α-Amino-γ-2-pyridinebutyric Acid (II) Monohydrate.—A solution of 38.5 g. (0.14 mole) of ethyl α-acetamido-α-cyano-γ-2-pyridinebutyrate in 75 ml. of concentrated hydrochloric acid was refluxed for six hours. After evaporation of the solution to dryness under reduced pressure, a small quantity of ice was added and the solution was made slightly basic by the addition of ammonia solution. It was warmed on a steam-bath until all the solid formed by the evaporation process had dissolved. The nearly neutral solution was again cooled, and the solid which formed was removed by filtration. After washing once with alcohol, 35 g. of solid was obtained (a mixture of the desired product with ammonium chloride), m.p. 230° dec. Recrystallization from a very small amount of water gave 14 g. (51%) of a chloride-free product, m.p. 276° dec. A second recrystallization from aqueous alcohol gave material which melted at 280° dec., when the m.p. bath was preheated to 240°.

Anal. Calcd. for $C_9H_{12}N_2O_2 \cdot H_2O$: C, 54.53; H, 7.12. Found: C, 54.91; H, 6.97.

DEPARTMENT OF PHARMACEUTICAL CHEMISTRY
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The Mechanism of the Pyrolyses of Pinenes

BY ROBERT L. BURWELL, JR.

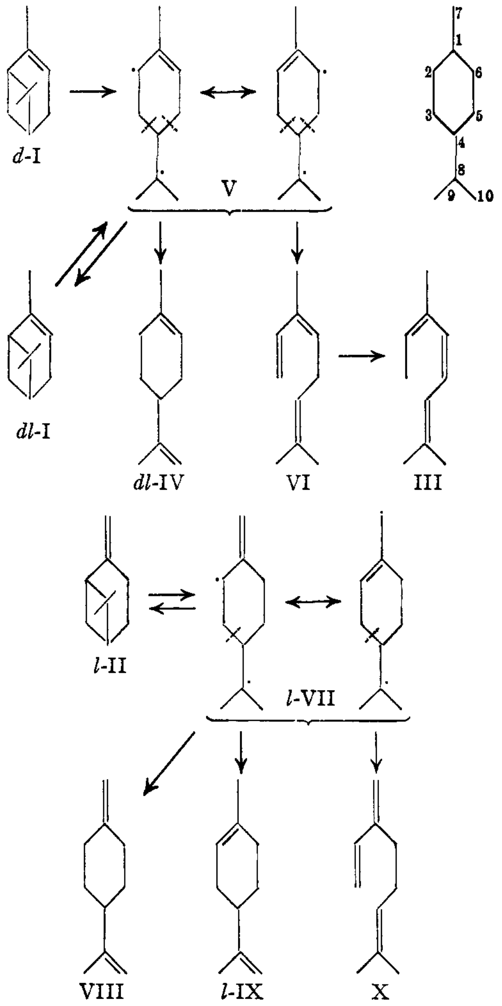
In view of the current interest in biradicals as reaction intermediates, it should be noted that a biradical provides an exceptionally attractive explanation of reactions occurring during pyrolyses of α-pinene (I) and β-pinene (II). The hypothesis permits one to deduce the relative rates of the reactions undergone by such biradicals. This biradical is unusual in that one of the odd electrons is part of an allylic resonance hybrid. The energetics, kinetics and products are consequent to this.

Savich and Goldblatt,[1] Fuguitt and Hawkins[2] and earlier workers have shown that vapor or liquid phase pyrolysis of α-pinene in the temperature range 200 to 500° results initially in three simultaneous reactions, all first order:[2] (a) racemization of α-pinene, (b) isomerization to *allo*-ocimene (III), and (c) isomerization to almost inactive limonene (IV). The relative rate of reaction (c) declines slowly with increasing temperature. The activation energy for the total reaction is about 41 kcal.[2] Frequency factors accord with those expected for unimolecular processes.[2]

If the three reactions are first order, racemization cannot involve either *dl*-limonene or *allo*-ocimene as an intermediate.[3] Furthermore, nearly *dl*-limonene is formed as such since *l*-limonene resists racemization under the reaction conditions.[1]

