GLC analysis of the oil eluted with pentane indicated the presence of a component with a retention time close to that of **3**. This component was isolated by GLC (yield 9 mg). Its IR spectrum possessed absorptions of medium intensity at 2920, 1460, 1380, 1365, and 872 cm^{-1}, in addition to other weak absorptions. A 220-MHz NMR spectrum showed signals at δ 5.63 (s, 1 H), 1.41 (s, 4 H, superimposed on a multiplet from δ 1.68 to 1.27, 5 H), 1.20 (s, 6 H), 1.08 (s, 6 H), 0.97 (s, 6 H), and 0.87 (doublet, J = 6 Hz, 6 H). The Raman spectrum possessed intense bands at 2200 and 1611 cm^{-1} in addition to other weak bands.

Anal. Calcd for $C_{20}H_{34}$: C, 87.51; H, 12.49. Found: C, 87.93; H, 12.47.

The mass spectrum of the oil eluted with pentane possessed peaks at m/e 274 (12.98), 259 (10.20), 205 (22.36), and 203 (20.51) (calculated mass of parent ion of **7**, 274). In addition, a peak at m/e 166 (4.11%) was present indicating the presence of 3,3,6,6-tetramethyl-1-ethylcyclohexene ($C_{12}H_{22}$, mol wt 166) in this oil. In the 10-eV mass spectrum, the intensities of the m/e 274 and 166 peaks increased to 44.35 and 27.01, respectively.

Registry No.—**1**, 37494-11-4; **3**, 59129-90-7; **6**, 61075-98-7; **7**, 61075-99-8; **8**, 18387-63-8; **9**, 61076-00-4; **10**, 61076-01-5; **11**, 61076-02-6; **14**, 61104-52-7; 1-trimethylsilyl-3-methylbut-1-yn-3-ol, 5272-33-2; 3-methyl-1-bromobutane, 107-82-4; 2,2,5,5-tetramethylcyclohexanone, 15189-14-7; 3,3,6,6-tetramethyl-1-ethylcyclohexene, 61076-03-7.

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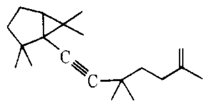

This and other possibilities are discussed in the Ph.D. Dissertation of C. N. Bush, University of Illinois, 1975.

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Notes

Optical Rotations and Absolute Configurations of 3-*tert*-Butylcyclohexene and of *trans*-3-*tert*-Butyl-6-methylcyclohexene

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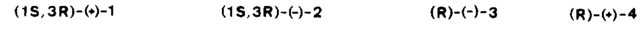
Received June 15, 1976

In connection with our interest in the asymmetric bromination of alkenes,[1] the chiroptical properties of some alkyl substituted cyclohexene derivatives were needed. In this paper we report the hitherto unknown relationship between optical rotations and absolute configurations of 3-*tert*-butylcyclohexene and of *trans*-3-*tert*-butyl-6-methylcyclohexene. The optical rotation of 4-*tert*-butylcyclohexene[1d] has also been revised.

