no complex was formed between osmium tetroxide and benzene.

Paper Chromatography of Osmium Tetroxide-Glycol Complexes. (1) **Ethylene Glycol-Osmium Tetroxide.**—Osmium tetroxide (0.1646 g.) was dissolved in 5 cc. of freshly distilled ethylene glycol. Immediately a chromatogram was prepared on Whatman No. 1 paper using 4 μl.-131 γ OsO_4 of the solution and another chromatogram with 4 μl. of ethylene glycol. Both were developed with a solvent mixture of benzene (80 vol.) and *n*-pentane (20 vol.). The ethylene glycol–osmium tetroxide complex chromatogram was colorless, but when sprayed with 2% thiourea in 5 *N* hydrochloric acid it developed a pink spot on white background with an R_f of 0.96. When a paper chromatogram is prepared with osmium tetroxide in ligroin and sprayed with the thiourea reagent the paper appears completely white with no pink-colored spots. Apparently the free osmium tetroxide evaporates while the complex remains on the paper. A chromatogram prepared from the ethylene glycol alone was sprayed with 1.5% solution of lead tetraacetate in glacial acetic acid containing 0.1% of acetic anhydride. It showed a white spot due to ethylene glycol which did not move from the place of application.

Another chromatogram was prepared after 4 hr. and the R_f of the complex was found to be the same. Finally, after 20 hr. of standing at room temperature the chromatogram showed again the same R_f for the complex. Moreover, in another chromatogram the complex was oxidized with lead tetraacetate and a white spot appeared on a brown background. This is an additional proof that the glycol was bound to osmium tetroxide.

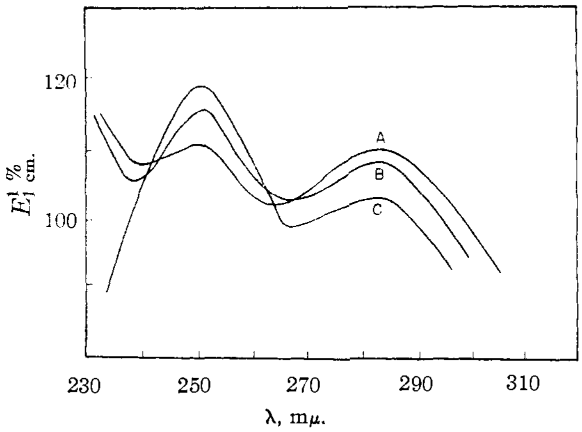

Fig. 4.—Ultraviolet absorption spectra of the osmium tetroxide–trimethylethylene glycol complex upon hydrogen peroxide addition: (A) before hydrogen peroxide addition; (B) 2 hr. after peroxide addition: (C) 1 day after peroxide addition.

(2) **Pinacol-Osmium Tetroxide.**—Anhydrous pinacol was dissolved in 1,2-dimethoxyethane to make a solution of 0.273 *M*. To this was added pure osmium tetroxide to make the solution with respect to osmium tetroxide 0.0256 *M*. A paper chromatogram (a) was then prepared with 50 μl.-325 γ OsO_4 and 1614 γ pinacol. This was developed with a mixture of benzene (80 vol.) and *n*-pentane (20 vol.). Two other chromatograms were prepared: (b) with the same solution as a and c with 10 μl.-360 γ of pinacol in absolute ethanol. A fourth chromatogram (d) was also prepared with 50 μl.-272 γ of osmium tetroxide alone in 1,2-dimethoxyethane. Chromatograms c and b were sprayed with lead tetraacetate solution while chromatograms a and d were sprayed with the thiourea reagent. The pinacol in c and the excess pinacol in b failed to move while the complex in a moved to the front and was colorless before spraying and pink colored after spraying with the thiourea reagent. Apparently traces of pink coloration which peared on the spot (d) which failed to move must be due to some other complex or reaction product between osmium tetroxide and 1,2-dimethoxyethane.

Acknowledgment.—The authors are indebted to Mrs. J. A. Hilton for technical assistance and in part to U. S. Public Health Service and Research Corporation for financial support of this investigation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Semipinacolic Deamination of Certain 1-Alkyl-2-amino-1-phenylethanols

BY HERBERT O. HOUSE AND EDWARD J. GRUBBS[1]

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The ketonic products obtained by the reaction of four 1-alkyl-2-amino-1-phenylethanols with nitrous acid in aqueous acetic acid have been determined. When the alkyl group was methyl, *n*-propyl or isopropyl, the only product detected was the corresponding alkyl benzyl ketone (phenyl migration). When the alkyl group was *t*-butyl, both the corresponding alkyl benzyl ketone and neopentyl phenyl ketone (*t*-butyl migration) were formed.

