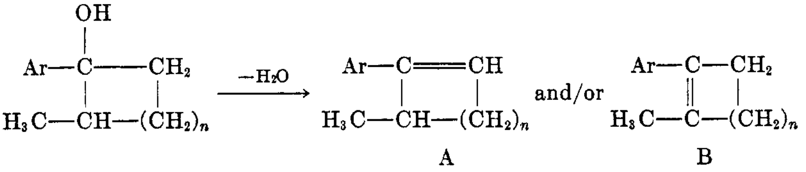
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

SOME VICINAL DISUBSTITUTED CYCLOPENTENES AND CYCLOHEXENES BEARING NAPHTHYL AND METHYL GROUPS[1, 2]

L. H. KLEMM AND HERMAN ZIFFER

Received September 7, 1954

Barring molecular rearrangement or migration of a double bond two isomeric olefins A and B are possible by dehydration of 2-methyl-1-aryl-1-cycloalkanols according to equation 1. Factors which might be expected to affect the direction of dehydration have been enumerated by Carlin and Landerl (1) but, at least in the cases where Ar = phenyl or naphthyl and n = 2 or 3, no record has been found of a proof of the location of the double bond in the product(s). In conjunction with our general program on the relation between coplanarity and chemical reactivity in arylcycloalkenes it became desirable to synthesize such methylated naphthylcyclopentenes and naphthylcyclohexenes and to ascertain (within a few per cent, if possible) the relative amounts of A and B present. This paper reports our initial results in this regard.



$$\begin{array}{l} \quad\;\; OH \\ \quad\;\;\; | \\ Ar—C——CH_2 \\ \quad\;\;\; |\qquad\;\; | \\ H_3C—CH—(CH_2)_n \end{array} \xrightarrow{-H_2O} \begin{array}{c} \begin{array}{l} Ar—C{=\!=}CH \\ \quad\;\;\; |\qquad | \\ H_3C—CH—(CH_2)_n \end{array} \\ A \end{array} \text{ and/or } \begin{array}{c} \begin{array}{l} Ar—C—CH_2 \\ \quad\;\;\; \|\quad\; | \\ H_3C—C—(CH_2)_n \end{array} \\ B \end{array}$$

(equation 1)

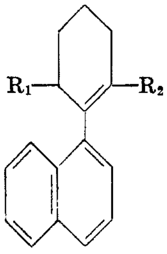
2-Methylcyclopentanone was prepared by the successive steps of (a) Dieckmann cyclization of diethyl adipate *via* sodium hydride (81% yield), (b) methylation of the resultant ketoester, (c) ring opening and hydrolysis with aqueous alkali, and (d) pyrolysis of the free diacid [42% over-all yield for steps (c) and (d)]. Efforts to accomplish direct hydrolytic decarboxylation of the product from (b) with aqueous acid according to the procedure of van Rysselberge (2) met with little success in our hands [*cf.* Treibs, Mayer, and Madejski (3)]. 2-Methylcyclohexanone was obtained by oxidation of 2-methylcyclohexanol. The four crude carbinols obtained by reacting each of these ketones with 1- and 2-naphthylmagnesium bromides were dehydrated by warming with anhydrous formic acid. After a preliminary distillation each resultant olefin was converted to a crystalline polynitroaromatic molecular compound (complex) for storage and further purification. In the cases of II and IV the 1:1 complexes with 1,3,5-trinitrobenzene (TNB) so obtained were recrystallized to constant narrow melting range. A like accomplishment was attained with the 1:1 complex from III and 2,4,7-trinitrofluorenone (TNF). I was not recrystallized in this fashion

---

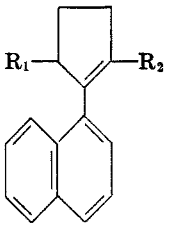
[1] Paper IV in the series on Chemical Reactivities of Arylcycloalkenes. Presented at the Northwest Regional Meeting of the American Chemical Society, Richland, Washington, June, 1954.

