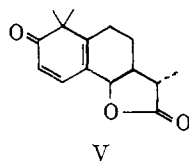


sensitizers such as benzophenone ($E_T = 68.5$ kcal.⁵) to santonin resulting in the photoconversion of santonin. The following comparison illustrates this point. One Pyrex tube contained a $1.95 \times 10^{-2} M$ solution of santonin which absorbed 58% of the incident radiation. Another tube contained a solution $4.3 \times 10^{-2} M$ in benzophenone and $1.95 \times 10^{-2} M$ in santonin such that the benzophenone absorbed 91% and the santonin 9% of the incident light. Both tubes were irradiated with the 3660-Å. line of mercury. The conversion of santonin to lumisantonin was 1.7 times as rapid in the tube containing the benzophenone. This indicated also that the photolysis of santonin alone was probably an efficient process, a surmise which was confirmed by the finding that this reaction has a quantum yield of approximately unity. On the other hand, Michler's ketone ($E_T = 61.0$ kcal.⁶) did not sensitize the photoconversion of santonin but acted only as a filter.

If the photolysis is carried out in piperylene as solvent, the photoconversion is completely quenched. This requires the intermediacy of triplets as the energy of the piperylene singlet (~ 2300 Å.) lies far higher than that of the incident radiation.⁷ However, the photoconversion of santonin does not cause the *cis-trans* isomerization of dilute solutions (*e.g.*, 0.2 *M*) of piperylenes or stilbenes.

From these results we conclude that the conversion of santonin to lumisantonin involves the following steps: excitation of santonin to a singlet state which crosses with near unit efficiency to the triplet state which undergoes a very rapid molecular rearrangement to lumisantonin.

In a similar fashion it has been possible to demonstrate the transfer of triplet character and energy from photosensitizers such as Michler's ketone to lumisantonin. The first isolable product of this reaction (and likewise of unsensitized reactions) is a new substance which has been shown to have structure III by physical and chemical methods and is identical with a substance isolated by Chapman and reported in an accompanying communication.⁸ This substance is very easily converted by dilute acid to an isomer V with the epimeric configuration at C-6, which is, in fact, the compound synthesized earlier by van Tamelen, *et al.*³ Such epimerization is known to be facile under acidic conditions.^{9,10} Further irradiation of III in the presence



of water yields photosantonin acid (IV).

From these results we conclude that the photochemistry of santonin, lumisantonin, and, by generalization, of other conjugated ketones involves the triplet state as the species which undergoes molecular rearrangements. It has been suggested¹¹ that the triplet state of similar systems is likely to be more polarizable and also more basic than the ground state. The photo-

chemical rearrangements of these systems can all be easily rationalized by assuming that the rearranging intermediate has negative character localized on the oxygen and positive character distributed through the conjugated system of the carbon skeleton.¹²⁻¹⁴ Thus, this demonstration of the intermediacy of triplet states in the photochemistry of santonin leads directly to the suggestion that the photochemical rearrangements of conjugated ketones proceed through triplet states having considerable charge separation which facilitates carbonium ion-type rearrangements of the carbon skeletons. An interesting possibility, which is in accord with the experimental facts just related and results on energies of $n \rightarrow \pi^*$ (triplet) and $\pi \rightarrow \pi^*$ (triplet) conversions,^{15,16} is that the excitation involved is not of the traditionally assumed $n \rightarrow \pi^*$ (triplet) type but rather involves a $\pi \rightarrow \pi^*$ (triplet) conversion which would explain even more convincingly the electron deficiency apparent in the carbon skeleton undergoing molecular rearrangement.

From the observed short lifetime of the santonin triplet, we had not anticipated observing any phosphorescence emission from santonin. However, in a MCIP (5:1 by volume methylcyclohexane:isopentane) glass at 77°K. the purest santonin we have been able to obtain showed a clear, broad phosphorescence emission ($\tau > 5 \times 10^{-4}$ sec.) at 68 ± 1 kcal. This may be interpreted in at least two ways: that the rigidity of the glass imprisoning the santonin prevents the molecular motions necessary for the molecular rearrangement to lumisantonin or that the observed emission comes from some triplet intermediate between santonin and lumisantonin.

