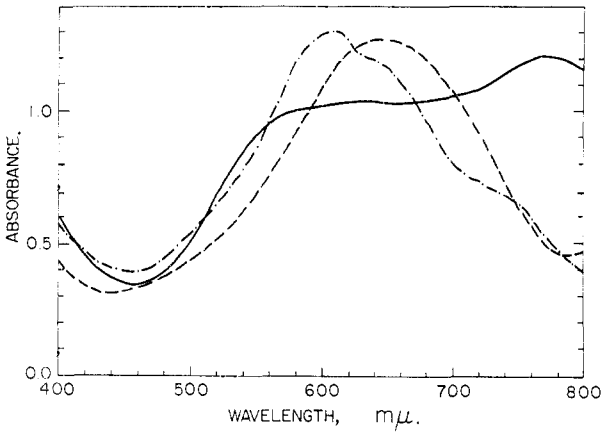

Fig. 2.—The visible spectra of indanthrone (-----); N-methylindanthrone (---·---·---); and N,N'-dimethylindanthrone (– – –) in KBr.

This finding confirms the assignment of the various modifications to polymorphism[29] and eliminates the possibility that some of these modifications could have resulted from the existence of indanthrone in different tautomeric forms (*e.g.*, I and III).

Since, in addition to the indanthrones, the structures of a large number of vat dyes consist of anthraquinone nuclei that are linked by one or more N–H bridge, the assignment of structure III to indanthrone may have far-reaching implications. If other anthraquinone dyes should also be found to exist in the analogous enol forms, it may be necessary to revise many of our existing views concerning dyes of this type. In that event it may also be possible to gain a better understanding of the forces that bind these dyes to the fibers and thus perhaps arrive at an answer to this problem which is of fundamental importance to dye chemistry.

Acknowledgments.—The author is indebted to Dr. J. Weinstein for his assistance with the experimental work and to Cpl. D. C. O'Brien for the mass spectrometric analysis of the deuterated indanthrones.

NATICK, MASSACHUSETTS

(29) G. Susich, *Anal. Chem.*, **22**, 425 (1950).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND THE CHANDLER LABORATORY OF COLUMBIA UNIVERSITY

The Stereochemistry of the SN2′ Reaction. I. Preparation of Pure *trans*-6-Alkyl-2-cyclohexen-1-ols

BY GILBERT STORK AND WILLIAM N. WHITE[1]

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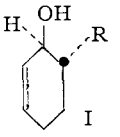
The synthesis of the substances mentioned in the title in which the alkyl groups are methyl, isopropyl and *t*-butyl is described. The reduction of *N-unsubstituted* anilines with lithium and ammoniai s shown to be an effective route to cyclohexenones.

Consideration of possible systems in which the SN2′ reaction might be expected to occur and which would allow one to demonstrate whether the displacing group enters *cis* or *trans* to the departing substituent, suggested the suitability of *trans*-6-alkyl-2-cyclohexen-1-ols (I) for this purpose.[2]



I

Suitable precursors of the cyclohexenols (I) appeared to be the corresponding cyclohexenones which are available by means of the Birch reduction of 2-alkylanisoles or N,N-dimethyl-2-alkylanilines.[3]

The compounds which were required for this study were those in which the alkyl group R in I is methyl, isopropyl and *t*-butyl, and the preparation and reduction of the corresponding 2-substituted anisoles was investigated first. 2-Methylanisole is, of course, readily available, while 2-isopropylanisole has been described[4]; we prepared it by methylation of commercially available 2-isopropylphenol. 2-*t*-Butylanisole has not been described, but the corresponding phenol is known. It was prepared by Hart[5] by treating *p*-bromophenol with isobutylene in the presence of sulfuric acid, followed by debromination by treatment with Raney nickel alloy and base. This preparation was repeated, and a similar route starting from *p*-chlorophenol was also followed. Both methods appeared to produce the same material which, although it did not appear completely homogeneous, produced the desired methyl ether in high yield. The Birch reduction of 2-*t*-butylanisole gave, however, unsatisfactory results and the synthesis of N,N-dimethyl-2-*t*-butylaniline was investigated in the hope that it would be more suitable for the reduction step. 2-*t*-Butylaniline is a known compound; it has been prepared by Shoesmith and Mackie[6] from 2,4-dinitro-*t*-butylbenzene, by selective reduction to 2-nitro-4-amino-*t*-butylbenzene followed by deamination and reduction. We followed this procedure, which gave the desired product in 30% over-all yield from benzene. The intermediate

(1) Public Health Service Predoctoral Fellow, 1951–1953.