[2] Performed under sponsorship of the Office of Ordnance Research, contract number DA-04-200-ORD-176.

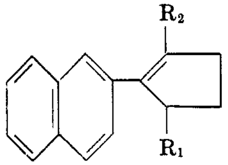
since test samples failed to yield narrowly melting complexes with TNB, TNF, picric acid, or *m*-dinitrobenzene. Nonetheless a spectrophotometric investigation showed the widely melting complex of I and TNB was again 1:1-type [*cf.* I with 1-phenylnaphthalene (4) and 1-(1-naphthyl)-1-cyclohexene (5) which also show discrepancies in complex formation]. Of the olefins recovered on dissociation of these complexes only II was crystalline, m.p. 53.5–54°, while the others were liquids. To help characterize I, its purity as a monoölefin was established by titration with perbenzoic acid.



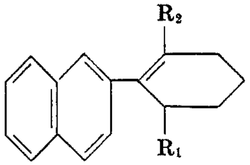
IA
IB



IIA
IIB



IIIA
IIIB

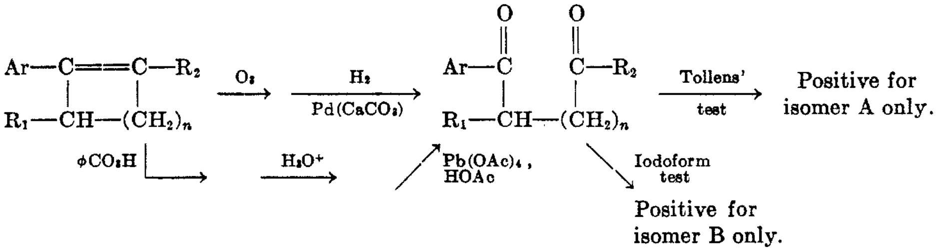


IVA
IVB

For A-isomers: $R_1 = CH_3$, $R_2 = H$
For B-isomers: $R_1 = H$, $R_2 = CH_3$

The location of the double bond in each sample was effected by Scheme I. Scission of the molecules at the double bonds to form dicarbonyl compounds was accomplished both by (a) successive epoxidation with perbenzoic acid in chloroform-benzene, hydrolysis with dilute aqueous acid, and glycol fission with lead tetraacetate in glacial acetic acid and (b) ozonolysis and subsequent catalytic hydrogenation. In the case of I the quantitative nature of the hydrolysis step was checked by titration of the crude glycol therefrom with periodic acid. Procedure (a) was selected first because of its ready susceptibility to quantitative evaluation of the intermediate steps. However, it had the disadvantage that changes in solvents necessitated isolation of the dried product at the end of each step. The dicarbonyl products, moreover, were dark in color and became more viscous on standing—perhaps as a result of self-condensation. Procedure (b) largely circumvented these difficulties since both steps were conducted in the same neutral solvent, ethyl acetate. The weight percentage yield (54–94%) of dicarbonyl compound was estimated gravimetrically by precipitation as the *bis*-2,4-dinitrophenylhydrazone.

SCHEME I



Positive for isomer A only.

Positive for isomer B only.

Qualitative tests on all of the dicarbonyl products from both procedures (a) and (b) were positive with ammoniacal silver nitrate solution while those with alkaline hypoiodite solution gave no obvious iodoform precipitate. An effort to adapt the potentiometric Tollens' titration method of Siggia and Segal (6) to use with our dicarbonyl compounds was then made. Though results were far from quantitatively reproducible they set a minimum value of about 40% to the amount of isomer A in each of the olefins. These results were checked on the dicarbonyl product (ketoaldehyde) obtained from 1-(1-naphthyl)-1-cyclohexene [formula I where $R_1 = R_2 = H$].

