The product was analyzed for its content of the *trans* isomer by the method of Suter and Lutz.[15] To a solution of 0.4334 g. of the compound in 100 ml. of boiling water containing three drops of phenolphthalein indicator was added, with stirring, 0.1140 *N* sodium hydroxide at a rate sufficient to keep the solution faintly pink. The following data were taken:

Time (min.)	Vol. of base	% Reaction
0:50	0.99	4.76
2:00	1.46	7.01
5:00	1.58	7.95
49:00	2.16	10.37

The product contained about 7% of the *trans* isomer.

Rearrangement of *cis*-1-Methyl-2-chloro-1-indanol.—The rearrangement of the bromomagnesium derivative of the *cis*-chlorohydrin was carried out in the absence of solvent as described for the case (A) of *cis*-2-chloro-1-indanol. A yield of 64% of 2-methyl-1-indanone (DNPH, m.p. 221–222°) was obtained.

2-Methyl-1-indanone was prepared by the method of Fuson, Ross and McKeever.[28] The 2,4-dinitrophenylhydrazone, prepared by the usual method, formed crimson crystals, m.p. 221.5–222° (from benzene).

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.33. Found: C, 58.95; H, 4.57.

Preparation and Rearrangement of *trans*-1-Methyl-2-chloro-1-indanol.—(A) The chlorohydrin prepared by shaking for six days an aqueous solution of N-chloroacetamide, containing a few drops of sulfuric acid, with 3-methylindene was converted into the bromomagnesium derivative and the latter heated for three hours at 100°. The reaction mixture was worked up as usual, affording a 58% yield (based on the analytically satisfactory chlorohydrin) of 2-methyl-1-indanone. Analysis of the starting material by the titration procedure[15] disclosed that the chlorohydrin consisted of about 73% of the *cis* isomer. The yield of the indanone thus corresponds to 79% of the *cis* chlorohydrin used.

(B).—A sodium hypochlorite solution was prepared by passing chlorine into a mixture of 4.1 g. of mercuric chloride and 31.7 g. sodium hydroxide in 300 g. of a mixture of crushed ice and water.[29] The resulting solution was found to be 1.23 molar in sodium hypochlorite. To 312 ml. of this solution was added a solution of 24.0 ml. of 16 *N* nitric acid in 225 ml. of water and 1 g. of sodium bicarbonate.

To a stirred mixture of 18.2 g. of 3-methylindene and 50 g. of ice was added 250 ml. of the hypochlorous acid solution (0.64 *M*) in portions of 100, 100, 25 and 25 ml., the total time required being 2.5 hours. The organic phase was taken up in ether and the ether solution washed with water (twice), 3 *N* sodium carbonate (once) and water (once). Removal of the ether after drying over magnesium sulfate left 23.3 g. of an oil.

Anal. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.41. Calcd. for $C_{10}H_{10}Cl_2$: Cl, 35.31. Found: Cl, 22.39.

Titration of a sample with alkali as described above gave the following data:

Time, min.	1.0	3.5	5.0	15.0
Reaction, %	28.8	39.1	44.5	51.2

These data show that the material contains less than 50% of the *trans* isomer, and probably about 35–40%. Because of the probable presence of some 1,2-dichloroindene the usual well-defined shoulder in the titration–time curve is absent, although the characteristic rapid initial reaction is clearly discernible.

(C).—**Rearrangement.**—After the addition of 81.6 ml. of 1.47 molar ethereal *t*-butylmagnesium chloride to a solution of 21.9 g. of the crude chlorohydrin, from (B), in 360 ml. of ether, the mixture was refluxed for an hour and the solvent removed through a sintered glass filter stick. The residue was washed with 100 ml. of ether, which was removed in the same way. The light brown solid residue (11.6 g., corresponding to 7.42 g. of chlorohydrin, or 34% of the crude material used) was heated at 100° for six hours. After hydrolysis and separation of the ethanol-soluble material from the black tarry substance which formed the bulk of the product, 0.75 g. of 2,4-dinitrophenylhydrazine and 1.5 ml. of concentrated hydrochloric acid were added to the ethanol solution (50 ml.). The red crystals of the DNPH of 2-methyl-1-indanone, which separated on standing, weighed 600 mg. This corresponds to a 4.5% yield of the ketone.