(2) The background and mechanism of the SN2′ reaction will be considered in the paper which follows. A preliminary communication containing some of this material has been published: G. Stork and W. N. White, THIS JOURNAL, **75**, 4119 (1953).

(3) A. J. Birch, *J. Chem. Soc.*, 593 (1946).

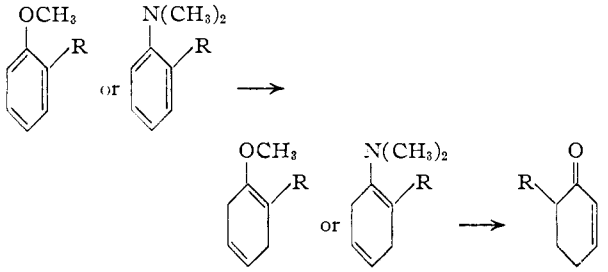
(4) V. Tambovsteva and I. P. Tsukervanik, *J. Gen. Chem. U.S.S.R.*, **15**, 820 (1945); M. Fileti, *Gazz. chim. ital.*, **16**, 113 (1886).

(5) H. Hart, THIS JOURNAL, **71**, 1966 (1949).

(6) J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2334 (1928).

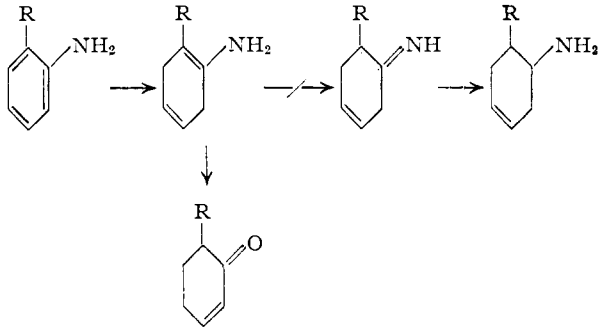
2-nitro-4-amino-*t*-butylbenzene was also prepared by a method which ensures its identity: 3-nitro-4-*t*-butylbenzoic acid[7,8] was converted by Hofmann degradation of its amide into the same monoamino compound which had been obtained by Shoesmith and Mackie.[6] Conversion into the N,N-dimethyl derivative was accomplished *via* formylation and lithium aluminum hydride reduction to the N-methyl compound; repetition of the process afforded the desired amine.

With the requisite starting materials available a study was made of the best conditions for the Birch reduction to the desired cyclohexenones. The expected results are



Initial attempts using sodium in liquid ammonia were not very encouraging, especially with 2-*t*-butylanisole which was almost completely unaffected; even N,N-dimethyl-2-*t*-butylaniline gave only about 10% reduction. These poor results, particularly with the difficultly accessible N,N-dimethyl-*t*-butylaniline, led us to give serious consideration to the possibility of reducing the more easily obtained primary amine. Birch[9] has noted that some cyclohexenone could be obtained by the reduction of aniline with sodium in liquid ammonia, but this suggestive observation was not pursued.

We have now found that the reduction of primary aromatic amines is a general reaction and gives substantially the same yields in the Birch reduction as that of the commonly used N,N-dimethyl derivatives. This result is of some practical significance as the primary amines are normally the precursors of the tertiary. It implies

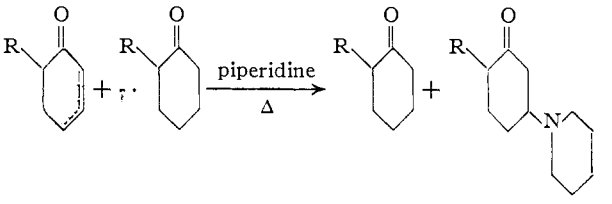


also that under the conditions of the Birch reduction, there is little tautomerization of the intermediate primary enamine to an imine, as the latter would have been reduced to an amine from which cyclohexenone derivatives could not be produced on hydrolysis.