As part of a general study of the migratory aptitudes of various groups in reactions involving molecular rearrangement, we have studied the semipinacolic deamination of a number of 1,1-disubstituted-2-aminoethanols I in aqueous acetic acid. Data comparing the effects of substitution on the ease of migration of aryl groups in this system are available[2]; these data are in agreement with the generalization that aryl group migration is facilitated by electron-donating substituents. Furthermore, this system is at least sterically similar to the presumed intermediate in the Baeyer–Villiger reaction[3-6] and some parallelism of relative migratory aptitudes is to be anticipated.

In the present study the migratory abilities of the alkyl groups methyl, *n*-propyl, isopropyl and *t*-butyl have been compared with the phenyl group by reaction of the amino alcohols II with nitrous acid. The reaction of the first member IIa of this series has been reported[7] to yield the ketone III (phenyl migration); none of the isomeric ketone IV could be isolated. We have confirmed this result and also demonstrated that the product IIIa contains less than 3% of the ketone IVa. The same result was also obtained with the amino alcohols IIb and IIc. In the latter case, the product III could have contained no more than 1% of the ketone

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[1] Eastman Kodak Co. Predoctoral Fellow, 1958–1959.

[2] D. Y. Curtin and M. C. Crew, THIS JOURNAL, **76**, 3719 (1954).

[3] M. F. Hawthorne, W. D. Emmons and K. S. McCallum, *ibid.*, **80**, 6393 (1958).

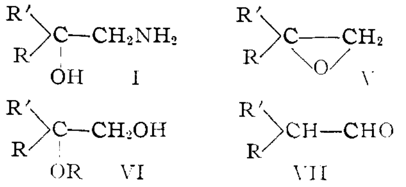
[4] M. F. Hawthorne and W. D. Emmons, *ibid.*, **81**, 6398 (1959).

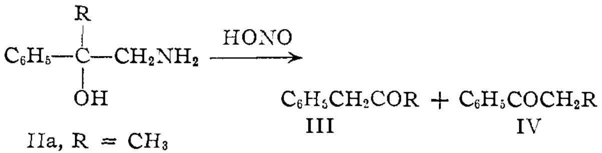
[5] W. von E. Doering and L. Speers, *ibid.*, **72**, 5515 (1950).

[6] S. L. Friess and N. Farnham, *ibid.*, **72**, 5518 (1950).

[7] M. Tiffeneau and H. Cahnmann, *Bull. soc. chim. France*, [5] **2**, 1876 (1935).

IV. The deamination of the amino alcohol IId produced a mixture of 75 ± 2% of the ketone III (phenyl migration) and 25 ± 2% of the ketone IV (*t*-butyl migration).



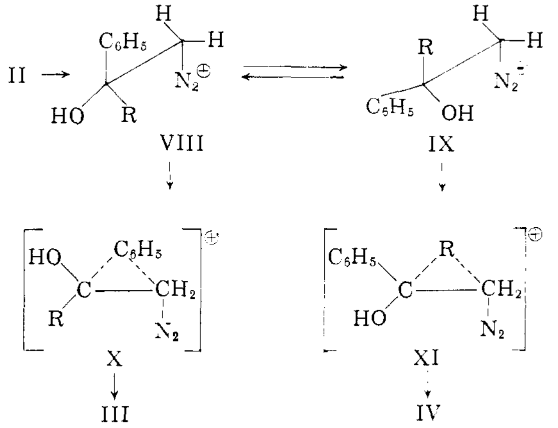

$$C_6H_5\text{—}C(R)(OH)\text{—}CH_2NH_2 \xrightarrow{HONO} \underset{III}{C_6H_5CH_2COR} + \underset{IV}{C_6H_5COCH_2R}$$

IIa, R = CH_3
b, R = $CH_3CH_2CH_2$
c, R = $(CH_3)_2CH$
d, R = $(CH_3)_3C$

Two explanations for the observed results not directly related to the question of migratory aptitude required consideration. The deaminations of amino alcohols of the type I could lead to disubstituted ethylene oxides V which might be supposed to be precursors of the ketonic products either by direct rearrangement or by solvolysis to the 1,2-diols or acetoxy alcohols VI (R = H or $COCH_3$) followed by rearrangement. However, examination of the literature reveals numerous examples of the isomerization of compounds of structure V or VI to form aldehydes VII and not ketones.[8,9]

The possibility also existed that the ketones IV were produced in the reaction mixture and were then selectively destroyed by the excess nitrous acid in the reaction mixture. The ketone IVd could be supposed to survive because of steric hindrance to reaction with nitrous acid. This possibility was excluded by demonstrating that the composition of a mixture of benzyl methyl ketone (IIIa) and propiophenone (IVa) was altered less than 1% (within the experimental error of the analytical method) by subjecting the mixture to the conditions of the deamination reaction.

