

dation of camphor hydrazone implicated diazo-camphane as an intermediate in the oxidation process, and established that the tricyclene produced as the major product in a variety of solvents did not incorporate deuterium when ethanol- d_1 was used as the solvent. The latter workers consequently suggested that protonation of diazocamphane by hydroxylic solvents does not occur.⁴

We now report the results of a joint study of this problem.

Table I summarizes the experimental findings for both reactions.

TABLE I

Solvent	Temp., °C.	Base	Percentage tricyclene ^a	
			Hydrazone ^b	Sulphonhydrazone
C ₂ H ₅ OH	79	—	75 ^c	
C ₂ H ₅ OH	79	+	65	
C ₂ H ₅ OH	138	+		86
CF ₃ CH ₂ OH	76	—	13 ^d	
(—CH ₂ OH) ₂	80	—	74	
(—CH ₂ OH) ₂	82	+	55	
(—CH ₂ OH) ₂	138	—	57	17
(—CH ₂ OH) ₂	138	+		25
HO(CH ₂) ₃ OH	80	—	75	
HO(CH ₂) ₃ OH	132	+		46
CH ₃ O(CH ₂) ₂ OH	80	—	62	
C ₂ H ₅ O(CH ₂) ₂ OH	132	+		92
(CH ₃ OCH ₂) ₂	81	—	98	

^a The volatile products are tricyclene and camphene.

^b The oxidation of camphor hydrazone has been found to be more sensitive to variations in the mercuric oxide than previously suspected. Using a uniform sample of mercuric oxide and freshly distilled camphor hydrazone, an error of $\pm 3\%$ was observed for experiments made over a 3–4 week period.

^c The discrepancy between this value and the $>97\%$ tricyclene reported earlier³ is probably due to the use of different samples of mercuric oxide. A third sample recently investigated gave 98% tricyclene under similar conditions.

^d Tricyclene is recovered unchanged after 1-hr. reflux in CF₃CH₂OH.

The striking change in the predominant product from the oxidation reaction, when β,β,β -trifluoroethanol is used as a solvent in place of ethanol is most reasonably interpreted in terms of the previously mentioned solvent protonation mechanism. The rather mediocre protonating ability of ethanol has been further demonstrated by the large proportion of tricyclene obtained from base-catalyzed decomposition of camphor sulphonhydrazone in ethanol at 138°.

The previously reported³ insensitivity of the mercuric oxide oxidation reaction to variations in the solvent is now thought to be due to at least two factors. First, none of the solvents investigated earlier were strongly protonating (in terms of the Bamford-Stevens reaction). Second, the heterogeneous mercuric oxide phase could easily catalyze the decomposition of diazocamphane to tricyclene. Evidence supporting this proposal may be found

in the smaller change in the tricyclene–camphane product ratio observed for the mercuric oxide oxidation reaction in ethylene glycol *vs.* ethanol (1.5 \times) as compared with the sulphonhydrazone decomposition reaction in the same two solvents (18 \times). This comparison is not strictly valid, since the temperatures at which these reactions are carried out are quite different. A higher temperature would, however, be expected to increase the rate of tricyclene formation.²

The rather slight effect that added base appears to have on product composition is expected if the protonation step is interpreted as proceeding mainly by general acid catalysis—*i.e.*, by ROH and not ROH₂⁺.

The experimental procedures used in this work have been described in previous papers.^{1a,3}

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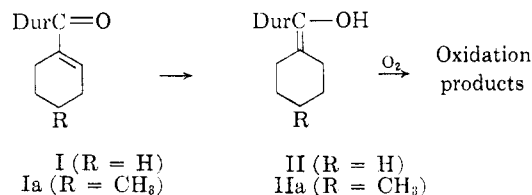
1,4-Reduction of 1-Duroylcyclohexenes

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In the synthesis of cyclohexyl duroyl ketone by reduction of the corresponding α,β -unsaturated ketone I with lithium aluminum hydride, cyclohex-



anone, and duroic acid were obtained as by-products. Since these compounds are the expected oxidative cleavage products² of the enol II of cyclohexyl duroyl ketone, it seemed likely that 1,4-reduction had occurred.³ Treatment of cyclohexyl duroyl ketone with lithium aluminum hydride, on the other hand, converted it nearly quantitatively into the corresponding carbinol.