The biradical (V) coördinates these facts. It is a resonance hybrid like the allyl free radical and is similarly stabilized. Reforming the broken bond leads to *dl*-I since recombination may occur to each stereochemical antipode. As models show, intramolecular hydrogen atom transfer is possible only from one of the six hydrogen atoms on the isopropyl residue (positions (9) and (10)) to the equivalent positions (2) or (6). Such a process forms *d*-IV and *l*-IV with equal probability. Rupture of either of the bonds indicated by dotted lines (3–4 or 4–5) forms VI which like ocimene[4] should readily conjugate to III at reaction temperatures. Intermediate V probably possesses a folded structure intermediate between *d*-I and *l*-I.

This mechanism, then, proposes a rate determining isomerization of I to the biradical which further reacts with probabilities which are temperature dependent.



Szwarc and Sheon[5] report the process $CH_2{=}CH{-}CH_2{-}CH_3 \rightarrow CH_2{=}CH{-}CH_2\cdot + CH_3\cdot$ to involve an activation energy of 62 kcal./mole. Allowance for the bond strain in a cyclobutane ring would reduce this value about to the activation energy reported for pyrolysis of α-pinene. The bond between carbon atoms (2) and (3) does not rupture at a rate detectable in comparison with the bond between (2) and (8) presumably owing to the greater stability of the tertiary free radical formed in the latter case.

Rice and Rice[6] proposed that a biradical like V should be formed from α-pinene and should im-

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[1] T. R. Savich and L. A. Goldblatt, THIS JOURNAL, 67, 2027 (1945).

[2] R. E. Fuguitt and J. E. Hawkins, *ibid.*, 67, 242 (1945); 69, 319 (1947).

[3] R. L. Burwell, Jr., *ibid.*, 70, 2865 (1948).

[4] J. L. Simonsen, "The Terpenes," 2nd ed., Vol. I, University Press, Cambridge, 1947, p. 20.

[5] M. Szwarc and A. H. Sheon, *J. Chem. Phys.*, 18, 237 (1950).

[6] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, p. 164.

mediately rearrange to ocimene (VI).[7] Other possible reactions of the intermediate and the stereochemical properties of the intermediate were not considered.

Application of the same concept to the pyrolysis of β-pinene (II) leads to the biradical (VII) which unlike V is asymmetric. Models show that hydrogen atoms from the isopropyl residue (positions (9) and (10)) may be transferred either to positions (2) or (7). One would expect transfer to position (7) with the formation of an internal olefin (IX) to be favored over that to position (2) which leads to an exo-structure (VIII). Limonene (IX) so formed should be optically pure. Recombination of the biradical (VII) unlike that of V would regenerate an unracemized pinene. Bond fission between carbon atoms (3) and (4) would lead to myrcene (X).

Goldblatt and Palkin[8] report the vapor phase pyrolysis of β-pinene to lead to myrcene (X) and *l*-IX of "singularly high rotation." The rotation of the isolated limonene was about 10% under the maximum possible.[9] No VIII was reported. The small deficit in rotation of IX might originate from the presence of a little VIII.

Hunt and Hawkins[10] report that the isomerization of β-pinene proceeds as a first order reaction unaffected by small quantities of hydroquinone. Dilution with *dl*-IV does not affect the rate constants. The reported activation energy is about 48 kcal.

Data which critically test the prediction that recovered β-pinene would be unracemized have not been reported.

The proposed mechanism provides a stereochemical correlation between *l*-β-pinene and *l*-limonene.

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[7] The formation of ocimene was later reported, F. O. Rice, U. S. Patent 2,190,369, February 13, 1940. No other investigator has reported ocimene.

[8] L. A. Goldblatt and S. Palkin, THIS JOURNAL, **63**, 3517 (1941).

[9] Ref. 4, p. 152 gives 126.8°; ref. 8 reports 114.9°.

[10] H. G. Hunt and J. E. Hawkins, THIS JOURNAL, **72**, 5618 (1950).