Using *o*-toluidine as a model compound, the effect of changing alkali metal, proton donor, concentration and order of addition was studied with the result that the best conditions were found to be the addition of a solution of 1 mole of amine in 400 ml. of dry *t*-butyl alcohol to a solution of 4 g. atoms of lithium in 1 liter of liquid ammonia. Under these conditions *o*-toluidine and 2-*t*-butylaniline were reduced in about 70 and 50% yields, respectively. Other reductions are mentioned in the Experimental section. After this phase of our work was completed Wilds and Nelson[10] described a very efficient reduction method for anisole derivatives which is very similar to the one above. Their very thorough study makes it likely that our results with anilines could be further improved by utilizing a co-solvent such as ether or 1,2-dimethoxyethane. One practical advantage of using amines as starting materials in the Birch reduction, which is perhaps worth emphasizing, is that the unreduced basic starting material is easily separated from the neutral ketonic products.

Infrared studies of the ketonic hydrolysis products showed that in all cases the expected unsaturated ketone was contaminated with the corresponding *saturated* ketone,[11] arising presumably from further reduction of the conjugated cyclohexadiene formed under the influence of the basic medium.

The presence of saturated ketone made it necessary to devise a method for the efficient purification of the desired cyclohexenones. Such a purification was attempted *via* dinitrophenylhydrazones and semicarbazones without success. It was eventually achieved by taking advantage of the quantitative addition of piperidine to the 6-alkyl-2-cyclohexen-1-ones when the components were refluxed for a few hours. Under these conditions the 2 alkylcyclohexanones did not react



The piperidinoketones were easily separated by extraction into dilute acid, and the saturated ketone could thus be completely eliminated. The procedure had the further advantage that, since the β,γ-unsaturated ketones could serve as well as their α,β-unsaturated isomers in this reaction, it was not necessary to use vigorous acid hydrolysis of the dihydroanilines from the Birch reduction, a procedure which conjugates the initially formed

(7) W. Kelbe and G. Pfeiffer, *Ber.*, **19**, 1723 (1886).

(8) This nitrobenzoic acid was prepared in this study by oxidation of 4-*t*-butyltoluene to 4-*t*-butylbenzoic acid (*cf. Org. Syntheses*, **27**, 84 (1941); also K. T. Serijan, H. E. Hipsher and L. C. Gibbons, THIS JOURNAL, **71**, 873 (1949)) which was converted to its methyl ester by Fischer esterification. The latter substance was nitrated (*cf.* "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 372) and the nitro ester was hydrolyzed to the known 3-nitro-4-*t*-butylbenzoic acid.

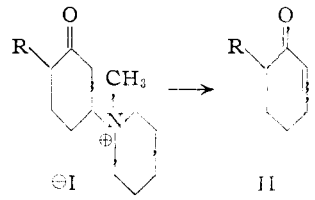
(9) A. J. Birch, *Nature*, **160**, 754 (1947).

(10) A. L. Wilds and N. A. Nelson, THIS JOURNAL, **75**, 5360 (1953).

(11) The relative amounts of saturated and unsaturated ketones in specific instances will be found in the Experimental section.

β,γ-isomer with considerable accompanying polymerization.[12]

Regeneration of the pure α,β-unsaturated ketones was effected by converting the piperidino ketones into their crystalline methiodides and warming these with pyridine



The over-all recovery of pure α,β-unsaturated ketone was about 80% by this procedure which was used to prepare the cyclohexenones (II) in which R is methyl, isopropyl and *t*-butyl.

Reduction of the cyclohexenones to cyclohexenols of the desired stereochemistry (I) was the next problem. It seemed likely that lithium aluminum hydride reduction would accomplish the desired end since this reagent is known to give predominantly the thermodynamically more stable of two possible alcohols—except in cases of extreme steric hindrance.[13]

When the alkylcyclohexenones discussed above were reduced with lithium aluminum hydride in ether for 30 minutes at 0°, unsaturated alcohols were formed. These were purified by conversion into their 3,5-dinitrobenzoates which were hydrolyzed, after crystallization to constant melting point, to give pure 6-alkyl-2-cyclohexen-1-ols (I) in which the alkyl group was methyl, isopropyl and *t*-butyl. The anticipated *trans* stereochemistry of these alcohols was demonstrated by catalytic hydrogenation to the corresponding 2-alkylcyclohexanols which were converted into their 3,5-dinitrobenzoates. These esters were obtained in about 90% yields from the original cyclohexenol and the homogeneity of the latter was further corroborated by the fact that the crude esters melted within 2–3° of the melting points of the pure esters; one recrystallization eliminated this discrepancy.