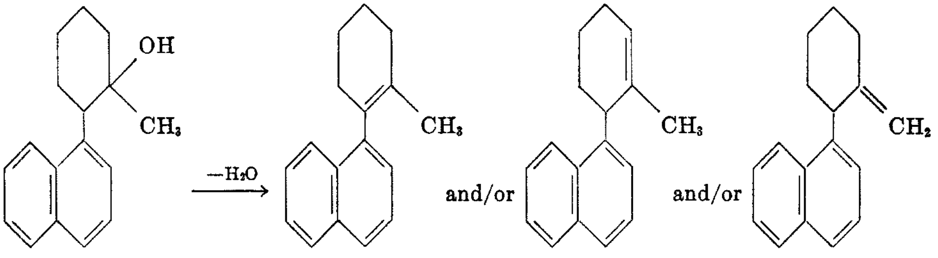
Somewhat better success was attained in establishing a maximum value for the amount of isomer B present in the olefins *via* gravimetric determination of the precipitate formed from treatment of the dicarbonyl product with excess hypoiodite. Taking into account the purity of the dicarbonyl products, assuming a 90% yield on the iodoform reaction (consistent with a control test), and assuming the precipitates formed were pure iodoform this would correspond to the calculated presence of 4–13% of isomers B in the olefins. However, the precipitates were obviously impure and did not have the characteristic odor associated with iodoform. In view of the consistency of these results for I–IV and the sharp melting points for II and the complexes of II–IV, we believe the preceding olefins I–IV were essentially chemically pure A-isomers.

Excluding purifications through polynitroaromatic complexes, our preparations of II and III followed almost exactly those of Bachmann and Kloetzel (7) for which they reported the formation of analytically impure liquids, assumed to have structures IIB and IIIB, respectively. In view of our structural studies it is more likely that their products consisted largely of A-isomers. Correspondingly, doubt must be cast on the assignment of angular positions for the methyl groups in the maleic anhydride adducts of their olefins.

Cook and Lawrence (8) and Mayer and Schiffner (9) reported the formation of I by dehydration of the carbinol resulting from the same Grignard reaction as used here. The former workers, however, used potassium bisulfate to effect dehydration to a liquid (probably identical with ours), while the latter ones obtained a crystalline product (needles from methanol, m.p. 55–56°) presumably from thermal dehydration.[3] We have now prepared an olefin having closely similar physical properties to those recorded for the Mayer and Schiffner product by thermal dehydration of carbinol V at 170° in an inert atmosphere. The structure of V was known from its method of synthesis from methylmagnesium iodide and 2-(1-naphthyl)cyclohexanone. On dehydration of V, however, three alternate structures, IB, IC, and ID, should be possible. Ozonolysis studies established the identity of our resultant olefin as IB inasmuch as the dicarbonyl product therefrom gave a positive iodoform test and a negative Tollens' test. It seems likely that the Mayer and Schiffner product is also IB.

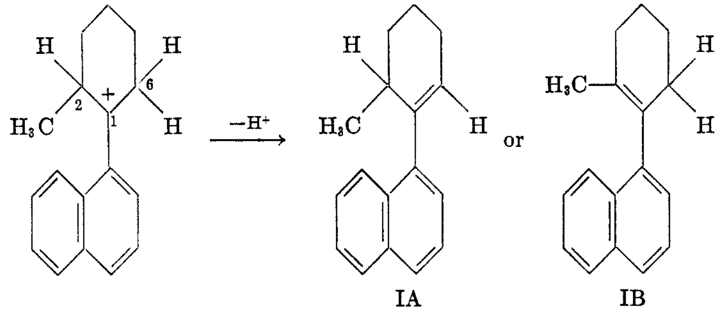
---

[3] Though Mayer and Schiffner did not specifically state the manner in which they effected dehydration they implied it was the same as used by Weiss and Woidich (12), *i.e.* apparently by pyrolysis. Both Mayer and Schiffner and Cook and Lawrence obtained 1-*o*-tolylnaphthalene on dehydrogenation of their products.