Acknowledgment.—We wish to thank Mr. A. Lamola for determining the emission spectrum of santonin, Prof. G. S. Hammond for stimulating discussions, and the National Science Foundation for financial support.

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(13) O. L. Chapman and S. L. Smith, *J. Org. Chem.*, **27**, 2291 (1962).

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(15) G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

(16) G. S. Hammond, P. A. Leermakers, N. Turro, J. Saltiel, A. Lamola, *et al.*, unpublished work.

(17) NSF Predoctoral Fellow.

(18) Alfred P. Sloan Research Fellow.

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Diene Studies. I. Relative Stabilities of Dihydrobenzenes and Hexahydronaphthalenes

Sir:

An understanding of the factors governing the relative thermodynamic stabilities of isomeric 1,3- and 1,4-dienes is particularly desirable now that methods for cleanly isomerizing dienes of this type are available.¹

(1) We found the adaptations described below of the method of N. Turnbull, U. S. Patent 2,316,136 (1943) (*Chem. Abstr.*, **37**, 5420 (1943)), to give less than 3% of side reactions (polymerization, disproportionation, etc.). Turnbull describes the conversion of VI to V in up to 71% yield, but does not mention what the remaining material is. For further base-catalyzed diene isomerizations, see: (a) H. Pines, J. A. Vesely, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **77**, 347, 6314 (1955); (b) H. Pines and L. Schaap, *ibid.*, **79**, 2956 (1957); (c) T. M. O'Grady, R. M. Alm, and M. C. Hoff, *Am. Chem. Soc. Div. Petrol. Chem. Preprints*, **4**, B65 (1959); (d) I. V. Gostunskaya and B. A. Kazanskii, *Zhur. Obshch. Khim.*, **25**, 1995 (1955); *Chem. Abstr.*, **50**, 8437 (1956); (e) J. H. Mitchell, Jr., H. R. Kraybill, and F. P. Zscheile, *Ind. Eng. Chem., Anal. Ed.*, **15**, 1 (1943); (f) J. Davenport, A. J. Birch, and A. J. Ryan, *Chem. Ind. (London)*, 136 (1956); (g) B. Sreenivasan and J. B.

(5) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4983 (1962).

(6) E. Herkstroeter, unpublished work.

(7) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(8) O. L. Chapman and L. F. Englert, *J. Am. Chem. Soc.*, **85**, 3028 (1963).

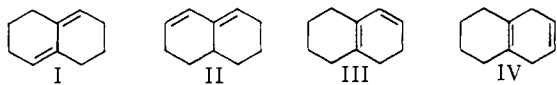
(9) H. Ishikawa, *J. Pharm. Soc. Japan*, **76**, 504 (1956).

(10) The configuration at C-6 is assigned on the basis of the n.m.r. spectral comparisons between V and 6-episantonin. Moreover, concomitant epimerization at C-11 is unlikely as the 5% hydrochloric acid in dimethylformamide, which causes epimerization at C-6, is without effect on the configuration at C-11.⁹

(11) J. M. Hirshon, D. M. Gardner, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **75**, 4115 (1953).

We have equilibrated the hexahydronaphthalenes with 1,3- and 1,4-diene systems and the dihydrobenzenes, and found that some new factors must be employed to explain the results.

