5-dihydrooxepine. Distillation of the *cis–trans* mixture through a 75-plate concentric tube column at 45 mm. failed to separate the isomeric oxides. The *cis–trans* epoxide mixture (ratio 1:2) gave the following physical constants: b.p. 107° (760 mm.)[10]; n^{25}_D 1.4520; d^{20}_4 0.899; infrared maxima (neat) 3.35 (m), 6.10 (m), 7.03 (m), 10.17 (s), 10.82 (vs), 11.50 (s), 12.10 (w), and 14.79 (s) μ.

Anal. Calcd. for C_6H_8O: C, 75.01; H, 8.33. Found: C, 74.88; H, 8.03.

Acknowledgment.—This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Ordnance under Contract No. DA-30-069-ORD-2487.

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[9] S. Searles, K. A. Pollart, and F. Block, *J. Am. Chem. Soc.*, **79**, 952 (1957).

[10] Determined by the inverted capillary tube technique.

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cis–trans Isomerism of Exocyclic α,β-Unsaturated Indanones and Tetralones

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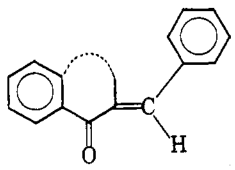
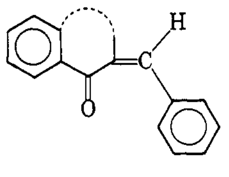
Exocyclic α,β-unsaturated ketones have a fixed *sym-cis* conformation of the C=C with respect to the C=O. Assignments of the *cis* and *trans* isomers of three such compounds by proton magnetic resonance spectroscopy are reported.



trans



cis

The deshielding effect resulting from the diamagnetic anisotropy of the carbonyl group leads to the vinyl proton in the *trans* isomer (with the proton *cis* to the carbonyl group) giving a signal at a greater chemical shift than in the *cis* isomer.

2-Benzal derivatives of 4,4-dimethyl-1-tetralone,[2] 1-indanone,[2] and 3,3-dimethyl-1-indanone,[3] as prepared by condensation with benzaldehyde in the presence of base, were isolated as sharp melting solids having the *trans* arrangement of phenyl and carbonyl groups (see Table I).

In methanol these *trans* isomers were largely converted by ultraviolet irradiation into the corresponding *cis* isomers. Chromatography of the crude irradiation products gave pure specimens of each of these *cis* iso-

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[1] To whom communications concerning this paper should be addressed.

[2] A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).

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TABLE I

PROPERTIES OF *cis* AND *trans* ISOMERS OF EXOCYCLIC α,β-UNSATURATED TETRALONES AND INDANONES

	2-Benzal-4,4-dimethyl-1-tetralone		2-Benzal-1-indanone		2-Benzal-3,3-dimethyl-1-indanone	
	trans	*cis*	*trans*	*cis*	*trans*	*cis*
M.p., °C.	110	Oil	109–111	95–96	80–82	Oil
Ultraviolet equilibration,[a] %	10	90	22	78	32	68
Chemical equilibration,[b] %	100	0	100	0	56	44
Chemical shifts in p.m.r. spectrum (τ)						
=CH (1)[c]	2.29	3.37	?[d]	3.11	2.35	3.20
$-CH_2$[e] (2)[c]	7.10	7.27	6.07	6.17		
$-CH_3$ (6)[c]	8.72	8.58			8.50	8.45
β to >C=O[f] (1)[c]	1.97	1.97	?	1.90	2.20	?
Mol. wt.[g]	(262)	258	(220)	219	(248)	251

[a] Irradiation of *trans* isomer in methanol. [b] Of either *trans* or *cis* isomer in acetonitrile. [c] Number of protons by integration. [d] Signal masked by aromatic peaks but $\tau < 2.7$. [e] Doublet, split by vinyl proton; $J_{ax} = 2$ c.p.s. [f] Doublet; $J_{ab} = 7$ c.p.s. [g] Determined by thermistor method [J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959)] using chloroform as solvent; values in parentheses are theoretical values.

mers. The *cis* isomers were of lower melting point, consistent with a *trans* to *cis* conversion.[4]

It can be seen from Table II that the ultraviolet spectral data, frequently found useful for assigning *cis* and *trans* isomers,[4] are of little assistance in assigning the isomers of these exocyclic α,β-unsaturated ketones. The infrared spectral data also present a confusing picture, but it is noteworthy that a peak assigned as due to C=C in the spectra of the *trans* isomers is absent in the spectra of the *cis* isomers.

