

and distribution. We have been unable to detect any annuloline in plants of *Lolium perenne*.

#### EXPERIMENTAL

*Annuloline hydrochloride.* Seed of *Lolium multiflorum* were germinated in lots of 350 grams on 47 × 51 cm. sheets of Whatman No. 1 filter paper. Water was supplied daily. The germination temperature varied between 22–25°. After 17 days the aerial portions of the seedlings were discarded and the roots together with the filter paper in which they were matted were extracted with petroleum ether (b.p. 62°–65°). Extraction was performed using 7–10 l. of solvent for each lot of roots and allowed to proceed for at least 24 hr. (with occasional stirring). The extraction was repeated 2–3 times with fresh solvent. The combined extracts from 2–3 lots of roots were concentrated to about 200–300 ml. After being stored for several days at –20° the concentrate was filtered through glass wool in order to remove the waxy solid which deposited. The concentrate was further reduced in volume to about 50 ml. and treated with anhydrous HCl whereupon crude annuloline hydrochloride was obtained as a yellow-gray ppt. The hydrochloride was triturated with about 5 ml. of ice cold absolute ethanol, the mixture centrifuged at 2° and the supernatant was discarded. The air dried product was further purified by trituration with 10–25 ml. of H<sub>2</sub>O and extraction with a sufficient number of 50-ml. portions of petroleum ether to remove the alkaloid which was now in the form of the free base. The petroleum ether solution was concentrated to 50–100 ml. and treated with HCl gas as before. The hydrochloride was washed with cold absolute ethanol and dried, m.p. 174–177°.

*Anal.*<sup>13</sup> Calcd. for C<sub>20</sub>H<sub>20</sub>NO<sub>4</sub>Cl: C, 64.30; H, 5.38; N, 3.75; Cl, 9.5. Found: C, 64.89; H, 5.28; N, 3.57; Cl, 8.57, 9.02.

*Annuloline.* The hydrochloride was converted to the free base by shaking its CHCl<sub>3</sub> solution with dilute alkali. The free base was obtained as a brown tar on removal of the CHCl<sub>3</sub>. After prolonged cooling in an ice bath and stirring, followed by overnight storage at room temperature, the material became transformed into a microcrystalline yellow powder. Recrystallization from hot benzene to which petroleum ether had been added to produce incipient cloudiness yielded fragile, light-yellow narrow rectangles, occurring mainly in clusters; m.p. 105–106°, remelting at same temperature. The product was neutral and tasteless but possessing a pleasant spicy resinous odor. The ultraviolet spectrum in cyclohexane showed a maximum at 354 mμ (log ε = 4.48) and a minimum at 285 mμ (log ε = 3.85).

*Anal.* Calcd. for C<sub>17</sub>H<sub>10</sub>NO(OCH<sub>3</sub>)<sub>3</sub>: C, 71.20; H, 5.64; N, 4.15; (OCH<sub>3</sub>)<sub>3</sub>, 27.6. Found: C, 70.59; H, 5.65; N, 4.16; OCH<sub>3</sub>, 26.1.

The methoxyl determinations<sup>14</sup> were made by the titrimetric method described by Niederl and Niederl.<sup>15</sup> Since recovery of OCH<sub>3</sub> from vanillin standards was 92% of theory, the value shown for annuloline has been adjusted accordingly. Dioxymethylene groups were shown to be absent by the procedure of Gaebel.<sup>16</sup>

*Annuloline picrate.* A 1% ethanolic solution of annuloline hydrochloride was treated with a slight excess of a 1% ethanolic solution of picric acid. The yellow fibrous crystals were recrystallized from hot 80% ethanol, m.p. 216–218°. One mole of picric acid per atom of N was found colorimetrically.

(13) Elementary analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, Colo.

(14) The methoxyl and dioxymethylene tests were carried out by Mr. R. S. Karimoto of this laboratory.

(15) J. B. Niederl and V. Niederl, *Organic Quantitative Micro-analysis*, J. Wiley and Sons, Inc., New York (1938), pp. 187–193.

(16) G. O. Gaebel, *Arch. Pharm.*, **248**, 226 (1910).

*Anal.* Calcd. for C<sub>20</sub>H<sub>19</sub>NO<sub>4</sub>·C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>O<sub>7</sub>: C, 55.10; H, 3.89; N, 9.89. Found: C, 55.18; H, 3.86; N, 10.05.

