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.

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[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.

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

$$2e\text{R}\cdot + O_2 \longrightarrow 2e\text{RO}_2\cdot$$

$$2e\text{RO}_2\cdot \longrightarrow \text{products; no } O_2 \text{ evolution}$$

$R_{O_2}/R_{N_2} = 2e$, 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.	$R_{O_2} \times 10^{3b}$	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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[1] National Science Foundation, Washington, D. C. 20550

[2] G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin, and R. S. Keys, *J. Am. Chem. Soc.*, **82**, 5394 (1960). Many earlier references are given in this paper.

[3] K. Ziegler, W. Parade, and W. Meye, *Ann.*, 567 (1950).

[4] M. Talât-Erben and N. Onol., *Can. J. Chem.*, **38**, 1154 (1960).

[5] G. S. Hammond, J. N. Sen, and C. N. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).