Oxidative cleavage has been observed also with 1-duroyl-4-methylcyclohexene (Ia). Reduction without addition of oxygen gave only the corresponding saturated ketone; when oxygen was passed into the reaction mixture just before and just after hydrolysis, however, 4-methylcyclo-

(3) W. Reusch, M. Di Carlo, and L. Traynor, *J. Org. Chem.*, **26**, 1711 (1961).

(4) Unfortunately the glycol solvents used in the sulphonhydrazone decomposition studies were not employed in the latter investigation.

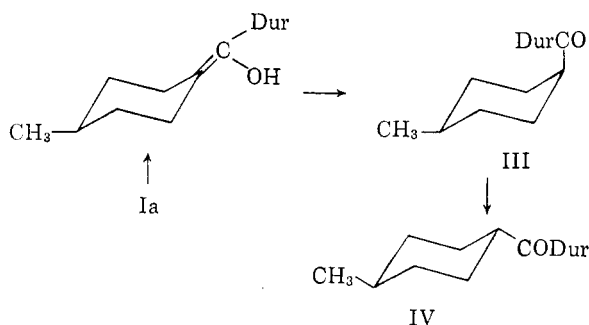
(1) Chas. Pfizer and Co. Fellow, 1960–1961.

(2) E. P. Kohler, *Am. Chem. J.*, **36**, 177 (1906).

(3) R. E. Lutz and D. F. Hinkley, *J. Am. Chem. Soc.*, **72**, 4091 (1950).

hexanone was formed, and the yield of the saturated ketone was reduced.

The *trans* isomer IV, prepared from durene and *trans*-4-methylcyclohexanecarbonyl chloride, proved to be different from the ketone obtained by the reduction; the latter accordingly was assigned the *cis* structure III, since this isomer would be expected if the intermediate enol IIa undergoes rate-controlled protonation on the less hindered side.⁴ It was not determined which substituent in the *cis* ketone occupies the axial position. This assignment is supported by the observation that, in the presence of sodium ethoxide, this ketone



isomerized to ketone IV, which is not altered by this treatment.

Experimental⁵

1-Duroylcyclohexene.—This ketone was prepared as described earlier⁶ and by acylation of durene with cyclohexene-1-carbonyl chloride.⁷ The yield by the latter method was 58%. Oxidation of 0.420 g. (0.00173 mole) of the ketone with alkaline hydrogen peroxide⁸ gave 0.377 g. (85%) of the epoxide, m.p. 93–94°.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.88; H, 8.55.

Cyclohexyl Duryl Ketone.—Acylation of durene (taken in excess) in methylene chloride with 1.23 g. (0.00842 mole) of cyclohexanecarbonyl chloride⁹ in the presence of aluminum chloride gave 1.20 g. (58%) of cyclohexyl duryl ketone, m.p. 106–107°. The infrared spectrum shows a carbonyl band at 1693 cm^{-1} .

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.65; H, 10.19.

Reduction of 1-Duroylcyclohexene.—A solution of 2.24 g. (0.00924 mole) of 1-duroylcyclohexene in 25 ml. of dry ether was added with stirring over a 7-min. period to slurry of 0.380 g. (0.0100 mole) of lithium aluminum hydride in 25 ml. of dry ether. The mixture was stirred for 10 min., cooled, and decomposed with dilute sulfuric acid. Extraction of the organic layer with 10% aqueous potassium hydroxide solution and acidification of this extract gave 25 mg. of solid which, when recrystallized from benzene, did not depress the melting point of duroic acid.