(R)-(−)-3-*tert*-Butylcyclohexene (**3**) of high optical purity was obtained through an improvement of the route already followed[1d] for the preparation of the optically active 4-*tert*-butyl isomer (**4**), consisting in the dehydrotosylation of the tosylate (**2**) of (+)-*cis*-3-*tert*-butylcyclohexanol (**1**) (Scheme I). The (1S,3R) configuration had been firmly established[2] for (+)-**1** by the ORD curve of (+)-3-*tert*-butylcyclohexanone arising from its oxidation. A value of $[\alpha]^{30}\mathrm{D}$ +7.9° has been reported[2] for **1** obtained by resolution of the acid phthalate through the brucine salt and a very high optical purity was suggested by the obtainment of (+)-3-*tert*-butylcyclohexanone with the same optical rotation ($[\alpha]^{24.5}\mathrm{D}$ + 25°) starting both from (+)-**1** and the diastereoisomeric (+)-*trans*-3-*tert*-butylcyclohexanol, which had been independently resolved through its 3β-acetoxy-Δ^5-etienate.[2] In our hands the resolution of the acid phthalate of (±)-**1** with brucine led to both enantiomeric alcohols, the dextrorotatory one having higher optical purity ($[\alpha]^{25}\mathrm{D}$ +8.9 and −8.1°). Treatment of both enantiomers with tosyl chloride afforded, after crystallization, the corresponding tosylates with very close absolute values of optical rotation ($[\alpha]^{25}\mathrm{D}$ −23.1 and +22.7°, respectively). Heating of (−)-**2** in quinoline gave a mixture of 3- and 4-*tert*-butylcyclohexene (**3** and **4**) in a 38:62 ratio. After chromatographic separation on a $AgNO_3/SiO_2$ column, the two olefins had the following rotations: (R)-**3**, $[\alpha]^{25}\mathrm{D}$ −6.2°; (R)-**4**, $[\alpha]^{25}\mathrm{D}$ +82.8°. The latter value is somewhat higher than the rough estimate of the maximum optical rotation previously made for **4**[1d] starting from a sample of (+)-**1** of lower optical purity and based on the maximum rotation ($[\alpha]^{30}\mathrm{D}$ +7.9°) reported at that time for **1**.

Scheme I

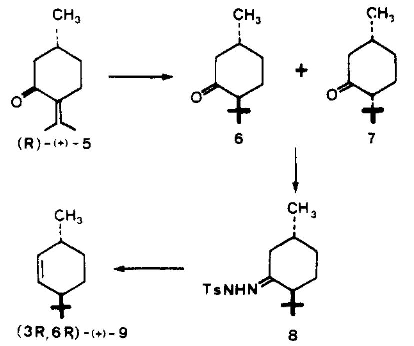


(1S,3R)-(+)-1 (1S,3R)-(−)-2 (R)-(−)-3 (R)-(+)-4

(3R,6R)-(+)-*trans*-3-*tert*-Butyl-6-methylcyclohexene (**9**), $[\alpha]^{25}\mathrm{D}$ +117.6 was obtained from optically pure natural (+)-pulegone (**5**) according to Scheme II.

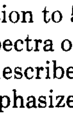
The addition of methylmagnesium iodide to (+)-**5** in the presence of cuprous chloride, which acts as catalyst for 1,4 addition,[3] gave, as reported,[4] a 7:3 mixture of ketones **6** and **7**. The major diastereoisomer **6** was separated as the tos-

Scheme II

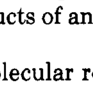


ylhydrazone **8**, which was transformed into pure **9**, which should also be optically pure, by treatment with an excess of butyllithium. Since the last reaction does not involve[5] the chiral centers C(2) and C(5), the (3*R*,6*R*) absolute configuration resulted for (+)-**9** from the known *R* configuration of (+)-pulegone[6] and from the established[4] trans relationship of the two alkyl substituents in the major product **6** of the 1,4 Grignard addition to **5**. This was unambiguously confirmed by the NMR spectra of several products of anti addition to **9**, which will be described elsewhere.[7]

It can be emphasized that the molecular rotation of (3*R*,6*R*)-**9**, [M]D +179.1°, is very similar to that of the corresponding *trans*-2-menthene (**10**, [M]D +185°).[8,9] According to Brewster's treatment of the optical activity of endocyclic olefins,[9] if a dextrorotatory contribution of 130° by the methyl group to the [M]D of (+)-**9** is assumed (a value leading to a reasonable agreement between calculated and experimental values of [M]D for several terpene olefins[9]), (*R*)-**3** would be expected to be dextrorotatory. This is in contrast with the experimental value of [M]D −8.6°.