V IB IC ID

Though we have not yet investigated the mechanisms of dehydration, circumstantial evidence and general considerations for elimination reactions (10) seem consistent with two plausible pathways for the transformations. (a) Assume the Grignard syntheses of the 2-methyl-1-(1- and 2-naphthyl)-1-cycloalkanols are stereospecific to give *cis* configurations of the vicinal methyl and naphthyl groups. Under acidic dehydrating conditions (formic acid or potassium bisulfate) these might then give A-isomers through *trans* elimination (11). (b) Alternatively formation of our A-isomers might be conditioned through formic acid dehydration, irrespective of stereoconfigurations in the carbinols, by an E_1-mechanism involving the intermediate formation of a carbonium ion (such as illustrated for the case of I by equation 2) in which the naphthalene ring and carbons 1, 2, and 6 should be coplanar. Stereo-preference for deprotonation ought then be dictated by the relative facilities of bringing the small hydrogen atom (as for IA) or the considerably larger methyl group (as for IB) into the plane. Clarification of the details of dehydration of such carbinols must await additional experimentation, some of which is currently under way in our laboratory.



(equation 2)

IA IB

EXPERIMENTAL[4]

2-Carboethoxycyclopentanone. To an apparatus similar to that described by Johnson and Daub (13), containing 110 g. (4.6 moles) of sodium hydride and 3.5 l. of dry benzene, was added 900 g. (4.5 moles) of diethyl adipate over a period of 2 hours. The mixture which solidified—stopping the stirrer—was allowed to stand for 2 days, whereupon it was treated successively with 20 ml. of glacial acetic acid and 3 l. of 10% hydrochloric acid. Evaporation

---

[4] Melting points are uncorrected. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

of the combined dried (magnesium sulfate) organic layer and benzene extracts of the aqueous phase and distillation of the residue gave 570 g. (81%) of product, b.p. 90–95° (5–6 mm.).

2-Methylcyclopentanone. A mixture of 337 g. (2.0 moles) of 2-methyl-2-carboethoxycyclopentanone [prepared from the preceding ketoester by the procedure of van Rysselberge (2)], 100 g. (2.5 moles) of sodium hydroxide, and 1.5 l. of water was refluxed one day, acidified with 227 ml. (2.6 moles) of concentrated hydrochloric acid, refluxed another day, treated with 40 g. (0.13 mole) of barium hydroxide octahydrate, and evaporated to dryness. On pyrolysis of the residue at 300° crude 2-methylcyclopentanone was collected by distillation. Refluxing of the residue with 50 ml. more of acid in 1 l. of water for another day, followed by evaporation and pyrolysis as before gave additional crude material. Fractionation of combined crude products *via* a column (9" x ¾") packed with glass helices gave 83 g. (42%) of ketone, b.p. 134–135° [reported (14a) b.p. 139°].

2-Methylcyclohexanone was prepared by oxidation of practical grade 2-methylcyclohexanol essentially according to the directions of Adams and Johnson (15) for cyclohexanone except that the alcohol was added slowly to the oxidizing mixture at a temperature of 0–40° and then the total mixture was maintained at 60–70° for 1 hour; yield (from 115 g. of carbinol) 61 g. (*ca.* 54%) of b.p. 163–166° [reported (14b) b.p. 166°].

Preparations of olefins IA–IVA. Following the directions of Bachmann and Kloetzel (7) as modified by Kleene (16) for the preparation of 1-(1-naphthyl)-1-cyclopentene, the Grignard reagent from 74 g. (0.36 mole) of 1- or 2-bromonaphthalene was treated with 41 g. (0.37 mole) of 2-methylcyclohexanone or 36 g. (0.37 mole) of 2-methylcyclopentanone. The resultant crude tertiary carbinol was dehydrated directly with anhydrous formic acid to the olefin which was distilled *in vacuo*; crude yields: IA, 35 g. (44%), b.p. 137–142° (1 mm.); IIA, 30 g. (40%), b.p. 110–125° (1 mm.); IIIA, 16 g. (21%), b.p. 120–128° (0.4 mm.); IVA, 23 g. (29%), b.p. 144–146° (1.4 mm.).

IA•TNB was obtained as yellow needles of constant melting range (89–110°) from methanol.