The authentic *trans*-2-alkylcyclohexanols needed for comparison were prepared by the reduction of the proper 2-alkylcyclohexanones with sodium in moist ether,[14,15] and the alcohols were transformed into their 3,5-dinitrobenzoates. *trans*-2-Methylcyclohexanol and *trans*-2-isopropylcyclohexanol have been prepared previously.[16,17]

(12) The method would presumably still be applicable should the saturated ketone form an enamine under these conditions, as the latter would be hydrolyzed during the acid extraction of the piperidinoketone.

(13) For a possible explanation of this result see J. H. Brewster, THIS JOURNAL, **76**, 6361 (1954).

(14) This process is known to give the thermodynamically more stable of the two possible alcohols, *trans* in the cases under discussion; see D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(15) 2-Methylcyclohexanone is commercially available. 2-Isopropylcyclohexanone and 2-*t*-butylcyclohexanone were prepared by Raney nickel reduction of the corresponding phenol, followed by oxidation with dichromate–sulfuric acid. They have been prepared previously; see references 17 and 18.

(16) (a) A. Skita and W. Faust, *Ber.*, **64**, 2878 (1931); (b) W. Hückel and K. Hagenguth, *ibid.*, **64**, 2892 (1931); (c) R. B. Turner, THIS JOURNAL, **72**, 878 (1950).

(17) G. Vavon and A. Callier, *Bull. soc. chim.*, **41**, 677 (1927).

(18) L. Schmerling, THIS JOURNAL, **69**, 1123 (1947).

Melting point comparisons with the dinitrobenzoates obtained after hydrogenation of our 6-alkyl-2-cyclohexen-1-ols I conclusively demonstrated the *trans* configuration of the latter substances which may now be used, after conversion of the hydroxyls into displacable groups, to study the occurrence and mechanism of the SN2′ reaction. This aspect of the problem is discussed in the following paper.

Experimental

2-Isopropylanisole.—Commercial 2-isopropylphenol was methylated with dimethyl sulfate and aqueous sodium hydroxide to give 2-isopropylanisole in 85% yield. This had b.p. 194.5–195.5° (reported[4] b.p. 198–199°).

2-*t*-Butylphenol.—This was prepared from *p*-bromophenol, following the procedure of Hart.[5] The over-all yield was 55% of colorless oil, b.p. 122–124° (18 mm.) (reported[5] b.p. 217–220°). There was some doubt about the purity of the product since, although it gave an aryloxyacetic acid derivative melting at 144.5–145° as reported,[5] it absorbed only 61% of the theoretical amount of hydrogen in the presence of Raney nickel catalyst at 150° and 100 atm., and approximately 20% of it was insoluble in 20% sodium hydroxide solution. In an attempt to get purer material, the preparation was carried out using *p*-chlorophenol as starting material: *t*-butyl alcohol (95 g.) was added dropwise over 2 hr. to a well stirred solution of 128 g. of *p*-chlorophenol, 150 cc. of concentrated sulfuric acid and 10 cc. of water. The mixture was kept at 65–75° during the addition and for an additional hour. After dilution with water, extraction with ether, washing with saturated ammonium chloride solution and drying over sodium sulfate, fractionation gave 107 g. (58%) of **4-chloro-2-*t*-butylphenol**, b.p. 144–146° (26 mm.).

Anal. Calcd. for $C_{10}H_{13}OCl$: C, 65.04; H, 7.09. Found: C, 65.40; H, 7.36.

Treatment of the chlorophenol with Raney nickel alloy and base, as described by Hart[5] for the corresponding bromo compound, gave material which did not appear much purer than the product from the bromo compound. Both samples were, however, suitable for conversion to the methyl ether.

2-*t*-Butylanisole.—Methylation with dimethyl sulfate and aqueous sodium hydroxide gave 2-*t*-butylanisole in 84% yield, b.p. 102.5–104.0° (22 mm.).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.57; H, 9.78.