In another experiment the bromomagnesium derivative was prepared in the manner described above (C) and heated for forty hours in boiling dibutyl ether. The yield of DNPH of 2-methyl-1-indanone, m.p. and mixed m.p. 221–222°, corresponded to a 3% yield of the ketone.

LOS ANGELES, CALIFORNIA RECEIVED SEPTEMBER 7, 1950

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(29) G. H. Coleman and H. F. Johnstone, "Org. Syn.," Coll. Vol. I, 2nd ed., John Wiley and Sons, New York 1, N. Y., 1941, p. 158.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Studies in Photochemistry and Radiation Chemistry of *i*-Propylbenzene and *t*-Butylbenzene[1,2]

BY THOMAS J. SWORSKI, ROBERT R. HENTZ[3] AND MILTON BURTON

Data on vapor phase photolyses of *i*-propylbenzene and *t*-butylbenzene with light of wave length near 2537 Å. are interpreted in terms of methyl radical production by a primary splitting of carbon-to-carbon bonds β to the benzene ring and hydrogen production principally via rupture of carbon-to-hydrogen bonds β and γ to the benzene ring. Liquid phase photolyses show almost complete suppression of hydrocarbon formation with total quantum yields of non-condensable gas 2.4×10^{-4} and 1.3×10^{-4}, respectively. Data for gas phase photolyses are sufficiently accurate only for the statement that the quantum yields are roughly of the same order of magnitude. Data on liquid-phase irradiations of these compounds with 1.5 Mev. electrons indicate that processes characteristic of excitation in the π-electron system make a relatively greater contribution to the over-all radiolytic effect than was apparent in previously reported data on toluene, mesitylene and ethylbenzene.

Introduction

Studies in the photochemistry of toluene, mesitylene and ethylbenzene[4] have shown that excitation in the π-electron system with light of wave length near 2537 Å. results in dissociation chiefly in bonds β to the benzene ring. In the case of ethylbenzene vapor, resultant ultimate products consist mostly of methane and ethane with but small amounts of hydrogen. Data on electron irradiation of these compounds in the liquid state[4] indicated that the observed radiolytic effects might be mainly the result of primary physical effects in the side group plus a contribution from processes ensuant on excitation in the π-system such as are observed in the vapor state photolyses.

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(1) Contribution jointly from the Radiation Chemistry Project operated by the University of Notre Dame under Atomic Energy Commission contract AT(11-1)-38 and the Sinclair Research Project.

(2) Abstract from a thesis submitted by Thomas J. Sworski in partial fulfillment of requirements for the degree of Doctor of Philosophy at the University of Notre Dame.

(3) Sinclair Fellow.

(4) R. R. Hentz and M. Burton, THIS JOURNAL, **73**, 532 (1951).

TABLE I

COMPARISON OF GAS COMPOSITIONS AND QUANTUM YIELDS IN PHOTOLYSES.[a] COMPARISON WITH ETHYLBENZENE

Liquid	$\gamma^b \times 10^4$	$\%H_2$	$\gamma_{(H_2)} \times 10^4$	$\%CH_4$	$\gamma_{(CH_4)} \times 10^4$	$\%C_2H_6$	$\gamma_{(C_2H_6)} \times 10^4$	$\gamma_{(CH_3)}{}^c \times 10^4$
Ethylbenzene[4]	3.4	94	3.2	3.1	0.11	2.6	0.088	0,29
i-Propylbenzene	2.4	96	2.3	2.6	.06	1.0	.024	.11
t-Butylbenzene	1.3	96	1.2	2.4	.03	1.6	.021	.07
Vapor								
Ethylbenzene[4]		14		50		36		
i-Propylbenzene		17		27		56		
t-Butylbenzene		12		32		56		

[a] All photolyses of the vapors of *i*-propylbenzene and *t*-butylbenzene were at a temperature of 150–160°. The vapor pressures of the materials exposed were those corresponding to a temperature of 25°. For conditions of ethylbenzene photolysis see ref. 4. [b] Number of moles of gas produced volatile at −120° per einstein absorbed. Quantum yields of the individual gases are calculated from these values and the analyses. [c] Estimated on basis of assumption that all methane and ethane is formed *via* free methyl radicals. $\gamma_{(CH_3)}$ is a rough measure of the rate of "available free radical" production because light intensity remained fairly constant in these experiments. "Available free radicals" are those which escape from the cage in which they are formed.