Anal. Calc'd for $C_{17}H_{18}\cdot C_6H_3N_3O_6$: TNB, 49.0.
Found:[5] TNB, 51.2.

IA was stored as the red-orange *picrate*, m.p. 55–120°,[6] obtained by evaporation *in vacuo* of the solvent from an equimolar mixture of the olefin and picric acid in absolute ethanol. Chromatographic dissociation according to the method of Klemm and Hodes (18) and two fractional distillations *in vacuo* under nitrogen gave *3-methyl-2-(1-naphthyl)-1-cyclohexene* (IA), colorless liquid, b.p. 133–134° (0.75 mm.) [reported (8) b.p. 125° (0.3 mm.)].

Anal. Calc'd for $C_{17}H_{18}$: C, 91.84; H, 8.16.
Found: C, 91.88; H, 8.24.

Complexes for purification of IIA–IVA were made by addition of olefin (20–30 g.) to a hot saturated solution of an equimolar amount of TNB in methanol or TNF in glacial acetic acid, followed by cooling the mixture, collecting the precipitate, and concentrating the mother liquor for a second crop; crude combined yields: IIA•TNB (95%), m.p. 87–95°; IIIA•TNF (85%), m.p. 123–124°; IVA•TNB (95%), m.p. 80–83°. Each complex was recrystallized from its respective solvent to constant m.p.: 95–96° for *IIA•TNB* as yellow needles, 123–124° for *IIIA•TNF* as red needles, 83–84° for *IVA•TNB* as yellow-orange needles.

Anal. Calc'd for $C_{16}H_{16}\cdot C_6H_3N_3O_6$: TNB, 50.7. Found for IIA•TNB:[5] TNB, 52.8.
Calc'd for $C_{16}H_{16}\cdot C_{13}H_5N_3O_7$: TNF, 60.2. Found for IIIA•TNF:[5] TNF, 60.4.
Calc'd for $C_{17}H_{18}\cdot C_6H_3N_3O_6$: TNB, 49.0. Found for IVA•TNB:[5] TNB, 50.7.

Each complex was dissociated by adding a benzene solution of it to a chromatographic column containing a 1:1 mixture (by volume) of silicic acid (Mallinckrodt S.L.) and Celite

---

[5] Determined spectrophotometrically by a procedure to be described elsewhere and developed by Mr. J. W. Sprague of the University of Oregon.

[6] We did not succeed in isolating a sharply melting picrate such as described by Bergmann and Weizmann (17).

(analytical grade) and elution with reagent grade petroleum ether (b.p. 30–60°). Distillation of the effluent *in vacuo* under nitrogen gave the purified olefin: *3-methyl-2-(1-naphthyl)-1-cyclopentene* (IIA), colorless liquid, b.p. 133–134° (1.2 mm.) [reported (7) b.p. 165–168° (1 mm.)], which solidified and was recrystallized thrice from methanol to produce prisms, m.p. 53.5–54°; *3-methyl-2-(2-naphthyl)-1-cyclopentene* (IIIA), colorless liquid, b.p. 133–134° (1.2 mm.) [reported (7) b.p. 180–182° (1 mm.)]; *3-methyl-2-(2-naphthyl)-1-cyclohexene* (IVA), pale yellow liquid, b.p. 144–146° (1.4 mm.).

Anal. Calc'd for $C_{16}H_{16}$: C, 92.26; H, 7.74.
Found IIA: C, 92.25; H, 7.68.
Found IIIA: C, 92.20; H, 7.93.
Calc'd for $C_{17}H_{18}$: C, 91.84; H, 8.16.
Found IVA: C, 91.73; H, 8.26.

A *picrate*, obtained from crude IVA, formed orange needles from 95% ethanol, m.p. 75–77°.