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### The Neopentyl and Neophyl Systems in Peracid Oxidation of Ketones<sup>1</sup>

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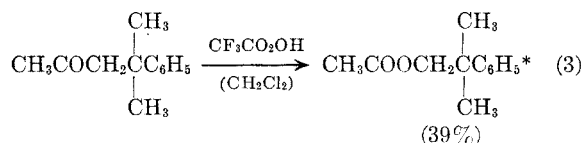
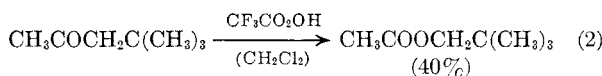
Received December 10, 1957

The suggestion of Emmons and Lucas<sup>2</sup> that the migrating group in the Baeyer-Villiger ketone oxidation<sup>3</sup> normally is the one most stabilized by hyperconjugative electron release appears to be substantiated by their work. Thus, in all the alkyl methyl ketones they reported, the methyl group was never observed to migrate, while the other alkyl group present in each case was capable of such hyperconjugative electron release and gave an acetate ester, as indicated below.



The yields were excellent (mainly 70–90%).

We have investigated *neopentyl* methyl ketone and *neophyl* ( $\beta$ -phenylisobutyl) methyl ketone in this reaction, following closely the directions of Emmons and Lucas. These ketones give *neopentyl* and *neophyl* acetates, as shown below, with no detectable amounts of methyl or other alkyl esters.



\* Yield based on consumed starting ketone.

The yields are poorer, however, than those noted in Emmons' work.

Because the neopentyl and neophyl systems have *no* hyperconjugative electron release (indeed, these systems often rearrange to the tert-amyl and benzyldimethylcarbinyl systems in order to achieve such hyperconjugative stabilization), we believe the present work shows that this hyperconjugative ability is not necessary for migration. It seems from all the work reported thus far that *any* alkyl group migrates preferentially to methyl. Hyperconjugative electron release may, nevertheless, be im-

(1) Abstracted from the thesis of Albert Danielzadeh to be submitted to the Graduate School of Loyola University for the degree of Master of Science, February 1958.

(2) W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955).

(3) A. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899) and other references to be found in the article cited in the previous footnote.

portant in determining the ease of oxidation and the yield of ester.

The retention of the neopentyl and neophyl skeletal systems in the product esters, with no indication of contamination by either tert-amyl or benzyldimethylcarbinyl acetates, incidentally affords support for the concerted (non-carbonium ion) type mechanism usually ascribed to this reaction.<sup>4</sup>

#### EXPERIMENTAL

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The infrared spectra were determined on liquid samples on Perkin-Elmer Model 21 Infrared Spectrophotometers by Miss E. Godar of this laboratory and by the Anderson Physical Laboratory, Champaign, Ill. Melting and boiling points are uncorrected.

**Materials.** *Trifluoroacetic anhydride* was commercial material (Halogen Chemicals), used as received. *Hydrogen peroxide* (90%) was generously supplied by the Becco Chemical Division of the Food Machinery and Chemical Corp., Buffalo, N. Y. *Neopentyl methyl ketone* was prepared as reported<sup>5</sup> by the dichromate oxidation of diisobutylene (Eastman) [44% yield, b.p. 124–127°,  $n_D^{20}$  1.404,  $d_4^{20}$  0.800, 2,4-dinitrophenylhydrazone m.p. 97° (lit.<sup>6</sup> m.p. 100°)]. *Neophyl methyl ketone* was prepared as reported<sup>7</sup> by the addition of mesityl oxide to benzene under aluminum chloride catalysis (61% yield, b.p. 61–62° at 1 mm.,  $n_D^{20}$  1.5115,  $d_4^{20}$  0.973 [lit.<sup>7</sup> b.p. 134° at 22 mm.,  $d_4^{25}$  0.972]). The 2,4-dinitrophenylhydrazone was prepared in the usual fashion, m.p. 98.5–99°.

*Anal.* Calcd. for  $C_{13}H_{20}N_4O_4$ : N, 15.71. Found: N, 15.56.

Authentic *neopentyl acetate* was obtained by the esterification of commercial neopentyl alcohol (Aldrich) in the usual manner with acetic acid and a trace of sulfuric acid [50% yield, b.p. 127°,  $n_D^{20}$  1.390,  $d_4^{20}$  0.855 (lit.<sup>8</sup> b.p. 127°,  $n_D^{20}$  1.3893,  $d_4^{20}$  0.8544)]. Authentic *neophyl acetate* was similarly obtained from neophyl alcohol<sup>9</sup> (60% yield, b.p. 105° at 5 mm.,  $n_D^{20}$  1.4959,  $d_4^{20}$  1.008).

*Anal.* Calcd. for  $C_{12}H_{16}O_2$ : C, 74.97; H, 8.38. Found: C, 75.17; H, 8.47.