Four hexahydronaphthalenes were detected² in the equilibrium mixture, prepared by heating $\Delta^{1,8}$ -hexahydronaphthalene³ (II) or $\Delta^{2,9}$ -hexahydronaphthalene⁴ (IV) with potassium *t*-amyloxide in *t*-amyl alcohol at 184° for 24 hr.: $\Delta^{1(9),5(10)}$ -hexahydronaphthalene (I), 53.7%; II, 25.5%; $\Delta^{1,9}$ -hexahydronaphthalene (III), 14.1%; IV, 6.4%. Taking statistical factors into account (*i.e.*, II and III are favored in isomerizations by factors of two over I and IV), these percentages indicate the other hexahydronaphthalenes to be less stable than I by 1.31 (II); 1.85 (III); 1.93 (IV); and at least 3.6 kcal./mole (other isomers, assuming that as much as 1% of another isomer would have been detected). At 95.0°, the equilibrium mixture of dihydrobenzenes (prepared from either isomer) contained 68.9% of 1,2-dihydrobenzene (V) and 31.1% of 1,4-dihydrobenzene (VI); with the statistical factor considered, V is only 0.07 kcal./mole more stable than VI at this temperature.



A well recognized factor affecting alkene stability is the degree of substitution by alkyl groups; although there is considerable disagreement as to the cause of the effect, its magnitude is known to be about 2–4 kcal./mole.⁵ This factor undoubtedly contributes to making I–IV the four most stable hexahydronaphthalenes.

It was surprising to find in the two systems that 1,4-cyclohexadienes (IV and VI) are of essentially the same stability as the corresponding 1,3-cyclohexadienes (III and V).⁶ This appears to be a special feature of cyclohexadienes, since in acyclic systems^{c,g,h,6} and cyclooctadienes,^{1c} the conjugated isomer is more stable than the unconjugated isomer by several kcal./mole, due to delocalization and/or hybridization.^{7,8} That some special destabilizing effect in 1,3-cyclohexadienes is not responsible is suggested by the heats of hydrogenation of cyclohexene and 1,3-cyclohexadiene⁷; there must, then, be a stabilizing feature of about 2 kcal./mole in 1,4-cyclohexadienes which is absent in other 1,4-dienes. This probably involves interaction between the double bonds; in what has been suggested as the most stable conformation,⁹ the π -electrons of

the two double bonds are quite close on one side of the ring.¹⁰

Another factor which is readily noticeable in the hexahydronaphthalene series is that *transoid dienes are more stable than cisoid dienes with the same degree of alkyl substitution by about 2–4 kcal./mole*.¹¹ Thus, I is more stable than III by 1.84 kcal./mole and $\Delta^{1(9),4}$ -hexahydronaphthalene (VII) by at least 3.6 kcal./mole; II, the other *transoid* hexahydronaphthalene, is more stable than $\Delta^{1(9),2}$ -hexahydronaphthalene by at least 2.9 kcal./mole.¹² This effect had been previously observed¹³ and given some theoretical basis¹⁴ for butadiene, but with butadiene the question of the contribution of the steric interaction between the "inside" protons on carbons 1 and 4 in *cisoid* butadiene always remained.^{8a} From the current results, it appears likely that this steric interaction is not the major factor causing the observed preference of butadiene for the *transoid* conformation.

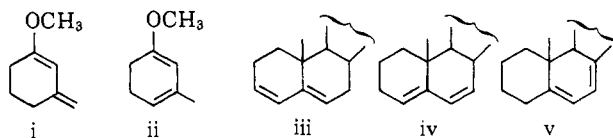
Isomerization studies on other dienes are in progress.¹⁵

(9) F. H. Herbstein, *J. Chem. Soc.*, 2292 (1959).

(10) For a suggestion of a similar effect in cycloheptatrienes, see R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, 839 (1962).

(11) Doering and co-workers (ref. 6) have noted this "destabilizing *cis* effect" in other systems.