Two possible explanations for the relative migratory aptitudes observed in this and previous studies are apparent. If the activation energy for rearrangement (and accompanying dissociation when applicable) is comparable in magnitude to the energy barrier to rotation of a single bond,[3,10,11] the observed relative migratory aptitudes could reflect little more than the relative concentrations of the various conformations of the intermediate.[11,12] For example, the two favored conformations of the diazonium ion derived from the amino alcohol II would be represented by structures VIII and IX. Alternatively, the relative migratory aptitudes could be a measure of the relative activation energies required to reach transition states such as X and XI for rearrangement. In an experimental determination of migratory aptitudes it is the sum of these two effects which is obtained although the effect of conformation may be negligible if the activation energy for rearrangement is appreciable.[12]



If the concentrations of conformations VIII and IX are presumed to be the sole factor determining the relative migratory aptitudes obtained in this study, it is necessary to assume that the concentration ratio of conformation VIII to conformation IX is at least one hundred when R is an isopropyl group and that the ratio is three when R is a *t*-butyl group. We consider these assumptions to be improbable since they imply an unusually large steric requirement for a phenyl group. It appears more profitable to consider that attainment of the transition state X for phenyl migration requires a lower energy than that required for transition state XI. This energy difference favoring phenyl migration could be ascribed to the greater orbital overlap possible in the transition state X which is comparable in structure to a phenonium ion intermediate. Although this explanation, based on differences in activation energy, appears to be more nearly compatible with the observed data, it seems probable that the magnitudes of the activation energies are sufficiently small so that the effect of concentrations of the conformations VIII and IX, discussed previously, is not completely obscured. Thus, the 25% of *t*-butyl group migration observed in the deamination of the amino alcohol IId could be attributed to conformation effects becoming comparable in importance to the difference in activation energies required to reach transition states X and XI.

Alternatively, the increased ability of the *t*-butyl group to migrate in competition with a phenyl group could be attributed either to an increase in the activation energy for the transition state X (R = *t*-butyl) as a result of steric interference[13] or to a decrease in the activation energy for the transition state XI (R = *t*-butyl), possibly because of an increased ability of the *t*-butyl group to distribute positive charge in the transition state.[3]

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(8) M. Tiffeneau, *Ann. chim. (Paris)*, [8] **10**, 145, 322 (1907).

(9) For example, see (a) A. Breuer and T. Zincke, *Ber.*, **11**, 1399 (1878); (b) R. Stoermer, *ibid.*, **39**, 2288 (1906); (c) A. Kotz and K. Richter, *J. prakt. Chem.*, **111**, 373 (1925); (d) H. O. House, THIS JOURNAL, **77**, 5083 (1955); (e) H. O. House, D. J. Reif and R. L. Wasson, *ibid.*, **79**, 2490 (1957).

(10) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

(11) A. Strietwieser, *J. Org. Chem.*, **22**, 861 (1957).

(12) For additional discussion of this point see D. Y. Curtin and M. C. Crew, THIS JOURNAL, **77**, 354 (1955).

(13) This argument has been applied to certain examples of the Baeyer-Villiger reaction by W. H. Saunders, *ibid.*, **77**, 4679 (1955).

Experimental[14]

α-Aminoacetophenone Hydrohalides.—Isonitrosoacetophenone[15] was converted to α-aminoacetophenone hydrochloride, m.p. 185° dec. (lit.[15] 185–186° dec.), by reduction with stannous chloride[16] (27% yield) and by hydrogenation over palladium-on-carbon in an anhydrous ethanol solution containing hydrogen chloride[17] (64% yield). The mixed hydrobromide and hydrochloride of α-aminoacetophenone was prepared in approximately 68% yield by reaction of phenacyl bromide with hexamethylene tetramine as previously described.[18]

2-Hydroxy-2-phenyl-3,3-dimethylbutylamine (IId).—To an ethereal solution of *t*-butylmagnesium chloride prepared from 78.7 g. (0.850 mole) of *t*-butyl chloride and 20.8 g. (0.855 g. atom) of magnesium was added, in portions and with stirring, 30 g. (approx. 0.14 mole)[18] of the mixed hydrobromide–hydrochloride salt of α-aminoacetophenone. After the mixture had been boiled under reflux with stirring for 7 hr., it was allowed to stand overnight under a nitrogen atmosphere and then poured into 50 ml. of a saturated, aqueous solution of ammonium chloride. The mixture was filtered and the two-phase filtrate was made alkaline with aqueous sodium hydroxide solution, heated to boiling, cooled and extracted with five 200-ml. portions of ether. The combined extracts were dried over magnesium sulfate and concentrated. An ethanolic solution of the residue deposited 0.46 g. (2.8%) of crude 2,5-diphenylpyrazine, m.p. 191–194°. Two additional crystallizations from ether afforded the pure pyrazine as colorless plates, m.p. 197.3–198° (lit.[19] 194–195°). The infrared spectrum[20] exhibits no absorption in the 3 μ region attributable to an N–H group and no absorption in the 6 μ region attributable to a carbonyl function.