10



11

Furthermore, the Mills[10] and Brewster[9] empirical rules predict a positive rotation for compounds having configuration **11** when the substituent X is more polarizable than hydrogen, unless C=C > X > CH_3 in polarizability. However, Eliel has suggested[11] that the *tert*-butyl group is less polarizable than methyl, which is less polarizable than vinyl, and the octet refraction values reported by Brewster[12] support this assumption. Therefore it can be concluded that, while the optical rotation of *trans*-3-*tert*-butyl-6-methylcyclohexene (**9**) is conformable to the expectation, that of the simple 3-*tert*-butyl derivative **3** is not.[13] We are currently investigating the cause of this apparent anomaly by far ultraviolet, ORD, and CD studies on the present and other simple substituted cyclohexenes.

Experimental Section

Melting points were determined on a Kofler block and are uncorrected. NMR spectra were registered with a JEOL C-60HL spectrometer from $CDCl_3$ solutions using Me_4Si as internal standard. GLC analyses of the mixture of **6** and **7** and of olefins **3**, **4**, and **9** were performed on a Perkin-Elmer Model F 11 instrument fitted with a 2-m glass column, 3 mm i.d., packed with 10% Carbowax 20M on silanized 80–100 mesh Chromosorb W. IR spectra for comparisons were registered on liquid films with a Perkin-Elmer Model 257 double-beam grating spectrophotometer. Optical rotations were measured in $CHCl_3$ solutions with a Perkin-Elmer Model 141 photoelectric polarimeter. The reference compounds (±)-**3** and (±)-**4** were prepared according to the reported methods.[14,15] $MgSO_4$ was always used as the drying agent. Petroleum ether refers to the fraction bp 30–50 °C.

(+)- and (−)-*cis*-3-*tert*-Butylcyclohexanol (1). The resolution of (±)-**1** was carried out as reported.[2] The brucine salt of *cis*-3-*tert*-butylcyclohexyl hydrogen phthalate was prepared by mixing 80 g of acid phthalate and 105 g of brucine in acetone. Most of the solvent was evaporated, benzene was added, and the solution was left overnight in a refrigerator. The precipitate (64 g) had $[\alpha]^{25}\mathrm{D}$ −18.8° (*c* 1.5). Concentration of the mother liquors gave a second crop (23 g), $[\alpha]^{25}\mathrm{D}$ −18.6°. Three crystallizations from benzene of a sample of the two combined fractions gave a brucine salt with $[\alpha]^{25}_{589}$ −18.7°, $[\alpha]^{25}_{546}$ −22.7°, $[\alpha]^{25}_{436}$ −55.0°, $[\alpha]^{25}_{365}$ −137.3°.

A warm solution of 50 g of this salt in MeOH was treated with 2 N aqueous HCl (30 ml), diluted with water, and extracted with ether. The extract was washed with 2 N HCl and water, dried, and concentrated. Dilution with petroleum ether yielded 20 g of crystalline *cis*-3-*tert*-butylcyclohexyl hydrogen phthalate. After recrystallization from ethyl ether–petroleum ether, this product had mp 123–123.5 °C, $[\alpha]^{25}_{589}$ +14.7°, $[\alpha]^{25}_{546}$ +16.9°, $[\alpha]^{25}_{436}$ +32.3°, $[\alpha]^{25}_{365}$ +58.7° (*c* 2.8) (lit.[2] mp 104.5–107 °C, $[\alpha]^{30}\mathrm{D}$ +14°).

Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 70.80; H, 7.90.

A suspension of the acid phthalate from several preparations (80 g), $[\alpha]^{25}\mathrm{D}$ +14.7°, in 50% aqueous KOH was steam distilled. Ether extraction and distillation under reduced pressure gave 40 g of pure **1**, mp 39–40 °C, $[\alpha]^{25}_{589}$ +8.9°, $[\alpha]^{25}_{546}$ +10.1°, $[\alpha]^{25}_{436}$ +17.0°, $[\alpha]^{25}_{365}$ +26.0° (*c* 4.4) (lit.[2] liquid at room temperature, $[\alpha]^{30}\mathrm{D}$ +7.9°).