Studies of *i*-propylbenzene and *t*-butylbenzene here reported give information on effect of increased number of methyl groups β to the benzene ring in photochemical studies and provide a more thorough test of the trends observed in electron irradiation data on toluene, mesitylene and ethylbenzene.

Experimental

Chemicals.—Eastman Kodak Co. White Label *t*-butylbenzene was fractionated in a 50-theoretical-plate column. A constant-boiling middle third was retained; $n^{20}D$ 1.4925; $n^{20}D$ (lit.) 1.4926.

Paragon Testing Laboratory *i*-propylbenzene was fractionated in the same 50-theoretical-plate column and a constant-boiling middle third was retained; $n^{20}D$ 1.4910; $n^{20}D$ (lit.) 1.4915.

After purification, these compounds were thoroughly degassed on a high vacuum system[4] and distilled into tubes with fresh sodium mirrors on the walls. Storage of the samples in these tubes for periods ranging from two days to several weeks ensured complete removal of water. Fresh sodium was always visible but hydrogen evolution had stopped long before the samples were used. Reaction cells were filled from these tubes on a high vacuum line. The degassing procedure was repeated on the liquid in the reaction cells to eliminate any hydrogen which may have resulted from the action of water in the samples on the sodium mirrors.

Procedures.—The Hanovia "L" burner was used in the photochemical studies. This lamp and the procedures employed have been described in a previous paper.[4] The cell used in this work for vapor-phase exposures was altered from that previously reported; it consisted of a quartz tube 15 mm. in internal diameter connected through a graded seal to a break-off seal and a Pyrex side arm. The liquid was contained in the side arm at room temperature and the vapor was exposed in the quartz tube at the temperature (150–160°) maintained by the lamp, which was enclosed in an aluminum cylinder open at the top.

Quantum yields were determined relative to liquid toluene. It was not found possible to obtain vapor phase quantum yields of sufficient reliability to warrant any conclusion other than that they are of the same order of magnitude as those for the liquid phase.

The analytical procedures have been described.[4] Mass spectrometric determinations were made on the condensable fraction and for positive identification of methane. The condensable fraction in the vapor phase photolysis was determined by mass-spectrometric analysis to be ethane. The yield of condensables in the liquid phase photolysis and electron bombardment was too low for accurate analysis.

All electron bombardments were made for five minutes at 1.50 Mv. and 2 μ amp. with the Radiation Chemistry Project HVEC Van de Graaff generator. Data on ethylbenzene showed no difference in effects of 1.50 Mv. and 1.80 Mv. electrons. Energy input was determined as previously described, except that in this work a Leeds and Northrup Speedomax recorder was employed.

As usual, all exposures produced a yellow coloration in the liquids or on the walls.

Results and Discussion

Photochemistry.—The data in Table I on vapor-phase photolyses of *i*-propylbenzene and *t*-butylbenzene again indicate that energy absorbed in the π-electron system of a compound containing a methyl group β to the benzene ring results in a low yield of hydrogen and a preponderance of methane and ethane. This result has been interpreted in terms of production of methyl radicals by a primary split of the β bond,[4] the strength of which has been estimated by Szwarc to be 63 kcal./mole.[5]

$$C_6H_5CR_2CH_3^* \longrightarrow C_6H_5CR_2 + CH_3 \qquad (1)$$

Reaction (1) may occur by internal conversion of electronic excitation energy into vibrational energy of the ground state with a subsequent maximum probability of rupture at the weakest bond in the molecule.