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.58; H, 5.11; N, 12.00.

Distillation of the residual material from the mother liquor of the above crystallization afforded 4.60 g. (17%) of the desired amino alcohol, b.p. 109–110° (1 mm.), which solidified on standing. Redistillation of a portion of the sample gave a supercooled liquid sample of the amino alcohol, b.p. 83–89° (0.5 mm.), $n^{28}\mathrm{D}$ 1.5259. The amino alcohol crystallized from petroleum ether as white prisms, m.p. 69–70°. The infrared spectrum[21] has a broad band with its center at 3440 cm.$^{-1}$ (OH and NH) and exhibits no absorption in the 6 μ region attributable to a carbonyl function.

Anal. Calcd. for $C_{12}H_{19}ON$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.26; H, 9.83; N, 7.29.

2-Hydroxy-2-phenyl-3-methylbutylamine (IIc).—An ethereal solution of isopropylmagnesium bromide, prepared from 112 g. (0.912 mole) of isopropyl bromide and 22.4 g. (0.922 g. atom) of magnesium, was treated with 26.0 g. (0.152 mole) of α-aminoacetophenone hydrochloride as previously described. After a reaction period of 2 hr. the mixture was poured into 150 ml. of saturated, aqueous ammonium chloride solution and the resultant slurry was mixed with solid sodium hydroxide and extracted with six 500-ml. portions of ether. After the ether extracts had been dried over magnesium sulfate and concentrated, the viscous residue was crystallized first from carbon tetrachloride and then from ethyl acetate. The crude **hydrochloride of 2-hydroxy-2-phenyl-3-methylbutylamine** separated as white crystals, m.p. 184.5–188.5°, yield 3.0 g. (9.2%). Two additional crystallizations from ethyl acetate afforded the pure amino alcohol hydrochloride, m.p. 192–193°.

Anal. Calcd. for $C_{11}H_{18}ONCl$: C, 61.24; H, 8.41; N, 6.49; Cl, 16.44. Found: C, 61.24; H, 8.34; N, 6.53; Cl, 16.50.

A 2.66-g. sample of the amino alcohol hydrochloride was mixed with 15 ml. of 20% aqueous sodium hydroxide, heated to boiling, cooled and extracted with 200 ml. of ether in 15-ml. portions. The combined extracts were dried over magnesium sulfate and concentrated. Distillation of the residue through a short path still (bath temperature 130°) at 0.2 mm. afforded the desired amino alcohol as a colorless liquid, $n^{29}\mathrm{D}$ 1.5528. The infrared spectrum[21] of the product has a broad band with its center at 3450 cm.$^{-1}$ (OH and NH) and no absorption in the 6 μ region attributable to a carbonyl function.

Anal. Calcd. for $C_{11}H_{17}ON$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.60; H, 9.45; N, 7.74.

2-Hydroxy-2-phenylamylamine (IIb).—The reaction of 15 g. (0.0877 mole) of α-aminoacetophenone hydrochloride with an ethereal solution of propylmagnesium bromide, prepared from 64.7 g. (0.526 mole) of propyl bromide and 13.0 g. (0.535 g.-atom) of magnesium, for a period of 3 hr. followed by use of the isolation procedure described for 2-hydroxy-2-phenyl-3,3-dimethylbutylamine yielded 3.23 g. (20.6%) of the desired amino alcohol as a yellow liquid, b.p. 110° (3.2 mm.). Distillation of the product through a short-path still at 0.2 mm. pressure afforded the pure amino alcohol as a colorless liquid, $n^{30}\mathrm{D}$ 1.5284. The infrared spectrum[21] of the product has a broad band centered at 3500 cm.$^{-1}$ (O–H and N–H) and no absorption in the 6 μ region attributable to a carbonyl function.

Anal. Calcd. for $C_{11}H_{17}ON$: C, 73.70; H, 9.56; N, 7.81; Found: C, 73.99; H, 9.63; N, 7.78.

2-Hydroxy-2-phenylpropylamine (IIa).—Application of the previously described procedure to 15.0 g. (0.0877 mole) of α-aminoacetophenone hydrochloride and an ethereal solution of methylmagnesium iodide, prepared from 74.7 g. (0.526 mole) of methyl iodide and 13.0 g. (0.535 g.-atom) of magnesium, afforded 2.71 g. (20.5%) of the amino alcohol, b.p. 97° (0.45 mm.) [lit.[7] b.p. 133–140° (14 mm.)], $n^{30}\mathrm{D}$ 1.5455–1.5469.

In addition 44.9 mg. of 2,5-diphenylpyrazine, m.p. 196.2–196.8°, was isolated. This product was shown to be identical with the sample previously described by a mixed melting-point determination and by comparison of the infrared spectra of the two samples.