The mother liquors from which the brucine salt was separated were evaporated and the residue was treated with 2 N aqueous HCl. Extraction with ether, evaporation, and crystallization from ethyl ether–petroleum ether yielded the (−)-acid phthalate, $[\alpha]^{25}\mathrm{D}$ −13.0°. Saponification of this product as described above afforded (−)-**1**, $[\alpha]^{25}\mathrm{D}$ −8.1°.

Tosylates of (+)- and (−)-*cis*-3-*tert*-Butylcyclohexanol (2). Tosyl chloride (9.5 g) was added to a stirred solution of (+)-**1** (5.8 g, $[\alpha]^{25}\mathrm{D}$ +8.9°) in dry pyridine (60 ml) at 0 °C. After standing overnight at 5 °C, the mixture was treated with cold 2 N aqueous HCl and extracted with ether. Evaporation of the washed (2 N aqueous HCl and water) and dried extract followed by crystallization of the residue from petroleum ether yielded 8.5 g of **2**, mp 85–87 °C [lit.[16] (±)-**2**, mp 58–59.5 °C], $[\alpha]^{25}_{589}$ −23.1°, $[\alpha]^{25}_{546}$ −26.3°, $[\alpha]^{25}_{436}$ −45.1°, $[\alpha]^{25}_{365}$ −71.0° (*c* 4.0), unchanged after two crystallizations.

Anal. Calcd for $C_{17}H_{26}SO_3$: C, 65.77; H, 8.44. Found: C, 65.80; H, 8.60.

A second crop of **2** had $[\alpha]^{25}\mathrm{D}$ −22.8°.

Similar treatment of (−)-**1**, $[\alpha]^{25}\mathrm{D}$ −8.1°, gave, after crystallization from petroleum ether, the dextrorotatory tosylate, mp 85–86 °C, $[\alpha]^{25}\mathrm{D}$ +22.7° (*c* 4.0). A sample with $[\alpha]^{25}\mathrm{D}$ +6° was obtained as the third crop from the mother liquors.

(−)-3-*tert*-Butylcyclohexene (3) and (+)-4-*tert*-Butylcyclohexene (4). A solution of (−)-**2** (5.0 g, $[\alpha]^{25}\mathrm{D}$ −23.1°) in dry quinoline (80 ml) was heated at 180 °C for 4 h, then treated with cold 2 N aqueous HCl and extracted with ether. Evaporation of the washed (2 N, HCl and water) and dried extract gave 2.6 g of a mixture of **3** and **4** in a 38:62 ratio (GLC), which was chromatographed on a 45 × 1.8 cm column filled with 10% $AgNO_3$ on silica gel (Woelm, dry-column grade) eluting with petroleum ether. Fractions (25 ml) were collected, whose composition was checked by GLC. Fractions 9–13 contained pure **3** which, after being freed from solvent by preparative GLC, had an IR spectrum identical with that of racemic **3**[14] (main absorption bands at 1387, 1362, 1223, 1136, 890, 865, 765, 723, 642 cm^{-1}); NMR δ 0.90 [s, $(CH_3)_3C$–, 9 H], 5.67 (m, $W_{1/2} \sim 4$ Hz, -CH=, 2 H); $[\alpha]^{25}_{589}$ −6.2°, $[\alpha]^{25}_{546}$ −7.4°, $[\alpha]^{25}_{436}$ −16.1°, $[\alpha]^{25}_{365}$ −32.3° (*c* 3.6). Fractions 14–16 consisted of mixtures of **3** and **4**; fractions 17–27 gave pure **4**, with an IR spectrum identical with that of racemic **4**,[15] $[\alpha]^{25}_{589}$ +82.8°, $[\alpha]^{25}_{546}$ +94.2°, $[\alpha]^{25}_{436}$ +160.3°, $[\alpha]^{25}_{365}$ +247.1°.