Because *t*-butylbenzene has no C–H bonds β to the ring, it is of special interest. Table I shows formation of hydrogen in photolysis of that compound, but in quantum yield of diminished amount. Since in work on photolysis of benzene it has been shown that the hydrogen yield is extremely low,[6] hydrogen produced in photolysis of *t*-butylbenzene probably comes practically entirely from γ C–H bonds. Some further speculation regarding origin of hydrogen in photolysis of all aromatic hydrocarbons so far investigated is contained in an Appendix to this paper.

Table I shows also that, in the liquid state, quantum yields of methane and ethane decrease in going from ethylbenzene to *i*-propylbenzene to *t*-butylbenzene successively. Speculation regarding coöperating and competing influences of (a) number of methyl radicals involved, (b) quantum yield of primary splits to give free methyl radicals, (c) influence of cage effect in reduction of number of free methyl radicals available for subsequent reaction, (d) effect of bond strength of the C–H link involved in methane production by reaction of free methyl with the particular substance (*i. e.*, whether it be primary, secondary or tertiary), and (e) effect

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(5) M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949).

(6) J. E. Wilson and W. A. Noyes, Jr., THIS JOURNAL, **63**, 3025 (1941); also S. Gordon, forthcoming publication.

of resultant steady-state concentration of free methyl on ethane production can be made to lead to a reasonably consistent picture of the variation both of quantum yields and of ratios of those yields. However, in view of the limited data, such qualitative speculation is not of particular value.

It is interesting that, as in earlier work, the data show a considerable suppression of hydrocarbon formation in liquid phase photolysis, such as may be expected from a Franck–Rabinowitch mechanism.[7]

Radiation Chemistry.—The yields of various products shown in Table II are compared with the relative number of parent groupings in Table III. In the work previously reported,[4] although there were some deviations from what might be expected on the basis of decomposition of the side group alone, the correlations were rather good. In this work, the deviation is greater than that observed in the original three compounds studied.[4] The G values (100 ev. yields) for hydrogen production decrease in order from ethylbenzene to *t*-butylbenzene as do the quantum yields in the liquid-phase photochemistry. The G value for hydrogen production from *t*-butylbenzene is actually less than that for such production from toluene. The relative G values for methane production are appreciably greater than the relative numbers of carbon-to-carbon bonds.

TABLE II

RESULTS OF 1.5 MEV. ELECTRON IRRADIATIONS OF LIQUIDS

	G^a	%H_2	%CH_4	%C_xH_y^{b}
i-Propylbenzene	0.25	67	29	3.7
t-Butylbenzene	.19	58	37	4.7

[a] The number of molecules of gas produced volatile at −120° per 100 ev. absorbed. [b] There is but little ethane in this fraction.

TABLE III

COMPARISON OF RELATIVE G VALUES FOR GAS PRODUCTION WITH THE RELATIVE NUMBER OF CORRESPONDING BONDS EXTERNAL TO THE BENZENE RING IN THE PARENT MOLECULE

	G'_t^{a}	B'_t^{b}	G'_{H_2}	B'_{C-H}	$G'_{CH_4+2C_xH_y}$	B'_{C-C}
i-Propylbenzene	1.79	1.67	1.29	1.50	9.1	3.00
t-Butylbenzene	1.36	2.00	0.85	1.75	8.8	4.00

[a] G'_t—this is the G value for total gas production relative to that in toluene as unity. The other G's have a corresponding significance. [b] B'_t—this is the ratio of the total number of bonds external to the C–C skeleton of the benzene ring in the given molecule to that in toluene. The other B's have corresponding significance for numbers of C–H and C–C bonds.

The data on the liquid state radiolyses are consistent with the idea that decomposition ensuant from highly excited states of the π-electron system tending to give products similar to those observed in the vapor phase photolyses (where a cage effect is inoperative) is an important part of the over-all decomposition. The data suggest that studies of vapor-phase irradiation might show that some suppression of hydrocarbon formation was occurring in the liquid state and that there is some correspondence between results of the photochemistry and of the radiation chemistry of the vapor phase.