Nitrous Acid Deaminations: A. The Deamination of 2-Hydroxy-2-phenylamylamine (IIb).—To a cold (0°) solution of 0.547 g. (0.00306 mole) of the amino alcohol in 50 ml. of 50% aqueous acetic acid (by volume)was added a solution of 0.828 g. (0.012 mole) of sodium nitrite in 10 ml. of water and the resulting mixture was stirred at 2° for 28 hr. The reaction mixture was treated with an excess of 10% aqueous sulfamic acid solution, diluted with 75 ml. of water and continuously extracted with pentane for 42 hr. The pentane extract was dried over anhydrous sodium carbonate and then concentrated. Distillation of the residue through a short path still afforded 0.366 g. (74%) of a neutral product, $n^{28.5}\mathrm{D}$ 1.4994. The gas chromatogram[22] of the product exhibited a single peak having the same retention time as an authentic sample of benzyl propyl ketone. This chromatogram also established that no more than 5% of valerophenone could be present in the reaction mixture. The infrared spectrum[21] of the reaction product was identical with the spectrum of an authentic sample of benzyl propyl ketone and the ultraviolet spectrum[23] of the reaction product indicated that no more than 3% of valerophenone could be present in the reaction product. The reaction product formed a 2,4-dinitrophenylhydrazone, m.p. 130–131°, in 52% yield which was shown to be identical with an authentic sample of benzyl propyl ketone 2,4-dinitrophenylhydrazone both by a mixed melting-point determination and by comparison of the infrared spectra of the two samples.

B. The Deamination of 2-Hydroxy-2-phenylpropylamine (IIa).—The deamination of 0.557 g. (0.00360 mole) of the amino alcohol as previously described yielded 0.367 g. (74.3%) of neutral product, $n^{28}\mathrm{D}$ 1.5130. The gas chromatogram[22] of the product exhibited a single peak having the same

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[14] All melting points are corrected; all boiling points are uncorrected. The infrared spectra were determined with either a Baird, model B, or a Perkin–Elmer, model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, model 11 MS. The microanalyses were performed by Dr. S. M. Nagy and his associates.

[15] Prepared as described by H. E. Baumgarten and F. A. Bower, THIS JOURNAL, **76**, 4561 (1954).

[16] H. Rupe, *Ber.*, **28**, 251 (1895).

[17] A. K. Mills and J. Grigor, *J. Chem. Soc.*, 1568 (1934).

[18] C. Mannich and F. L. Hahn, *Ber.*, **44**, 1542 (1911); K. H. Slotta and H. Heller, *ibid.*, **63**, 1024 (1930). The mixed salt was reported to be composed of 90% of the hydrobromide and 10% of the hydrochloride. The calculations reported in this paper assume this composition.

[19] S. Gabriel, *ibid.*, **41**, 1127 (1908).

[20] Determined in chloroform solution.

[21] Determined in carbon tetrachloride solution.

[22] Determined with a column packed with Dow Silicone Fluid No. 550 suspended on ground firebrick.

[23] Determined in ethanol solution.

retention time as an authentic sample of benzyl methyl ketone, n^{28}_{D} 1.5136. Since authentic samples of benzyl methyl ketone and propiophenone were not completely resolved by gas chromatography,[22] this method of analysis could not be used. The infrared spectrum[21] of the product was identical with the spectrum of an authentic sample of benzyl methyl ketone and the ultraviolet spectrum[23] of the product indicated that no more than 3% of propiophenone could have been present. The reaction product afforded a 2,4-dinitrophenylhydrazone, m.p. 149.3–150.3°, which was shown to be identical with an authentic sample of benzyl methyl ketone 2,4-dinitrophenylhydrazone, m.p. 151.3–152.3° (lit.[24] 152–153°), both by a mixed melting-point determination and by comparison of the infrared and ultraviolet spectra of the two samples.

As a control experiment a solution containing a 0.495-g. sample composed of 50.5% benzyl methyl ketone and 49.6% propiophenone in 50 ml. of 50% aqueous acetic acid was treated with a solution of 0.8 g. of sodium nitrite in 10 ml. of water and the resulting solution was stirred at 2° for 24 hr. The ketone mixture, recovered as previously described, amounted to 0.405 g. (82% recovery). The infrared spectra of the original and recovered samples were superimposable. The ultraviolet spectra of the two samples differed in extinction at 241 mμ by less than 1%.