**The oxidation of neopentyl methyl ketone.** A solution of peroxytrifluoroacetic acid was prepared by the dropwise addition of trifluoroacetic anhydride (37.8 g., 25.4 ml., 0.18 mole) to an ice cold solution of hydrogen peroxide (90%, 5.1 g., 4.1 ml., 0.15 mole) in methylene chloride (50 ml.). This solution was added dropwise over a 45-min. period to a stirred suspension of neopentyl methyl ketone (11.4 g., 0.1 mole) in methylene chloride (75 ml.) containing dry, finely powdered disodium hydrogen phosphate (65 g.). The exothermic reaction was controlled by the rate of addition and was completed by refluxing for 2 hr. after the addition was completed. The customary<sup>2</sup> work-up of the reaction mixture gave pure neopentyl acetate (5.25 g., 40% yield, b.p. 127–29°,  $n_D^{20}$  1.390,  $d_4^{20}$  0.863). The material gave a positive hydroxamic acid test for esters.

The infrared spectra of this product and authentic neopentyl acetate (see above) were identical, with indicative bands at 5.75  $\mu$  (saturated ester C=O), 6.76  $\mu$  ( $CH_2$ ), 7.27  $\mu$  ( $C\equiv C$ ) and 8.05  $\mu$  (acetate C—O—).

(4) Cf. footnote 2 for leading references.

(5) E. H. Man, F. C. Frostick, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **74**, 3229 (1952).

(6) L. Schmerling, *J. Am. Chem. Soc.*, **68**, 1650 (1946).

(7) A. Hoffman, *J. Am. Chem. Soc.*, **51**, 2542 (1929).

(8) O. R. Quayle and H. M. Norton, *J. Am. Chem. Soc.*, **62**, 1170 (1940).

(9) F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., *J. Am. Chem. Soc.*, **65**, 1469 (1943).

**The oxidation of neophyl methyl ketone.** A solution of peroxytrifluoroacetic acid was prepared as before, using double those amounts, and added as before to a solution of neophyl methyl ketone (35.2 g., 0.2 mole) in methylene chloride (150 ml.) containing dry, finely powdered disodium hydrogen phosphate (130 g.). Treatment of the reaction mixture in the usual fashion<sup>2</sup> gave neophyl acetate contaminated with much unchanged ketone (20 g., b.p. 90–100° at 4 mm.,  $n_D^{20}$  1.500,  $d_4^{20}$  0.989). Purification was effected by means of Girard's reagent T in the usual manner<sup>10</sup> and furnished pure neophyl acetate [11.0 g., 28.5% yield (38.5% yield based on consumed ketone), b.p. 89–90° at 2 mm.,  $n_D^{20}$  1.4960,  $d_4^{20}$  1.003]. This material was ketone free and gave a positive hydroxamic acid test for esters.

The infrared spectra of this product and authentic neophyl acetate (see above) were identical, with indicative bands at 5.76  $\mu$  (saturated ester C=O), 6.75  $\mu$  ( $CH_2$ ), 7.26  $\mu$  ( $C\equiv C$ ) and 8.00–8.16  $\mu$  (acetate C—O—), along with the expected peaks associated with aromatic unsaturation and mono-substitution.

**Acknowledgment.** We thank Miss E. Godar for certain of the infrared spectral measurements.

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(10) As, for instance, described in L. F. Fieser, *Experiments in Organic Chemistry*, D. C. Heath and Company, Boston, Mass., third edition (Revised) 1957, p. 89.

### Configuration of Two Dinitroölefins

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Received December 13, 1957

Work by Freeman and Emmons<sup>2</sup> on the addition of dinitrogen tetroxide to acetylenes led them to assign *cis* and *trans* configurations to isomers of two pairs of dinitroölefins. Through calculations of dipole moments from dielectric constant measurements on two of these same compounds we can add evidence to confirm their assignment. Dipole moments of 5.79 D and 5.16 D were obtained for 3,4-dinitro-3-hexene, m.p. 31–32°, and 2,3-dinitro-2-butene, m.p. 28.0–28.5°, respectively, the isomers obtained from treatment of 1-chloro-1-nitro alkanes with alkali. Since the dipole moment of a nitro group in an alkane is about 3.3 D, the measurement constitutes strong evidence for the *cis* configuration in these compounds. Courtauld models of the *cis* isomers suggest that the two nitro groups may not be co-planar with the double bond. There is room for this interpretation in the values of the dipole moments, which are less than expected for *cis* nitro groups coplanar with the double bond.

A distorted *cis* structure for the two compounds is

(1) Taken from the M.S. thesis of T. E. Mead, Brown University, 1957.

(2) J. P. Freeman and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 1712 (1957).