Evaporation of the solvent from the base-extracted organic layer left an oil which, when taken up in ethanol, gave 0.875

g. (33%) of cyclohexyl duryl ketone. The ketone did not depress the melting point of the product obtained by acylation of durene with cyclohexanecarbonyl chloride. The ethanol filtrate from which the ketone separated was treated with a solution of 2,4-dinitrophenylhydrazine, and the reaction mixture was allowed to stand for 10 hr. at room temperature. The red precipitate, after recrystallization from ethanol-ethyl acetate, weighed 0.460 g. and did not depress the melting point of the 2,4-dinitrophenylhydrazone of cyclohexanone, m.p. 160–161°. The yield of cyclohexanone was 18% based on this derivative.

Reduction of Cyclohexyl Duryl Ketone.—Addition of a solution of 2.00 g. (0.00820 mole) of cyclohexyl duryl ketone in ether to a solution of 1.21 g. (0.0328 mole) of lithium aluminum hydride in ether gave, after the usual hydrolysis, 1.96 g. (97%) of cyclohexyldurylcarbinol, m.p. 94–95°. The infrared spectrum was a broad hydroxyl group band at 3420–3560 cm^{-1} .

Anal. Calcd. for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.68; H, 10.37.

1-Duroyl-4-methylcyclohexene (Ia).—Acylation of durene with 1.72 g. (0.0109 mole) of 4-methyl-1-cyclohexenecarbonyl chloride, prepared from the corresponding acid,⁹ gave 1.92 g. (69%) of the desired ketone, m.p. 130–132°. The infrared spectrum has bands at 1652, 1634, and 800 cm^{-1} , which were assigned, respectively, to a carbonyl group, a carbon-carbon double bond, and a trisubstituted olefin.

Anal. Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.41; H, 9.45.

Treatment of 0.130 g. of this ketone with 0.05 g. of 10% palladium on charcoal at 300° for 1 hr. gave a solid that melted at 144–145° after recrystallization from ethanol and did not depress the melting point of *p*-tolyl duryl ketone.¹⁰

Reduction of 1-Duroyl-4-methylcyclohexene.—When 1.50 g. (0.00586 mole) of the unsaturated ketone Ia was treated with 0.890 g. (0.0234 mole) of lithium aluminum hydride under approximately the conditions that caused cleavage of 1-duroylcyclohexene, the only product found was the saturated ketone III (1.23 g., 81%). It melted at 95–96° after recrystallization from ethanol.

Anal. Calcd. for $C_{18}H_{26}O$: C, 83.66; H, 10.14. Found: C, 83.46; H, 10.06.

The yield of saturated ketone decreased to 26% when oxygen was passed through the reaction mixture for 5 min. just before and just after hydrolysis. When the ethanol filtrate from which this solid crystallized was treated with 2,4-dinitrophenylhydrazine solution, 0.083 g. of orange material was produced; it did not depress the melting point of the corresponding derivative of 4-methylcyclohexanone, m.p. 130–131°. The yield of 4-methyl-cyclohexanone, based on this derivative, was 5%.

***trans*-1-Duroyl-4-methylcyclohexane (IV).**—Acylation of durene with 1.66 g. (0.0104 mole) of *trans*-4-methylcyclohexanecarbonyl chloride, prepared from *trans*-4-methylcyclohexanecarboxylic acid¹¹ with thionyl chloride, gave 1.67 g. (63%) of the *trans* ketone IV, m.p. 109–110°. The infrared spectrum of this material is almost identical with that of the ketone obtained by lithium aluminum hydride reduction of 1-duroyl-4-methylcyclohexene (Ia).

Isomerization of the Ketone III to *trans*-1-Duroyl-4-methylcyclohexane (IV).—Treatment of 0.200 g. of the ketone III with sodium ethoxide in ethanol⁴ gave 0.180 g. of solid that melted at 109–110° without purification and did not depress the melting point of *trans*-1-duroyl-4-methylcyclohexane. The latter was unchanged by this treatment.

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(5) All melting points are uncorrected. Microanalyses were carried out by Mr. Josef Nemeth and Mrs. A. S. Bay.

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