C. The Deamination of 2-Hydroxy-2-phenyl-3-methylbutylamine (IIc).—The deamination of 0.487 g. (0.00272 mole) of the amino alcohol as previously described yielded 0.372 g. (84%) of a neutral product. Although the gas chromatogram[22] of the product exhibited a single peak with the same retention time as benzyl isopropyl ketone, the alternative product, isovalerophenone, would not have been resolved under the conditions of the chromatogram. The infrared spectrum[21] of the product was identical with the spectrum of an authentic sample of benzyl isopropyl ketone and the ultraviolet spectrum of the product indicated that less than 1% (in each of two experiments) of isovalerophenone was present in the mixture. The product formed a semicarbazone, m.p. 139–140°, in 43% yield which was shown to be identical with an authentic sample of benzyl isopropyl ketone semicarbazone both by a mixed melting-point determination and by comparison of the infrared spectra of the two samples.

D. The Deamination of 2-Hydroxy-2-phenyl-3,3-dimethylbutylamine (IId).—The deamination of 0.500 g. (0.00259 mole) of the amino alcohol as described earlier yielded 0.334 g. (73%) of a neutral product, n^{29}_{D} 1.4986. The gas chromatogram[22] of the product had a single peak with a retention time corresponding to either benzyl *t*-butyl ketone or phenyl neopentyl ketone. The ultraviolet spectrum[23] of the product suggested the presence of 25 ± 2% (average value from three runs) of phenyl neopentyl ketone in the product. Infrared analysis of the mixture indicated the presence of 25 ± 3% of phenyl neopentyl ketone and 75 ± 3% of benzyl *t*-butyl ketone in the mixture. A 0.180-g. sample of the product was converted to a mixture of 2,4-dinitrophenylhydrazones which was partially separated by a combination of fractional recrystallization from ethanol and chromatography. Two pure 2,4-dinitrophenylhydrazone samples were isolated; namely, 41 mg. of the benzyl *t*-butyl ketone derivative, m.p. 140–140.7°, and 15 mg. of the higher-melting phenyl neopentyl ketone derivative, m.p. 156–156.6°. Both products were identified by mixed melting point determinations with authentic samples and by comparison of the infrared spectra of the samples.

Benzyl Propyl Ketone (IIIb).—An ethereal solution of the Ivanov reagent prepared from 11.1 g. (0.0702 mole) of sodium phenylacetate, 8.73 g. (0.0710 mole) of propyl bromide and 1.75 g. (0.0720 g.-atom) of magnesium was treated with 7.49 g. (0.0704 mole) of butyryl chloride. After the resulting mixture had been refluxed with stirring for 3 hr., the mixture was poured into dilute hydrochloric acid and heated until carbon dioxide was no longer being liberated. The neutral product, isolated in the usual manner and distilled under reduced pressure, amounted to 1.48 g. (13%), $n^{27.5}_{D}$ 1.5037 (lit.[25] n^{20}_{D} 1.5063). The product formed a 2,4-dinitrophenylhydrazone which crystallized from ethanol as orange needles, m.p. 129.5–130.5° (lit.[26] 129.5–130.5°). The infrared spectrum[21] of the ketone has a band at 1710 cm.$^{-1}$ (C=O); the ultraviolet spectrum[23] has a maximum at 287 mμ (ϵ 830) with a molecular extinction of 552 at 242 mμ. The corresponding values in the spectra of valerophenone are 1690 cm.$^{-1}$ (conj. C=O) and λ_{max} 242 mμ (ϵ 14,800). The ultraviolet spectrum[20] of benzyl propyl ketone 2,4-dinitrophenylhydrazone has a maximum at 364 mμ (ϵ 24,100).

Benzyl Isopropyl Ketone (IIIc).—Reaction of the Ivanov reagent from sodium phenylacetate with isobutyryl chloride by the procedure previously described yielded the desire ketone, b.p. 106–108° (6–8 mm.), $n^{29.5}_{D}$ 1.4965 (lit.[27] b.p. 113–116° (14.5 mm.), n^{25}_{D} 1.5040), in 9% yield. The product formed a semicarbazone which crystallized from ethanol as white needles, m.p. 140–140.5° (lit.[27] 140.5-141.5°), in 38% yield. The infrared spectrum[21] of the ketone has a band at 1711 cm.$^{-1}$ (C=O); the ultraviolet spectrum[23] has maxima at 258 mμ (ϵ 620) and 288 mμ (ϵ 600) with a molecular extinction of 533 at 243 mμ. The corresponding values in the spectra of isovalerophenone are 1690 cm.$^{-1}$ (conj. C=O) and λ_{max} 243 mμ (ϵ 12,200).