TABLE II

ULTRAVIOLET AND INFRARED SPECTRA OF *cis* AND *trans* ISOMERS OF EXOCYCLIC α,β-UNSATURATED TETRALONES AND INDANONES

	Ultraviolet spectra[a]		Infrared spectra[b] (cm.$^{-1}$/absorption of 10 mg. per ml. of soln.)	
Compound	λ_{max}, mμ	$\epsilon \times 10^{-3}$		
trans-2-Benzal-4,4-dimethyl-1-tetralone[c]	307	16.5	$\gamma_{C=O}$	1673/94
	227	11.4	$\gamma_{C=C}$	1610/90
			γ_{Ar}	1605/90
cis-2-Benzal-4,4-dimethyl-1-tetralone	311	11.3	$\gamma_{C=O}$	1676/82
	269	9.3	γ_{Ar}	1602/54
	234	9.7		
trans-2-Benzal-1-indanone[d]	320	28.0	$\gamma_{C=O}$	1706/100
	227	10.0	$\gamma_{C=C}$	1640/85
			γ_{Ar}	1615/76
cis-2-Benzal-1-indanone	316	21.0	$\gamma_{C=O}$	1700/75
	228	9.4	γ_{Ar}	1619/71
trans-2-Benzal-3,3-dimethyl-1-indanone[d]	310	17.5	$\gamma_{C=O}$	1705/98
	275 (sh)	11.5	$\gamma_{C=C}$	1627/80
	224	7.8	γ_{Ar}	1612/85
cis-2-Benzal-3,3-dimethyl-1-indanone	322	17.8	$\gamma_{C=O}$	1695/96
	280 (sh)	7.1	γ_{Ar}	1615/89
	230	7.8		

[a] In methanol. [b] In carbon tetrachloride. [c] See ref. 2. [d] See ref. 3.

The melting points and the p.m.r. spectra of the products show that equilibration of 2-benzal-4,4-dimethyl-1-tetralone and 2-benzal-1-indanone in acetonitrile by means of hydrogen bromide or piperidine[5] leads to the pure *trans* isomer, irrespective of whether one starts with the *trans* or *cis* isomer.

Equilibration of 2-benzal-3,3-dimethyl-1-indanone gave a product which was shown by analysis of its p.m.r. spectrum to consist of about 56% *trans* isomer and 44% *cis* isomer (see Table III).

TABLE III

cis–trans ISOMER RATIOS AFTER TREATMENT OF AN ACETONITRILE SOLUTION OF *cis*- OR *trans*-2-BENZAL-3,3-DIMETHYL-1-INDANONE WITH VARIOUS ADDITIVES

Olefin	[Olefin]	Additive	[Additive]	Time, hr.	Temp., °C.	% *cis*
trans	0.025	None		72	105	0
trans	0.049	NEt_4Br	0.20	43	90	0
trans	0.048	$C_5H_{11}N$	0.20	9	25	16
trans	0.017	$C_5H_{11}N$	0.10	168	25	42
trans	0.048	$C_5H_{11}N$	0.20	2	90	43
trans	0.049	$C_5H_{11}N$	0.20	43	90	44
trans	0.053	$C_5H_{11}N$	0.10	48	105	46
trans	0.048	HBr	0.16	23	25	38
trans	0.043	HBr	0.16	21	90	44
cis	0.049	$C_5H_{11}N$	0.17	44	25	45
cis	0.020	$C_5H_{11}N$	0.17	1.5	90	44
cis	0.037	$C_5H_{11}N$	0.17	43	90	41
cis	0.030	HBr	0.16	23	25	44

The ultraviolet spectrum of the *trans*-2-benzal-3,3-dimethyl-1-indanone has previously been found to indicate steric hindrance between a hydrogen atom attached to the aromatic nucleus of the 2-benzal substituent and a 3-position methyl group.[3] The presence of a considerable proportion of *cis* isomer on equilibration of this exocyclic α,β-unsaturated indanone is almost certainly related to this presence of steric hindrance in the *trans* isomer.