(−)-*trans*-2-*tert*-Butyl-5-methylcyclohexanone Tosylhydrazone (8). Natural (+)-pulegone (**5**) [$[\alpha]^{20}\mathrm{D}$ +22.5° (neat), 100% optical purity,[17] 35 g] was reacted with methylmagnesium iodide (from 6.2 g of magnesium and 36 g of methyl iodide) in the presence of freshly prepared cuprous chloride[18] (0.75 g), as described,[4] except that ethyl ether was used as the solvent instead of tetrahydrofuran. The 7:3 mixture (GLC) of **6** and **7** obtained (28 g) was dissolved in absolute ethanol (200 ml), tosylhydrazine (31 g) was added, and the mixture was refluxed for 8 h. Evaporation of the solvent left a semisolid residue which was dissolved in methanol. After standing overnight at −10 °C, the tosylhydrazone **8** crystallized (20 g), mp 138–140 °C. Concentration of the mother liquors and standing at −10 °C yielded a second fraction (8 g), identical with the first one. After repeated recrystallizations from methanol until a constant optical rotation and melting point were reached, **8** had mp 145–146 °C, $[\alpha]^{25}_{589}$ −33.7°, $[\alpha]^{25}_{546}$ −39.0°, $[\alpha]^{25}_{436}$ −72.3°, $[\alpha]^{25}_{365}$ −126.5° (*c* 3.1); NMR δ 0.86 [overlapping s and d, $(CH)_3C$– and CH_3–, 12 H], ~1.1–2.1 (7 cyclohexane H), 2.41 (s, $CH_3C_6H_4$–, 3 H), 2.70 [2 m, *J* ~ 10 Hz, >$CHC(CH_3)_3$, 1 H], 7.32 and 7.92 (2 d, $-C_6H_4-$, 4 H), 8.38 (m, >NH, 1 H).

Anal. Calcd for $C_{18}H_{28}N_2SO_2$: C, 64.26; H, 8.39; N, 8.33; S, 9.53. Found: C, 63.98; H, 8.20; N, 8.18; S, 10.05.

(+)-*trans*-3-*tert*-Butyl-6-methylcyclohexene. A 2.2 M solution of butyllithium in hexane (75 ml) was added dropwise to a stirred suspension of the tosylhydrazone **8** (13.2 g) in anhydrous ethyl ether (140 ml) at 0 °C under a nitrogen atmosphere. The solid **8** first dissolved, then a white precipitate was formed, which turned to yellow and finally to orange. The reaction mixture was stirred at 0 °C for 2 h, left for 12 h at room temperature under nitrogen, and then hydrolyzed. The organic layer was separated, washed with 10% aqueous Na_2CO_3 and water, dried, and evaporated. The residue was dissolved in petroleum ether and filtered through a 40 × 2.5 cm column of silica gel. Evaporation and distillation of the eluate yielded pure (GLC) **9**: bp 72–73 °C (18 mm); $[\alpha]^{25}_{589}$ +117.6°, $[\alpha]^{25}_{546}$ +134.3°, $[\alpha]^{25}_{436}$ +235.5°, $[\alpha]^{25}_{365}$ +378.2° (*c* 6, $CHCl_3$); NMR δ 0.86 [overlapping s and d, $(CH_3)_3C-$ and CH_3-, 12 H], 5.52 (m, $W_{1/2} \sim 4$ Hz, $-CH=$, 2 H).

Anal. Calcd for $C_{11}H_{20}$: C, 86.60; H, 13.24. Found: C, 86.84; H, 13.25.

Acknowledgment. Financial support by the Consiglio Nazionale delle Ricerche (Roma) is gratefully appreciated.

Registry No.—(+)-**1**, 61116-78-7; (+)-**1** phthalate, 61062-48-4; (−)-**1**, 61116-79-8; (+)-**2**, 61138-74-7; (−)-**2**, 31062-01-8; **3**, 61062-49-5; **4**, 61062-50-8; **5**, 89-82-7; **6**, 56782-80-0; **7**, 56816-94-5; **8**, 61062-51-9; **9**, 61116-80-1.