(12) There are cases in which *transoid* dienes have been shown to be more stable (qualitatively) than *cisoid* dienes with more alkyl substituents, *e.g.*, i is more stable than ii (A. J. Birch, E. M. A. Shoukry, and F. Stansfield, *J. Chem. Soc.*, 5376 (1961)) and iii (J. C. Eck and E. W. Hollingsworth, *J. Am. Chem. Soc.*, **63**, 107 (1941)) and iv (K. Dimroth and G. Trautmann, *Ber.*, **69**, 669 (1936); H. E. Stavely and W. Bergmann, *J. Org. Chem.*, **1**, 575 (1937)) are more stable than v.



(13) (a) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946); (b) W. B. Smith and J. L. Massingill, *J. Am. Chem. Soc.*, **83**, 4301 (1961).

(14) R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

(15) We gratefully acknowledge financial support from the National Science Foundation (Fellowship to R. H. C.) and the Public Health Service (GM-07689, R. B. B. and C. E. S.).

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Diene Studies. II. Relative Stabilities of Some Pentadienyl Carbanions

Sir:

Pentadienyl carbanions have long been proposed as intermediates in nucleophilic aromatic substitution,¹ and more recently in Birch reductions of aromatic compounds and in base-catalyzed isomerizations of 1,3- and 1,4-dienes.² Possibly the best evidence that they are intermediates in the latter case is that double bonds in 1,3- and 1,4-dienes migrate far more rapidly in base than isolated double bonds³ and when a particularly stable carbanion is involved or a particularly strong base is used, their metal salts have been obtained in high concentration.^{1a,2c,4} Pentadienyl carbanions

(1) (a) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); (b) J. Miller, *J. Am. Chem. Soc.*, **85**, 1628 (1963).

(2) (a) A. J. Birch, *Quart. Rev.*, **4**, 69 (1950); (b) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959); (c) A. J. Birch, E. M. A. Shoukry and F. Stansfield, *J. Chem. Soc.*, 5376 (1961); (d) W. von E. Doering, G. Schroeder, K. Trautner, and S. Staley, 144th National Meeting of the American Chemical Society, 1963, p. 14M.

(3) We have found that the isomerization of *cis*- Δ^1 -octahydronaphthalene to $\Delta^{9,10}$ -octahydronaphthalene is slower than the isomerization of I to II by a factor of at least 10⁵.

(4) R. Paul and S. Tchelitcheff, *Compt. Rend.*, **239**, 1222 (1954); G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957).

Brown, *J. Am. Oil Chemists' Soc.*, **33**, 521 (1956); (h) H. B. White, Jr., and F. W. Quackenbush, *ibid.*, **36**, 653 (1959).

(2) All of the dienes described were characterized using their n.m.r., ultraviolet, and infrared spectra, and elemental analyses. III (which shows one sharp peak in the vinyl region of its n.m.r. spectrum) was distinguished from VII by the presence of vinyl proton absorption in the n.m.r. spectrum of its adduct with tetracyanoethylene.

(3) Prepared by dehydrating $\Delta^{1(9),2}$ -octalol (H. Böhme and G. Peters, *Z. Naturforsch.*, **12b**, 5 (1957)) with 3,5-dinitrobenzoyl chloride in pyridine and removing *cisoid* conjugated dienes by adduct formation with tetracyanoethylene.

(4) C. B. Wooster, U. S. Patent 2,182,242 (1939) (*Chem. Abstr.*, **34**, 1993 (1940)); A. J. Birch, *J. Chem. Soc.*, 430 (1944).

(5) See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 247. It is important to note that this generalization holds well for the octahydronaphthalenes (A. S. Hussey, J.-F. Sauvage, and R. H. Baker, *J. Org. Chem.*, **26**, 256 (1961)).

(6) W. von E. Doering, G. Schroeder, K. Trautner, and S. Staley, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, California, 1963, p. 14M. These authors have also isomerized the dihydrobenzenes, finding a similar small difference in stability when the statistical factor of 0.6 kcal./mole is taken into account.

(7) See, for example, G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 80.

(8) (a) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959); (b) M. J. S. Dewar and H. N. Schmeising, *ibid.*, **5**, 166 (1959); (c) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).