There are two possible explanations for the correspondence between the results of the radiation chemistry and the photochemistry of these compounds. Primary excitation and ionizations of the π-electron system may greatly predominate over any others. There is no apparent reason why this should be so. It is more likely that a transfer of excitation or ionization occurs from the orbital in which it is primarily produced to a π-orbital in a time short compared to that required for decomposition from most of the primarily excited or ionized states. The fact that the ionization potential of a π-electron is less than that of any other electron in the molecule supports this view.

In the compounds ethylbenzene, *i*-propylbenzene and *t*-butylbenzene mass spectrometric data show the ion resultant from the loss of fifteen mass units to constitute from 60 to 75% of the total ionization.[8] Taking for ethylbenzene an approximate value of 50% of the total number of ions formed to be as in process (2), and assuming an average energy expenditure of 25 ev. per ion pair formed in the liquid, an average of 50 ev. would be expended per methyl radical produced.

$$C_6H_5CH_2CH_3 \rightsquigarrow C_6H_5CH_2^+ + CH_3 + e \quad (2)$$

If each methyl radical yielded methane the G value for methane production would be 2. This is almost a factor of ten times the over-all G value. This result indicates either that methyl radicals are disappearing largely in polymer formation or that the liquid state is suppressing reaction (2). If the latter explanation is correct the vapor phase should give an appreciably larger G value and the products should be richer in methane. We have not made any observations on this point.

Appendix

In photolysis of aromatic hydrocarbons hydrogen may result either from primary rupture of a bond or from a primary rearrangement process. The latter may be illustrated, in the cases we have studied, by ethylbenzene and by *i*-propylbenzene.

$$C_6H_5CRHCH_3 \longrightarrow C_6H_5CR{=}CH_2 + H_2$$

Since such a process requires less energy than a rupture its possibility cannot be denied. However, it is reasonable to suppose that it is nevertheless somewhat less probable. Yields of product are very small and possible styrene production has not been determined so that these remarks are on a purely speculative level.

Regarding rupture processes, low quantum yields in benzene photolysis[6] indicate that α_{C-H} makes practically no contribution. Thus, all hydrogen in photolysis of toluene is traceable to primary β_{C-H} splits and all hydrogen from *t*-butylbenzene to primary γ_{C-H} splits.

Table IV is an effort to reconcile the quantum

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[7] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[8] American Petroleum Institute Research Project 44, National Bureau of Standards, Catalog of Mass Spectral Data, Serial No. 305, 310, 319, contributed by the Humble Oil and Refining Company, Baytown, Texas.

TABLE IV

ANALYSIS OF QUANTUM YIELDS OF HYDROGEN IN THE LIQUID-PHASE PHOTOLYSES OF VARIOUS AROMATIC COMPOUNDS

	$\gamma \times 10^4$				
Source	Mesitylene[4] C_6H_3-$(CH_3)_3$	Toluene[4] C_6H_5-CH_3	Ethylbenzene[4] C_6H_5-CH_2CH_3	*i*-Propylbenzene C_6H_5CH-$(CH_3)_2$	*t*-Butylbenzene C_6H_5C-$(CH_3)_3$
Rearrangement (by difference)			2.1	1.2	
β_{C-H}	3.4	1 →	0.7 →	0.3	
γ_{C-H}	↑	↑	0.4 ←	0.8 ←	1.2
Total $(H_2) \times 10^4$	3.4	1	3.2	2.3	1.2

yields of hydrogen observed in photolyses of these compounds on the basis of these speculations. The guiding idea is that but a very small fraction of the excited molecules decompose. The amount of the decomposition *via* a particular path (*e. g.*, rupture of a β_{C-H} bond) then depends largely on the number of equivalent paths and the probability of decomposition along one such path. According to the scheme proposed each group makes a characteristic contribution to the total quantum yield (*i. e.* $\sim 1 \times 10^{-4}$ for β_{C-H} and $\sim 0.4 \times 10^{-4}$ for γ_{C-H}). The total quantum yields of hydrogen, $\gamma(H_2)$, were alone determined. The arrows indicate the direction of the speculations. The results are obviously consistent but data on the yields of the styrenes would be required to verify the suggested mechanisms.