For *trans*-2-benzal-3,3-dimethyl-1-indanone the relationship between the peak at τ 2.35 and the vinyl proton was confirmed by preparing *trans*-2-(α-deuteriobenzal)-3,3-dimethyl-1-indanone by condensing 3,3-dimethyl-1-indanone with deuteriobenzaldehyde. The spectra were identical except that the signal at τ 2.35 was absent.

For the *cis* and *trans* isomers of both 2-benzal-4,4-dimethyl-1-tetralone and 2-benzal-1-indanone, a long-range coupling between the vinyl proton and the methylene protons is observed. The methylene protons appear as a doublet ($J \sim 2$ c.p.s.) and the vinyl proton as a somewhat ill-defined triplet. Deuterium substitution for the vinyl proton in *trans*-2-benzal-1-indanone

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[4] For an excellent discussion of the physical properties of geometrical isomers of olefins, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 12, Section 12-3.

[5] See ref. 4, p. 344, for a discussion of the mechanism of these acid and secondary amine promoted interconversions.

resulted in a sharp singlet for the methylene protons, consistent with the proposed coupling.[6]

Experimental[7]

Preparation of the *cis* Isomers.—Solutions containing about 1 g. of *trans* isomer in 100 ml. of methanol were irradiated, in a Pyrex flask, for 1–2 days by means of a B-100A Blakray source (Ultra-Violet Products, Inc.). Evaporation gave a product whose p.m.r. spectrum was analyzed to give the *cis–trans* isomer ratios for equilibration in the presence of the ultraviolet irradiation; this data is presented in Table I.

The product was chromatographed on Alcoa F-20 alumina using as eluent 1% benzene in petroleum ether (b.p. 60–70°). In this way samples were obtained whose p.m.r. spectra indicated pure *cis* isomers. Only the *cis*-2-benzal-1-indanone was a solid, m.p. 93–96°. The two oils obtained had the correct molecular weights (Table I) and one of them, *cis*-2-benzal-4,4-dimethyl-1-tetralone, was analyzed.

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 87.03; H, 6.84.

Spectral characteristics for the *cis* isomers are recorded in the first two tables.

Irradiation of 2-benzal-4,4-dimethyl-1-tetralone in carbon tetrachloride led to 80% *cis* isomer and irradiation of 2-benzal-3,3-dimethyl-1-indanone in acetonitrile to 74% *cis* isomer in the equilibrium mixtures.

Equilibration of the *cis* and *trans* Isomers.—Small quantities of either the pure *cis* or pure *trans* isomer were dissolved in acetonitrile together with 0.1 to 0.2 *M* amounts of hydrogen bromide or piperidine. Eventually, the solutions were evaporated to dryness and the *cis–trans* ratio in the product was determined by analysis of its p.m.r. spectrum. When equilibrations were carried out at elevated temperatures, sealed bulbs were used.

Acknowledgment.—This work was supported in part by Grant G-20149 from the National Science Foundation.

[6] D. N. Kevill, G. A. Coppens and N. H. Cromwell, *J. Am. Chem. Soc.*, **86**, 1553 (1964).

[7] Infrared spectra were measured with a Perkin-Elmer Model 21 double beam recording instrument employing sodium chloride optics and matched sodium chloride cells with 10 mg./ml. carbon tetrachloride solutions. The ultraviolet spectra were determined with a Cary Model 11-MS recording spectrophotometer using reagent grade methanol solutions. The proton magnetic resonance spectra were obtained with a Varian A-60 instrument using carbon tetrachloride solutions containing a trace of tetramethylsilane (τ 10.00) as internal reference.