2-*t*-Butylaniline.—This was prepared essentially by the procedure of Shoesmith and Mackie[6] over the route 2,4-dinitro-*t*-butylbenzene → 4-amino-2-nitro-*t*-butylbenzene → 2-nitro-*t*-butylbenzene → 2-*t*-butylaniline. The intermediates had the reported physical constants and the over-all yield from *t*-butylbenzene was 40%. Rigorous proof of the position of the amino group in the partial reduction product of 2,4-dinitro-*t*-butylbenzene was obtained by making 4-amino-2-nitro-*t*-butylbenzene in the following manner: 3-nitro-4-*t*-butylbenzoic acid[7,8] was converted into its acid chloride by refluxing for 5 hr. a mixture of 169 g. of nitro acid with 125 cc. of thionyl chloride. The excess thionyl chloride was distilled off at atmospheric pressure and the residue was distilled to give 169 g. (92%) of **3-nitro-4-*t*-butylbenzoyl chloride** as an almost colorless oil, b.p. 174–176° (16 mm.).

Anal. Calcd. for $C_{11}H_{12}O_3NCl$: C, 54.67; H, 5.01. Found: C, 54.72; H, 4.95.

The acid chloride was transformed into **3-nitro-4-*t*-butylbenzamide** by passing a rapid stream of gaseous ammonia through a cooled solution of 165 g. of 3-nitro-4-*t*-butylbenzoyl chloride in 500 cc. of dry ether for 1 hr. The mixture was poured into 500 cc. of water and the separated ether layer was washed with sodium bicarbonate and dried over potassium carbonate. Removal of the ether left a residue which was crystallized from benzene to give 142 g. (94%) of large, colorless crystals, m.p. 85.0–86.0°.

Anal. Calcd. for $C_{11}H_{14}O_3N_2$: C, 59.45; H, 6.35. Found: C, 59.43; H, 6.28.

A Hofmann degradation was run by mixing 18.0 g. of the powdered amide with a solution of 16 g. of bromine in 100

cc. of 10% sodium hydroxide solution. After the solid had dissolved, 40 cc. of 30% sodium hydroxide solution was added and the mixture was heated on the steam-bath for 1 hr. After addition of 100 cc. of water, the separated oil was taken up in ether and the ether layer was dried over potassium carbonate and distilled, giving an orange solid, b.p. 143–147° (2.5 mm.), m.p. 48–53°, raised to 57.5–58.5° by recrystallization from cyclohexane (59% yield). This was identical with the material obtained more conveniently by the procedure of Shoesmith and Mackie.[6] Reductive deamination was performed with ethanol as described by Shoesmith and Mackie[6] and was not improved by using hypophosphorus acid or sodium hypophosphite as the reducing agents, the yield in all cases being about 65%. Final reduction of 2-nitro-*t*-butylbenzene with Raney nickel and hydrogen (1 atm.) in ethanol gave the desired 2-*t*-butylaniline as a colorless oil, b.p. 103.0–104° (11 mm.), as reported.[6] The N-acetyl derivative had m.p. 161.0–161.6° after crystallization from benzene (reported[6] m.p. 161°).

N,N-Dimethyl-2-*t*-butylaniline.—Transformation of the aniline to its dimethyl derivative was accomplished by successive formylation and reduction; a mixture of 13.7 g. of 2-*t*-butylaniline, 14.0 g. of 88% formic acid and 60 cc. of toluene was refluxed 1 hr. A water separator was attached to the system and refluxing was continued until 9.0 cc. of water was collected (5 hr.). Distillation of the reaction mixture gave 15.5 g. (95%) of **2-*t*-butylformanilide** as a colorless liquid, b.p. 132–132.5° (2.5 mm.), which was crystallized from ligroin; m.p. 75.5–76.5°.

Anal. Calcd. for $C_{11}H_{15}ON$: C, 74.54; H, 8.53. Found: C, 74.43; H, 8.38.