NOTRE DAME, IND. RECEIVED NOVEMBER 9, 1950

[A CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF CONNECTICUT]

The Raman and Infrared Spectra of Nortricyclene

BY ELLIS R. LIPPINCOTT

Spectroscopic data for nortricyclene, tricyclo[2.2.1.0^{2,6}]heptane, C_7H_{10}, are reported. These include the Raman spectrum of the liquid with depolarization factors and the infrared spectrum of the vapor and solid in the region from 3500 to 250 cm.$^{-1}$. These spectral data, along with those for related molecules, have been considered in terms of postulated models. It is concluded that the best model for nortricyclene is one having a C_{3v} symmetry.

Nortricyclene, tricyclo[2.2.1.0^{2,6}]heptane, C_7H_{10}, has been synthesized by Roberts, Trumbull, Bennett and Armstrong.[1] From its chemical properties and method of preparation, they reasoned that the most probable molecular structure was one where the carbon atoms were connected by single bonds to form three five-membered rings and one three-membered ring, these being such that the molecule possessed a threefold axis of symmetry and three vertical planes of symmetry (see Fig. 1). Such a configuration would belong to a C_{3v} point group. Other structures of lower symmetry such as one containing two five-membered rings and two four-membered rings were not excluded but considered less likely from chemical evidence.

The purpose of this paper is to report the infrared spectrum of solid and gaseous nortricyclene in the region 3 to 40 μ, the Raman spectrum of the liquid with depolarization factors and to form conclusions about its structure from the data presented. These will be drawn from empirical characteristics of the spectra, such as the presence or absence of typical bond frequencies, and also from a comparison of spectral features with those expected from selection rules of the corresponding point groups. Additional data from related compounds has been used to determine the presence or absence of degenerate modes of vibration.

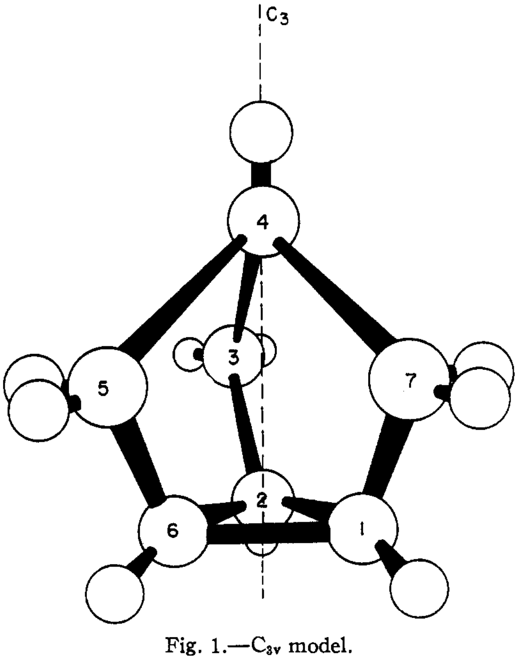

Fig. 1.—C_{3v} model.

Experimental

Infrared Spectra.—A sample of nortricyclene with b.p. 106° and m.p. 56° was kindly supplied for this work by Professor J. D. Roberts of the Chemistry Department, Massachusetts Institute of Technology. The infrared spectra were obtained on a modified Perkin-Elmer model 12B spectrometer in the Spectroscopy Laboratory at the Massachusetts Institute of Technology.[2] Prisms of calcium fluoride, sodium chloride, potassium bromide and thallium bromide–iodide were used in the appropriate regions from 3500 to 250 cm.$^{-1}$. Spectra of the solid were obtained by using liquid absorption cells of standard design. Liquid nortricyclene was placed in these cells and allowed to solidify. A Beckman IR-2 spectrometer in the Department of Chemistry at the University of Connecticut was used to rerun the spectrum of solid nortricyclene and to obtain spectra of liquid 3-bromonortricyclene in the region from 3500 to 660 cm.$^{-1}$. A suitable temperature control was not available to keep the sample liquid and consequently no liquid spectra were taken. The vapor spectra were obtained at

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[1] Roberts, Trumbull, Bennett and Armstrong, THIS JOURNAL, **72**, 3116 (1950).

[2] Lord, Lynch, Schumb and Slowinski, *ibid.*, **72**, 522 (1950).