DEPARTMENT OF CHEMISTRY
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The Association of Tri-*p*-xenylmethyl

BY TING-LI CHU AND S. I. WEISSMAN

Recent measurements of the magnetic susceptibility of solutions in toluene of tri-*p*-xenylmethyl[1] show that over the temperature range 0 to 60° and the concentration range 0.018 to 0.032 mole per liter the molar susceptibility is constant. Use of the conventional correction for diamagnetism leads to a constant degree of association of 0.20.

In connection with other work we have investigated the absorption spectra of solutions of tri-*p*-xenylmethyl in toluene. We find that the Beer–Lambert law is obeyed over the concentration range 2×10^{-4} to 4.5×10^{-3} mole per liter, and that the molar extinction coefficient is independent of temperature over the range 10 to 40°. The shape of the absorption curves obtained by us is identical with those already given in the literature.[2,3] The molar extinction coefficient at the peak at 6150 Å. is 1525. These results indicate that tri-*p*-xenylmethyl is not associated in toluene solution.

Our solutions were prepared on the vacuum bench by the method already described by Lewis, Lipkin and Magel.[2] A solution of a weighed sample of pure tri-*p*-xenylcarbinol[4] in freshly distilled acetyl chloride was refluxed for 12 hours. The resulting solution was made up to a known volume and an aliquot pipetted into a Pyrex absorption cell. The cell was quickly attached to the vacuum line where all subsequent operations were carried out. The acetyl chloride was evaporated and the solid halide subjected to prolonged evacuation at about 80°. Any trace of acid remaining in the system was neutralized by introduction of triethylamine vapor. A measured volume of toluene and a trace of triethylamine (each dried over sodium–potassium alloy) were distilled into the cell containing the halide, and silver amalgam was then introduced by a vacuum dumper. The cell was sealed off under vacuum, and reduction effected by several minutes shaking of the solution with the amalgam. The free radical solutions prepared in this way remained unchanged during several days storage in the dark at room temperature.

We may report, in addition, that α-naphthylphenyl-*p*-xenylmethyl also obeys Beer's law with a temperature-independent extinction coefficient. A mixture of this free radical with tri-*p*-xenylmethyl, however, does not obey Beer's law, nor is the absorption at fixed concentration independent of temperature. The two free radicals apparently associate in toluene solution.[5] According to our data ΔF^0 for the association is about -4 kcal. per mole at 25°, while ΔH is about -12 kcal. per mole.

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[1] P. W. Selwood and R. M. Dobres, THIS JOURNAL, **72**, 3860 (1950).

[2] G. N. Lewis, D. Lipkin and T. T. Magel, *ibid.*, **66**, 1579 (1944).

[3] It has been demonstrated (ref. 2) that unless extreme precautions are taken, tri-*p*-xenylmethyl is converted to another free radical of unknown constitution. The pure tri-*p*-xenylmethyl is blue-green, the other free radical red. In a recent paper Dobres and Selwood (THIS JOURNAL, **72**, 5731 (1950)) describe tri-*p*-xenylmethyl as "deep burgundy." Apparently our blue-green substance and the one studied by Dobres and Selwood are different.

[4] This material was generously supplied by Professor Lipkin. It is a portion of the preparation used in the work of Lewis, Lipkin and Magel.

[5] A result pointing in the same direction has been obtained by C. S. Marvel and Chester M. Himel, THIS JOURNAL, **64**, 2227 (1942).

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Rate of Oximation and Extent of Enolization of Alkyl Aryl Ketones[1]

BY MARY J. CRAFT,[2] BILLY F. LANDRUM,[2] EDGAR C. SURATT[2] AND CHAS. T. LESTER[3]

We have previously reported the rate of oxime formation of four series of ketones.[4] We have ex-

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[1] This work was made possible through a contract with the Office of Naval Research.

[2] Taken from respective Ph.D. Dissertations, Emory University, 1950.

[3] Responsible co-author.

[4] (a) E. C. Suratt, J. R. Proffitt, Jr., and C. T. Lester, THIS JOURNAL, **72**, 1561 (1950); (b) M. J. Craft and C. T. Lester, *ibid.*, **73**, 1127 (1951).