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(7) The addition of XY reagents to **9** gave anti diaxial and diequatorial adducts, in all of which the protons α to X and Y clearly appeared to be coupled with axial protons α to the methyl and *tert*-butyl groups, showing that both the alkyl substituents were equatorial. This also ruled out the possibility of epimerization of ketone **6** at C(2) prior to tosylhydrazone formation (work in progress from this laboratory).

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Mechanistic Aspects of the Wolff–Kishner Reaction. 6. Comparison of the Hydrazones of Benzophenone, Fluorenone, Dibenzotropone, and Dibenzosuberone

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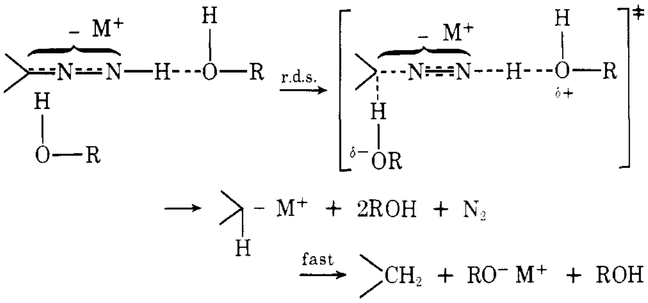
Received June 15, 1976

A careful determination[1] of the kinetic and activation parameters of the Wolff–Kishner reaction of benzophenone hydrazone in two hydroxylic solvents (butyl carbitol and 1-decanol) as a function of the cation (K, Na, Li, and Mg) in the alkoxide catalyst, the concentration of the latter, and as a function of the presence of dicyclohexyl-18-crown-6 has led to the conclusion that the rate-determining step involves the hydrazone anion and a minimum of two solvent molecules: one hydroxylic solvent molecule that functions as a proton source, and another solvent molecule that acts as a base in the scission of the N–H bond. The rate-limiting step for the Wolff–Kishner reaction of benzophenone hydrazone in a hydroxylic solvent can thus be represented as follows:



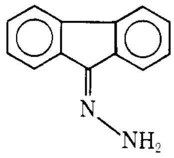
(M+ is solvated)

The experimental results also suggest that the reactivity of the hydrazone anion increases with the dissociation of the ionic pair.

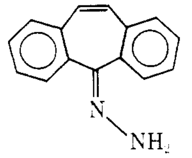
In this paper we wish to report the comparison of the behavior of benzophenone hydrazone (I) in the Wolff–Kishner reaction with that of three structurally related compounds (II, III, IV) in which the stabilization of the partial negative charge at the reactive carbon atom should vary as a function of the differences in coplanarity, aromaticity, and antiaromaticity.[2]

Results and Discussion

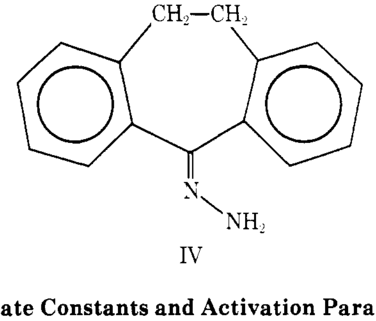
The kinetics of the Wolff–Kishner reaction of I–IV were determined in butyl carbitol using the sodium butyl carbito-



II



III



IV

Table I. Rate Constants and Activation Parameters for the Wolff-Kishner Reaction of I-IV

Compd	$k^{150.5°} \times 10^3$, $M^{-1}\,s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol[c]	$\Delta S^{\ddagger}$, eu[c]
I	2.71[a]	28.8 ± 0.5	−3.1 ± 1.1
II	254[a,b]	25.6 ± 0.4	−1.5 ± 0.9
III	1.62[a]	29.1 ± 1.5	−3.3 ± 3.2
IV	0.280[a]	30.2 ± 0.7	−4.4 ± 1.6

[a] Standard deviations of these values are less than 5%. [b] Extrapolated from 91.7–131.0 °C. [c] Errors quoted in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are equal to 1.96 × (standard errors) which gives a 96% "confidence level" (N. C. Barford, "Experimental Measurements: Precision, Error and Truth", Addison-Wesley, Reading, Mass., 1967).