Phenyl Neopentyl Ketone (IVd).—To a suspension of 14.7 g. (0.110 mole) of aluminum chloride in 65 ml. of benzene, cooled in an ice-bath, was added, dropwise and with stirring over a period of 1 hr., a solution of 9.40 g. (0.0698 mole) of *t*-butylacetyl chloride[28] in 20 ml. of benzene. After the reaction mixture had been allowed to stand for 4 hr. the ketone was isolated in the usual manner. The product was collected at 112–114° (10 mm.), $n^{27.8}_{D}$ 1.5051–1.5055 (lit.[29] 115.2–116.2° (10–11 mm.), n^{25}_{D} 1.5056). The gas chromatogram[22] of the product exhibits a single peak; the ultraviolet spectrum[23] of the product has a maximum at 244 mμ (ϵ 11,900). The infrared spectrum[21] exhibits two peaks of nearly equal intensity in the 6 μ region at 1691 and 1677 cm.$^{-1}$. The spectrum of the product in chloroform solution has a band at 1668 cm.$^{-1}$ with a shoulder of lower intensity at 1685 cm.$^{-1}$. The nuclear magnetic resonance spectrum[30] has the following peaks (expressed as cycles per second relative to the proton resonance of water, a positive shift denoting a shift in the direction of increasing resonance frequency at constant magnetic field strength): a singlet at −168 sec.$^{-1}$ (CH_3 bonded to a carbon atom bearing no hydrogen atoms), a singlet at −99 sec.$^{-1}$ (CH_2 adjacent to carbonyl function and bonded to a carbon atom bearing no hydrogen atoms), and two multiple peaks in the ranges +86 and +107 sec.$^{-1}$ (aromatic C–H). Thus all of the physical properties of the product except the presence of a double carbonyl band in the infrared suggest that the ketone is a single substance, and we are led to believe that the split carbonyl absorption is attributable either to conformational effects or, possibly, to Fermi resonance.

Because of question about the purity of this product, the reported[29] conversion of phenyl neopentyl ketone to two isomeric 2,4-dinitrophenylhydrazones was also reinvestigated. Chromatography of the mixed 2,4-dinitrophenylhydrazones, m.p. 106–138°, on Merck acid-washed alumina resulted in the elution (with 1% ether in petroleum ether) of two fractions: A, yellow plates melting over the range 110–133° (lit.[29] 108–136°) and B, orange needles melting at 156–157° (lit.[29] 157.6–158.2°). The higher-melting fraction, B, was equilibrated by refluxing a solution of 43 mg. of the material in 4 ml. of ethanol containing 0.5 ml. of 6 *N* hydrochloric acid. Chromatography of the recovered derivative and subsequent recrystallization of the eluates afforded 9 mg. of golden plates, m.p. 109–115°, and 18 mg. of orange needles, m.p. 154.6–156.6°. The ultraviolet spectrum of the higher-melting form, m.p. 156–157°, has a maximum at 378 mμ (ϵ 28,100); the lower melting from, m.p. 109–115°, has a maximum at 369 mμ (ϵ 23,700). The ready interconvertibility of the two materials provides compelling evidence that the two are geometrical and not structural isomers. The ob-

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[24] F. C. Whitmore and T. K. Sloat, THIS JOURNAL, **64**, 2968 (1942).

[25] A. I. Vogel, *J. Chem. Soc.*, 610 (1948).

[26] R. T. Gilsdorf and F. F. Nord, THIS JOURNAL, **74**, 1837 (1952).

[27] A. T. Nielsen, C. Gibbons and C. A. Zimmerman, *ibid.*, **73**, 4696 (1951).

[28] The acid chloride, prepared by the reaction of the acid with thionyl chloride, was characterized as its amide, m.p. 127–131°, obtained in 48% yield. The pure amide crystallized from ether as white needles, m.p. 130.2–131.1°. A. H. Homeyer, F. C. Whitmore and V. H. Wallingford [THIS JOURNAL, **55**, 4209 (1933)] reported a melting point of 132° for this compound. There was no evidence that a second amide was present.

[29] E. Berliner and F. Berliner, *ibid.*, **72**, 222 (1950).

[30] Determined as a pure liquid with a Varian Associates high-resolution nuclear magnetic resonance spectrometer, model V4300B. The ratio signal used had a frequency of 40 mc.

served differences in ultraviolet absorption of the derivatives are in accord with this interpretation.[31]

Benzyl *t*-Butyl Ketone (IIId).—To an ethereal solution of benzylmagnesium chloride, prepared from 99.0 g. (0.783 mole) of benzyl chloride and 19.2 g. (0.790 g.-atom) of magnesium, was added, in portions with stirring over a period of 30 min., 19.7 g. (0.195 mole) of trimethylacetamide. The resulting solution was refluxed with stirring for 22 hr. and then poured into a mixture of ice and hydrochloric acid. The neutral products, isolated in the usual way, were subjected to a series of fractional distillations, the course of the distillation being followed by gas chromatography. After the separation of 0.119 g. of unchanged amide, m.p. 152–153°, and 1.94 g. of bibenzyl, m.p. 50–51.5° (lit.[32] 52.5–53.5°), the yield of pure ketone, b.p. 130–131° (21 mm.), $n^{29}\mathrm{D}$ 1.4984–1.4989, amounted to 8.52 g. (25%).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.72; H, 9.08.