The formamide was reduced by adding, over a period of 20 minutes, a solution of 9.7 g. of 2-*t*-butylformanilide in 30 cc. of dry tetrahydrofuran to a stirred suspension of 2.5 g. of lithium aluminum hydride in 150 cc. of dry ether. After refluxing for 2 hr., the mixture was cooled and 20 cc. of ethyl acetate was added cautiously, followed by 100 cc. of 15% sodium hydroxide solution. The residue after removal of the ether was steam distilled until 500 cc. had been collected. The distillate was extracted with ether, and drying and fractionation gave 8.5 g. (95%) of **N-methyl-2-*t*-butylaniline** as a clear liquid, b.p. 110–112° (12.5 mm.).

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50. Found: C, 80.65; H, 10.62.

The formylation procedure described above was repeated on N-methyl-2-*t*-butylaniline and gave **N-methyl-2-*t*-butylformanilide** in 94% yield as a very viscous oil, b.p. 109–110° (2.3 mm.).

Anal. Calcd. for $C_{12}H_{17}ON$: C, 75.35; H, 8.96. Found: C, 75.52; H, 9.00.

Lithium aluminum hydride reduction as described above gave 95% yield of the desired N,N-dimethyl-2-*t*-butylaniline, b.p. 214–215° at atmospheric pressure.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80. Found: C, 81.38; H, 11.00.

The **picrate** was crystallized three times from ethanol and had m.p. 169–170°.

Birch Reductions.—The preparation of 6-alkyl-2-cyclohexenones by Birch reduction was carried out by the following method: Lithium (1.4 g., 0.2 mole) was dissolved in 100 cc. of liquid ammonia with stirring and a solution of 0.05 mole of the aniline or anisole in 20 cc. of *t*-butyl alcohol was stirred in during five minutes. The mixture was stirred until decolorization (about 1 hr.), and 150 cc. of water was then added cautiously. The water solution was allowed to warm to 25° and was extracted with ether. After removal of the ether and *t*-butyl alcohol, 100 cc. of ice-cold 5% hydrochloric acid was added, and the mixture was heated from 0 to 90° in 20 minutes, with swirling. After cooling, the mixture was extracted with ether; the ether solution was dried over potassium carbonate and fractionated. When the starting material was an aniline, it could be recovered from the acid solution by making basic and extracting with ether.

The reaction products were separated into saturated and unsaturated ketones by the addition of piperidine to the distilled ketonic products resulting after hydrolysis of the Birch reduction mixtures, following the procedure described below. After addition of amine was complete, separation into basic and neutral fractions gave the yields of unsaturated and saturated ketones which are shown in Table I.

TABLE I

Compound	Yield of saturated ketone, %	Yield of unsaturated ketone, %
Anisole	10	49
Aniline	27	42
N,N-Dimethylaniline	32	37
o-Cresol	0	0
2-Methylanisole	17	52
o-Toluidine	18	50
N,N-Dimethyl-*o*-toluidine	22	43
2-Isopropylanisole	13	13
2-*t*-Butylanisole	5	10
2-*t*-Butylaniline	23	25
N,N-Dimethyl-2-*t*-butylaniline	20	24

3-(1-Piperidyl)-6-alkylcyclohexanones.—One-tenth of a mole of the ketone mixture from the Birch reduction was refluxed with 0.3 mole of piperidine for 4 hr. The mixture was cooled and poured into 200 cc. of 10% hydrochloric acid solution. The resulting solution was extracted four times with ether (these extracts could be worked up to obtain the saturated ketone or a mixture of the ketone and an aromatic ether if the latter was the starting material in the Birch reduction). The acid solution was made alkaline with 20% sodium hydroxide and extracted with ether. The ether solution was dried over potassium carbonate and fractionated to give yields corresponding to quantitative conversion of the unsaturated ketone to the aminoketone. The properties of the 3-(1-piperidyl)-6-alkylcyclohexanones thus prepared are given in Table II.