2-Methyl-1-(1-naphthyl)-1-cyclohexene (IB). To the Grignard reagent from 0.32 g. (0.013 mole) of magnesium, 0.9 ml. (0.014 mole) of methyl iodide, and 25 ml. of anhydrous ether was added, dropwise, a solution of 2.73 g. (0.012 mole) of 2-(1-naphthyl)cyclohexanone [prepared according to Orchin (19), m.p. 85–86°; reported m.p. 83.5–85°] in a mixture of 10 ml. of anhydrous ether and 15 ml. of anhydrous benzene. After 7 hours of refluxing, the mixture was poured into ice and dilute hydrochloric acid. After separation of layers and two extractions of the aqueous phase with ether the dried (magnesium sulfate) combined organic layers were evaporated. The dark residual liquid was heated at 170° for 40 minutes (while a steady stream of nitrogen was bubbled through it) and then was distilled, yield 1.60 g. (64%) of colorless liquid, b.p. 128–130° (0.85 mm.), which solidified and was recrystallized twice from methanol to give needles, m.p. 56–57° [reported[7] (9) needles from methanol, m.p. 55–56°].

Anal. Calc'd for $C_{17}H_{18}$: C, 91.84; H, 8.16.
Found: C, 91.68; H, 8.28.

Ozonolysis studies. (*a*) *Procedure.* Ozone was generated from air by means of a Scottdale Ozone Company (Scottdale, Pa.) ozonizer (adjusted to 10,000 volts) and was passed through a train similar to that described elsewhere (20), yield about 0.3 millimole of ozone per minute as determined by iodimetric titration. The procedure was adapted from the work of Henne and Perilstein (21). Into a solution (at room temperature) of 5 millimoles (1.0–1.1 g.) of olefin in 80 ml. of c.p. ethyl acetate contained in a low-pressure hydrogenation bottle was passed a total of *ca.* 5.5 millimoles of ozone. Then 0.5–1.0 g. of 1% palladium hydroxide-on-calcium carbonate catalyst (22) was added and the contents were shaken for 24 hours under 2–3 atm. hydrogen pressure. The catalyst was removed by filtration.

(*b*) *Qualitative tests.* For IB only a Tollens' test (23a) was made directly on the preceding solution (result: negative). In all cases the solvent was evaporated and samples of the residual liquid or solid were tested with Tollens', sodium hypoiodite (23b), and 2,4-dinitrophenylhydrazine (24) (DNP) reagents. IA–IVA gave positive tests with Tollens' and DNP reagents and negative tests with NaOI. IB gave positive tests with DNP and NaOI and a negative test with Tollens' reagent. 1-(2-Naphthyl)-1-cyclopentene (18) [formula III, $R_1 = R_2 = H$] used as a control sample for ozonolysis gave positive tests with Tollens' and DNP reagents (not tested with NaOI).

(*c*) *Quantitative iodoform tests.* The iodoform test was also conducted on larger amounts (250–500 mg.) of the products from IA–IVA. Each gave 20–50 mg. of crude tan semisolid (weight percentage yields: IA, 10; IIA, 14; IIIA, 5; IVA, 10) which did not smell like iodoform and in which no *bona fide* iodoform was apparent. A test on 50 mg. of 2-acetylnaphthalene to ascertain the sensitivity of the method produced a quantitative yield (0.12 g.) of crude iodoform, m.p. 100—105°.

(*d*) *Quantitative estimation of extent of ozonolysis.* A weighed amount (*ca.* 0.4 g.) of the

---

[7] See discussion for possible identicalness of this compound.

preceding ozonolyzed product (from IA–IVA) was treated with a calculated excess (5%) of standard DNP-reagent (24). The precipitate (ppt. #1) which formed was collected by filtration, dried in air, and weighed. The filtrate (*ca.* 15 ml.) was diluted to 250 ml. and allowed to stand 1 hour. The resultant precipitate (ppt. #2) was collected and treated as for ppt. #1. Assuming ppt. #1 consists of all the inert material and the *bis*-DNP derivative of the dicarbonyl compound (x moles) while ppt. #2 is unreacted DNP, then one has the equations for material balance sample weight $+ 2x$ DNP $\rightarrow 2x\ H_2O +$ ppt. #1 and $(y - 2x)$ DNP = ppt. #2, where y = total moles of DNP used. The two independent values of x thus obtained for each product were used to calculate the weight % yield (difference in values 4–16% for the two methods) of dicarbonyl compound by means of the equation

$$\text{Weight \% yield} = \frac{100x\ (\text{molecular weight of dicarbonyl compound})}{\text{sample weight}};$$

average weight % yields: IA, 54; IIA, 70; IIIA, 94; IVA, 75.[8]