Radical Efficiency from 2,2′-Azobis(2-methylpropionitrile)

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The decomposition of 2,2′-azobis(2-methylpropionitrile) (ABN) has been studied by many workers,[2] and it has been shown that the production of cyanopropyl radicals is appreciably inefficient. Ziegler[3] reported that ABN decomposition in the presence of air does not produce a pressure change since the nitrogen evolved is exactly compensated by simultaneous oxygen uptake by cyanopropyl radicals. Talât-Erben[4] isolated 2-cyano-2-propyl hydroperoxide (stable to 120°) from ABN decomposition in xylene under oxygen.

It was of interest to study ABN decomposition in chlorobenzene under oxygen under conditions similar to those used in autoxidation studies with ABN initiation. A definite oxygen uptake is found, which we assume is due to the following reactions.

$$\mathrm{ABN} \longrightarrow \mathrm{N_2} + 2e\mathrm{R}\cdot + (1 - e)\ \mathrm{R\text{-}R}\ \text{(in solvent cage)}$$

$$2e\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow 2e\mathrm{RO_2}\cdot$$

$$2e\mathrm{RO_2}\cdot \longrightarrow \text{products; no } \mathrm{O_2} \text{ evolution}$$

$R_{O_2}/R_{N_2} = 2e$, where e = efficiency of radical production from ABN, R = cyanopropyl radicals, R-R = tetramethylsuccinonitrile (or other nonoxygen consuming products), and R = rate of reaction.

The data in Table I show that R_{O_2}/R_{N_2} is 1.17 at 60–65° and, therefore, $e = 0.59$ which compares favorably with the value reported by Hammond[5] (0.57–0.60). This result favors the assumed reactions and formation of 2-cyano-2-propyl hydroperoxide which is stable under our experimental conditions. A repeat of the oxidation inhibition method, using cumene oxidation in chlorobenzene, inhibited by 2,6-di-*t*-butyl-4-methylphenol, as used by Hammond,[5] gave $e = 0.60$ at 60°

TABLE I

ABN DECOMPOSITION IN CHLOROBENZENE[a]

Wt. of ABN, g.	Temp., °C.	$R_{O_2} \times 10^3$ [b]	R_{N_2}	R_{O_2}/R_{N_2}
0.5987	60.0	0.162	0.942	1.17
0.7030	60.0	0.215	1.10	1.20
0.6508	65.0	0.289	1.78	1.16
0.7519	65.0	0.302	2.06	1.15
			Av.	1.17

[a] Total pressure, 1 atm. of oxygen; chlorobenzene partial pressure, 63 mm. at 60.0° and 79.5 mm. at 65.0°. Each run was made for 100 min. in 10 ml. of chlorobenzene, and the rate was taken for the linear portion which was approximately over the 20–90 min. interval. [b] All rates are ml. (STP) × sec.$^{-1}$; R'_{O_2} is the observed rate of oxygen consumption; R_{O_2} is the true rate of oxygen consumption and equals $R'_{O_2} + R_{N_2}$ where R_{N_2} is the measured rate of nitrogen evolution under nitrogen.

Experimental

ABN was Eastman Organic Chemicals, No. 6400, and chlorobenzene was No. 10 from the same source. Reaction cells were 50-ml. erlenmeyer flasks connected by 0.25-in. neoprene to a constant temperature gas buret using mercury. The reaction flasks were shaken in an oil bath controlled to 0.05° and temperatures were read on an N.B.S. certified mercury-glass thermometer. By variation of shaking rates, it was shown that the reaction was not diffusion controlled. Straight lines were computed from the data using a least-squares method on an IBM Model 1620 computer. R_{N_2} from ABN in chlorobenzene, under nitrogen at 50–65°, gave values in good agreement with the literature and an activation energy of 30.1 kcal.

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