TABLE II

Alkyl group	B.p., °C.	Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Picrate m.p., °C.
Methyl	110	2.0	73.79	73.69	10.84	10.89	174–174.1
Isopropyl	116	1.2	75.28	75.07	11.28	11.23	161.5–161.9
t-Butyl	123	1.1	75.89	75.65	11.47	11.23	180–180.1

3-(1-Piperidyl)-6-alkylcyclohexanone Methiodides.—The piperidinoketone obtained as above (0.1 mole) was dissolved in 0.8 mole of methyl iodide. The mixture was kept at 5° for 3 hr., and the temperature was allowed to rise to 20° over a 3-hr. period. After staying at that temperature for 10 hr., the solid mass was scraped from the flask, pressed on a filter and dried in air. It was crystallized from *n*-butyl alcohol to give the following 3-(1-piperidyl)-6-alkylcyclohexanone methiodides:

Alkyl group	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	91	174.5–175	46.30	46.50	7.17	7.31
Isopropyl	93	177.5–178	49.32	49.37	7.73	7.70
t-Butyl	96	205.5–206	50.66	50.75	7.97	8.12

6-Alkyl-2-cyclohexen-1-ones.—One-tenth of a mole of 3-(1-piperidyl)-6-alkylcyclohexanone methiodide was mixed with 0.3 mole of pyridine and heated on the steam-bath with occasional stirring until solution was complete. The solution was then heated and stirred 1 more hr. at 90° and was then poured, while still warm, into 200 cc. of 10% hydrochloric acid solution. This mixture was extracted with ether and the ether solution was dried and fractionated to yield the spectroscopically pure α,β-unsaturated ketones. The properties of these 6-alkyl-2-cyclohexen-1-ones are given in Table III.

TABLE III

Alkyl group	Yield, %	B.p., °C.	Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl[a]	82	74–75	24				
Isopropyl[b]	90	94–94.3	18	78.21	78.06	10.21	10.19
t-Butyl	80	106–106.5	24	78.89	79.00	10.59	10.56

[a] 2,4-Dinitrophenylhydrazone, m.p. 161–162° (reported[3] m.p. 156–157°). [b] 2,4-Dinitrophenylhydrazone, m.p. 133–134°.

trans-**6-Alkyl-2-cyclohexen-1-ols.**—A solution of 0.2 mole of 6-alkyl-2-cyclohexen-1-one in 100 cc. of dry ether was added dropwise over a period of 15 minutes to a stirred suspension of 4.5 g. of powdered lithium aluminum hydride in

300 cc. of dry ether kept at 0° by external cooling. The mixture was stirred an additional 15 minutes and 25 cc. of acetone was then added cautiously, followed by 25 g. of ice. The reaction mixture was poured with stirring into 350 cc. of cold 5% hydrochloric acid solution. The ether layer was separated and dried over potassium carbonate. The ether was evaporated and the residue was distilled. The infrared spectra showed complete absence of ketonic material in the alcohols which were obtained (crude) in almost quantitative yields.

The alcohols were converted into the 3,5-dinitrobenzoates by adding a solution of 0.1 mole of the alcohol in 0.2 mole of dry pyridine to a solution of 0.11 mole of 3,5-dinitrobenzoyl chloride in 0.6 mole of pyridine. The mixture was warmed on a hot-plate until homogeneous and was allowed to stand at 25° for several hours. It was then poured into 100 cc. of concentrated hydrochloric acid and 200 g. of ice. The resultant suspension was extracted with benzene, and the benzene solution was washed with 100 cc. of 10% hydrochloric acid solution, water and 10% sodium bicarbonate solution. The benzene solution was dried over potassium carbonate and evaporated on the steam-bath at atmospheric and then water-pump pressures. The residue was recrystallized from ligroin (lig.) or cyclohexane (cy.) until a pure product had been obtained. The properties of the 6-alkyl-2-cyclohexen-1-yl 3,5-dinitrobenzoates obtained are given in Table IV.

TABLE IV

Alkyl group	Cryst. solvent	No. of cryst.	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	Cy.	9	53	117.9–118.6	54.90	55.21	4.61	4.90
Isopropyl	Lig.	3	57	79.7–80.7	57.48	57.73	5.43	5.63
t-Butyl	Cy.	11	36	105.7–106.4	58.61	58.89	5.79	6.03

The pure dinitrobenzoates were hydrolyzed by treating a solution of 0.15 mole of ester in 250 cc. of methanol with a solution of 25 g. of sodium hydroxide in 125 cc. of water and refluxing for 40 minutes. After cooling and dilution to 1000 cc. with water, the mixture was extracted several times with ether; the ether was dried over potassium carbonate and the product was recovered by distillation, yielding pure *trans*-6-alkyl-2-cyclohexen-1-ols with the following properties:

Alkyl group	Yield, %	B.p., °C.	B.p., Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	80	93.3–93.8	45	74.95	75.07	10.78	10.63
Isopropyl	91	88.8–89.0	11	77.09	76.92	11.50	11.38
t-Butyl	80	91.7–92.2	11	77.86	77.98	11.76	11.84

Proof of the *trans* Configuration of the 6-Alkyl-2-cyclohexen-1-ols.—A solution of 0.01 mole of 6-alkyl-2-cyclohexen-1-ol (from the hydrolysis of its constant melting dinitrobenzoate) in 10 cc. of methanol was added to 0.10 g. of prereduced platinum oxide in 5 cc. of methanol. The mixture was hydrogenated at 25° and 1 atmosphere for 2 hr., at which point hydrogen uptake was complete. Removal of the catalyst, evaporation of the solvent and distillation produced the saturated alcohol which was converted to its 3,5-dinitrobenzoate as previously described for the unsaturated alcohols. The melting points of the crude dinitrobenzoates thus obtained were found to be within 2° of those of the pure esters, obtained after one recrystallization from the smallest possible amount of cyclohexane. Melting points of mixtures with authentic *trans*-2-alkylcyclohexanol 3,5-dinitrobenzoates established the *trans* structure of the reduced alcohols and, consequently, of the parent cyclohexenols. The data are given in Table V.

TABLE V

Alkyl group	B.p. of reduced alc., °C.	Mm.	Dinitrobenzoate m.p., °C.	Mixed m.p. with authentic *trans*-DNB, °C.
Methyl	90–91	53	113–114	113.4–114.4
Isopropyl	91–92	13	131.1–132	131.5–132.5
t-Butyl	143–144	100	121.5–122.5	122–122.8

Authentic *trans*-2-Alkylcyclohexanols.—The *trans*-cyclohexanols were prepared by the reduction of the corresponding ketone with sodium in moist ether; sodium (7.0 g.) was added in small chunks over a period of 15 minutes to well-stirred mixtures of 0.1 mole of 2-alkylcyclohexanone, 8.0 cc. of water and 100 cc. of ether, kept at 0° by external cooling. Eight cc. of water was then added during 5 minutes, followed by an additional 7.0 g. of sodium over 15 minutes. More water (35 cc.) was then added over 30 minutes and the mixture was stirred for 6 hours at 0°; then water (75 cc.) was added cautiously to destroy the excess sodium. The ether layer was separated, washed with saturated salt solution and dried over potassium carbonate. Evaporation of the ether and distillation of the residue gave the desired *trans*-2-alkylcyclohexanols which were obtained in 90–95% yields. The preparation of ***trans*-2-methylcyclohexanol** has been carried out previously[16]; it gave a pure 3,5-dinitrobenzoate, m.p. 113.9–114.7° (reported[16a] m.p. 115°) in 59% yield, after 4 recrystallizations from cyclohexane. It was further characterized by its hydrogen phthalate, m.p. 124°, as reported.[16b,c] ***trans*-2-Isopropylcyclohexanol** has also been made previously.[17] It gave a pure **3,5-dinitrobenzoate**, m.p. 132.2–133.2°, in 81% yield after 3 recrystallizations from cyclohexane and was identified by its hydrogen phthalate, m.p. 120–120.8° (reported[17] m.p. 121°), and by hydrolysis of the dinitrobenzoate to the pure alcohol, m.p. 63–64° as reported.[17]

***trans*-2-*t*-Butylcyclohexanol** was obtained as a solid which did not melt sharply (70–75°). It was characterized by its **3,5-dinitrobenzoate**, m.p. 122.2–123°, obtained in 77% yield after four recrystallizations from cyclohexane.

Anal. Calcd. for $C_{17}H_{22}O_6N_2$: C, 58.27; H, 6.33. Found: C, 58.36; H, 6.40.

Hydrolysis of the pure ester gave ***trans*-2-*t*-butylcyclohexanol**, b.p. 139–140° (95 mm.), m.p. 84.5–85.0°.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.93; H, 12.81.

The 2-*t*-butylcyclohexanol, m.p. 52–53°, obtained by Schmerling[18] is evidently a mixture of isomers.

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