The infrared spectrum[21] of the product has a band at 1711 cm.$^{-1}$ (C=O); the ultraviolet spectrum[23] has a maximum at 258 mμ (ε 220) with a molecular extinction of 121 at 244 mμ.

The ketone formed a 2,4-dinitrophenylhydrazone which separated from ethanol as yellow needles, m.p. 139.3–140.3°, yield 70%. An additional recrystallization raised the melting point to 140.1–140.8°. The ultraviolet spectrum[20] has a maximum at 365 mμ (ε 25,200).

Anal. Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.52; H, 5.76; N, 15.52.

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[31] F. Ramirez and A. F. Kirby, THIS JOURNAL, **76**, 1037 (1954).

[32] F. D. Greene, W. A. Remers and J. W. Wilson, *ibid.*, **79**, 1416 (1957).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polymerization of Higher α-Diolefins with Metal Alkyl Coordination Catalysts[1]

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The α-diolefins of the general formula $CH_2{=}CH(CH_2)_nCH{=}CH_2$ where *n* is equal to 4, 5, 6, 7, 8, 9, 10, 11, 12, 14 and 18, have been prepared and polymerized with the system aluminum triisobutyl–titanium tetrachloride. The polymers obtained consist of both soluble and insoluble, cross-linked fractions. The results of quantitative infrared and bromination determinations indicate that the soluble polymers possess cyclic units, open chain units containing terminal unsaturation as is present in the monomer, and open chain units containing internal unsaturation resulting from a rearrangement of the double bond from the terminal position.

In a recent publication,[2] was described the polymerization of 1,5-hexadiene and 1,6-heptadiene by means of the aluminum triisobutyl–titanium tetrachloride catalyst system to yield polymers which contained repeating cyclic units separated by methylene bridges. The present paper reports a study of the action of the coördination catalysts on longer chain α-diolefins.

The preparation of 1,7-octadiene (I) and 1,13-tetradecadiene (II) was carried out by allowing the appropriate ω-unsaturated alkylenemagnesium bromide to react with allyl bromide.

$$\mathrm{CH_2{=}CH(CH_2)_nMgBr} \xrightarrow{\mathrm{CH_2{=}CHCH_2Br}} \mathrm{CH_2{=}CH(CH_2)_{n+1}CH{=}CH_2}$$

I, $n + 1 = 4$
II, $n + 1 = 10$

The use of allyl chloride has been reported to yield only 15% of 1,7-octadiene,[3] but our yields were about 65%. Also the preparation of 1,13-tetradecadiene only in low yields in a manner similar to that described here has been reported[4] before.

The use of the appropriate α,ω-alkylenedimagnesium halides afforded good yields of 1,11-dodecadiene (III) (72%),[5] 1,14-pentadecadiene (IV) (54%) and 1,15-hexadecadiene (V) (56%). In addition to the main products, small amounts of α-diolefins containing an increased number of carbon atoms were isolated. From the synthesis of 1,14-pentadecadiene and 1,15-hexadecadiene were isolated, respectively, 1,23-tetracosadiene (VI) (12%) and 1,25-hexacosadiene (VII) (11%). These are new compounds and represent the longest known members of the straight-chain α-diolefin series.

$$\mathrm{Br(CH_2)_nBr} \xrightarrow{\mathrm{Mg}} \xrightarrow{\mathrm{CH_2{=}CH{-}CH_2Br}} \mathrm{CH_2{=}CH(CH_2)_{n+2}CH{=}CH_2} +$$

III, $n + 2 = 8$
IV, $n + 2 = 11$
V, $n + 2 = 12$

$$\mathrm{CH_2{=}CH(CH_2)_{2n+2}CH{=}CH_2}$$

VI, $2n + 2 = 20$
VII, $2n + 2 = 22$

1,14-Pentadecadiene has not been previously reported in the literature. 1,15-Hexadecadiene has been obtained only as a by-product from the reaction of 1,5-pentanedimagnesium bromide with allyl bromide.[6] The constants for these compounds reported earlier do not agree with those obtained here and they are not consistent with those expected in the α-diolefin series.

1,12-Tridecadiene (IX) has not been previously reported in the literature. The Boord olefin synthesis provided an easy route to this diolefin from undecylenyl bromide. The intermediate, α-(10-undecenyl)-β-bromoethyl ethyl ether (VIII), was obtained in 75% yield by allowing the Grignard reagent of undecylenyl bromide to react with α,β-dibromoethyl ethyl ether. However, it was difficult to find conditions which would permit formation and isolation of 1,12-tridecadiene from this

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[1] The work discussed herein was sponsored by a grant (NSF-G-2626) from the National Science Foundation.

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[6] J. N. Reformatsky, E. Grischkewitsch-Trochimowsky and A. Semensow, *Ber.*, **44**, 1885 (1911).