Perbenzoic acid oxidations. (*a*) *Titration of IA.* The procedure was adapted from that used for conversion of styrene to styrene oxide (25). About 22 mg. of IA was shaken intermittently for 45 minutes with an excess (50%) of standard (0.17 *N*) perbenzoic acid in 90% chloroform-10% benzene (by volume) and then refrigerated (0–5°) for 24 hours. Unreacted perbenzoic acid was determined iodimetrically; % unsaturation found: 99.7, 99.4, 98.3. A control run on naphthalene showed no unsaturation.

(*b*) *Hydroxylation of IA–IVA.* A sample of 2–3 g. of olefin was treated with a 10% excess of perbenzoic acid in the aforementioned manner. The solution was then washed successively with dilute aqueous sodium hydroxide and water, dried (magnesium sulfate), and evaporated. The residual oil was refluxed for 50–60 hours with 200 ml. of 1.3% sulfuric acid. Combined ethereal extracts (two) of the solution were dried (magnesium sulfate) and evaporated. The residual glycol was dried at room temperature for 1 hour at 1 mm. pressure.

Glycol fission. (*a*) *Titration of IA glycol.* To a 10-ml. aliquot portion of the preceding glycol from IA dissolved in glacial acetic acid (total volume of solution 100 ml.) was added a ten-fold excess of standard (26) 0.02 *M* periodic acid solution. The mixture was allowed to stand for 3–4 hours, whereupon acidified aqueous potassium iodide solution was added and the liberated iodine was titrated as before; found: 0.97 moles HIO_4 consumed per mole of IA originally taken.

(*b*) *Lead tetraacetate oxidation.* The procedure was adapted from that of Baer, Grosheintz, and Fischer (27). To a solution of the glycol (from hydroxylation) in 50 ml. of glacial acetic acid was added a warm solution of lead tetraacetate (10% excess) in 50 ml. of the same solvent. The mixture was stirred for 3 hours, treated with 25 ml. of 1 *N* sulfuric acid, filtered, and evaporated almost to dryness *in vacuo* at room temperature. The residue was made alkaline with solid sodium carbonate and extracted with ether. The washed (with water) ethereal layer was dried (magnesium sulfate) and evaporated to give a dark liquid which was dried at 1 mm. pressure and room temperature for several hours. Iodoform tests on all of the products were negative.

Tollens' titration. The procedure was adapted from that of Siggia and Segal (6). A solution (in about 20 ml. of methanol) of a measured amount (about 0.08 g.) of product from the preceding lead tetraacetate oxidation was stirred for 6–50 hours at room temperature with 50 ml. of freshly prepared Tollens' solution. A slight measured excess of standard 0.1 *N* potassium iodide was added and the solution was stirred for 15–20 minutes. Excess iodide was titrated potentiometrically with standard 0.1 *N* silver nitrate. Values found

---

[8] The maximum percentage of isomer B in one of these olefins (*cf.* discussion) can be calculated from the formula

$$\frac{100\ (\text{wt.} - \%\ \text{yield in iodoform test})(\text{mol. wt. of dicarbonyl compound})}{(\text{wt.} - \%\ \text{yield in DNP test})(394)(0.9)}.$$

for the molar percentage of aldehyde present (assuming pure dicarbonyl product were used) were IA, 30–50; IIA, 40; IIIA, 45–70; IVA, 40–65. Checks on benzaldehyde (used directly) and 1-(1-naphthyl)-1-cyclohexene (18) [formula I, $R_1 = R_2 = H$] (oxidized as for IA–IVA) were 35–55% and 55–95%, respectively. Use of aqueous dimethylformamide in place of methanol or use of temperatures up to 85° did not improve the accuracy or reproducibility of the method.

SUMMARY

1. Dehydration *via* anhydrous formic acid of the four 2-methyl-1-(1- and 2-naphthyl)-1-cyclopentanols and cyclohexanols gave 3-methyl-2-naphthyl-1-cycloalkenes.

2. Thermal dehydration of 1-methyl-2-(1-naphthyl)-1-cyclohexanol produced 2-methyl-1-(1-naphthyl)-1-cyclohexene.

3. Structures of the five olefins were determined by oxidative fission at the double bonds to crude dicarbonyl products which were tested for the presence of the aldehydo and methylketo groups.

EUGENE, OREGON

REFERENCES

(1) CARLIN AND LANDERL, *J. Am. Chem. Soc.*, **75**, 3969 (1953).
(2) VAN RYSSELBERGE, *Bull. Classe sci. Acad. roy. Belg.*, [5] **12**, 171 (1926).
(3) TREIBS, MAYER, AND MADEJSKI, *Ber.*, **87**, 356 (1954).
(4) ORCHIN, *J. Org. Chem.*, **16**, 1165 (1951).
(5) KLEMM AND SPRAGUE, *J. Org. Chem.*, **19**, 1464 (1954).
(6) SIGGIA AND SEGAL, *Anal. Chem.*, **25**, 640 (1953).
(7) BACHMANN AND KLOETZEL, *J. Am. Chem. Soc.*, **60**, 2204 (1938).
(8) COOK AND LAWRENCE, *J. Chem. Soc.*, 1431 (1936).
(9) MAYER AND SCHIFFNER, *Ber.*, **65**, 1337 (1932).
(10) INGOLD, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, pp. 464–471.
(11) PRICE AND KARABINOS, *J. Am. Chem. Soc.*, **62**, 1159 (1940).
(12) WEISS AND WOIDICH, *Monatsh.*, **46**, 453 (1925).
(13) JOHNSON AND DAUB, *Org. Reactions*, **6**, 46–47 (1951).
(14) HEILBRON, *Dictionary of Organic Chemistry*, Vol. II, Oxford University Press, New York, 1936, (a) p. 667, (b) p. 660.
(15) ADAMS AND JOHNSON, *Laboratory Experiments in Organic Chemistry*, 4th Ed., Macmillan Company, New York, 1949, p. 249.
(16) KLEENE, *J. Am. Chem. Soc.*, **63**, 631 (1941).
(17) BERGMANN AND WEIZMANN, *J. Org. Chem.*, **9**, 352 (1944).
(18) KLEMM AND HODES, *J. Am. Chem. Soc.*, **73**, 5181 (1951).
(19) ORCHIN, *J. Am. Chem. Soc.*, **70**, 495 (1948).
(20) SMITH, GREENWOOD, AND HUDRLIK, *Org. Syntheses*, **26**, 63 (1946).
(21) HENNE AND PERILSTEIN, *J. Am. Chem. Soc.*, **65**, 2183 (1943).
(22) BUSCH AND STÖVE, *Ber.*, **49**, 1063 (1916).
(23) SHRINER AND FUSON, *The Systematic Identification of Organic Compounds*, 3rd Ed., John Wiley and Sons, Inc., New York, 1948, (a) p. 145, (b) pp. 138–139.
(24) JOHNSON, *J. Am. Chem. Soc.*, **73**, 5888 (1951).
(25) HIBBERT AND BURT, *Org. Syntheses*, Coll. Vol. I, 2nd Ed., p. 494 (1941).
(26) SIGGIA, *Quantitative Organic Analysis via Functional Groups*, John Wiley and Sons, Inc., New York, 1949, p. 8.
(27) BAER, GROSHEINTZ, AND FISCHER, *J. Am. Chem. Soc.*, **61**, 2607 (1939).