pared by the method of Overhoff and Provst[7] from 63 g. (0.40 mole) of 2-bromopyridine, 24 g. (0.60 g.-atom) of magnesium, and 20 g. (0.184 mole) of ethyl bromide. The complex which resulted from a 12-hr. reflux of this reagent with 22 g. (0.40 mole) of propionitrile was decomposed with 4 moles of anhydrous methanol. Several grams of dipyridyl, in addition to the ketimine, was obtained on distillation of the reaction filtrate.

Anal. Calcd. for $C_8H_{10}N_2$: N, 20.89; neut. equiv., 67.10. Found: N, 20.81; neut. equiv., 67.20.

Melting points of the phenylhydrazone and 2,4-dinitrophenylhydrazone of the hydrolyzed ketimine agreed with those reported for the corresponding derivatives of ethyl 2-pyridyl ketone.

2-Thienyl 5-acridyl ketimine. The Grignard reagent prepared from 63 g. (0.30 mole) of 2-iodothiophene and 8 g. (0.30 g.-atom) of magnesium with 300 ml. of tetrahydrofuran as the solvent was allowed to react with 15.8 g. (0.077 mole) of 5-cyanoacridine during a 15-hr. reflux. The complex was decomposed by addition of 1 mole of anhydrous methanol; the ketimine was precipitated as a saline complex from the decomposition filtrate by addition of two volumes of diethyl ether. Following recrystallization from tetrahydrofuran, the precipitate was sublimed to give pure 2-thienyl 5-acridyl ketimine.

Anal. Calcd. for $C_{18}H_{12}N_2S$: N, 9.72; neut. equiv., 96.12. Found: N, 9.66; neut. equiv., 96.50.

Methyl ethyl ketimine. A complex was prepared by reaction of 22 g. (0.40 mole) of propionitrile with the Grignard reagent from 71 g. (0.50 mole) of methyl iodide and 12 g. (0.50 g.-atom) of magnesium.

When the complex was decomposed with methanol and the filtrates from the decomposition mixture were distilled, intractable tars resulted, even when the pot temperatures were held below 10°. Treatment of these filtrates with anhydrous hydrogen chloride gave a white solid which proved to be mostly ammonium chloride. Treatment of the filtrates with 2,4-dinitrophenylhydrazine reagent resulted in the formation of the 2,4-dinitrophenylhydrazone of methyl ethyl ketone (m.p. 115°).

Decomposition of the complex by ammonia gave filtrates in which no trace of ketimine was found.

DURHAM, N. C.

---

(7) J. Overhoff and W. Provst, *Rec. trav. chim.*, **57**, 179 (1938).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

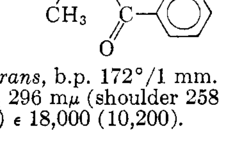
cis- and *trans-*Dypnones[1, 2]

ROBERT E. LUTZ AND LANDRY T. SLADE

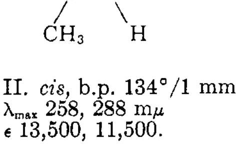
Received June 5, 1961

Practical preparations of *cis*-dypnone and *cis*-*p*,*p*'-dibromodypnone by irradiation of the *trans* isomers, have been developed. Lability of the *cis* isomers was shown by catalyzed rearrangements to the *trans* isomers by acid, base, or peroxide. Configuration and absorption characteristics are correlated. *cis*- and *trans*-Dypnones were converted by alkaline hydrogen peroxide into similar mixtures of epoxides; by *N*-bromosuccinimide under prior *cis*-to-*trans* inversion to *trans*-γ-bromodypnone; and by bromine at −80° to the same dibromide, from which *trans*-α-bromodypnone was obtained upon dehydrohalogenation.

trans-Dypnone (I)[2,3] has as its main structural features the α,β-unsaturated ketone system of a chalcone, and a β-methyl group activated through conjugation with the carbonyl group. The existence of *cis*-dypnone (II) had previously been demonstrated spectrophotometrically in irradiated $5 \times 10^{-5}M$ solutions.[4] Like *cis*-chalcone,[5] it would of necessity have the relatively nonplanar arrangement II, with the phenyl group sandwiched, and the benzoyl group overlapping the phenyl and itself deviating from coplanarity. These configurations and conformations are consistent with the marked differences between the ultraviolet absorption spectra of the isomers; *trans*-dypnone has a relatively simple and strong *trans*-chalcone-type band at 296 mμ, and the *cis* isomer has two well-separated *cis*-chalcone-like bands at 257 and 284 mμ, the latter of relatively low ε value. It was the object of this research to isolate and characterize the *cis* isomer and to study the effects of configuration, conformation, and substituents on the reactions.



I. *trans*, b.p. 172°/1 mm. λ_{max} 296 mμ (shoulder 258 mμ) ε 18,000 (10,200).



II. *cis*, b.p. 134°/1 mm. λ_{max} 258, 288 mμ ε 13,500, 11,500.

---

(1) This work was supported by research grants from the National Science Foundation.

(2) (a) R. E. Lutz and L. T. Slade, a paper presented at the New York ACS Meeting, September 1960, abstracts p. 99P; (b) L. T. Slade, M.S. thesis, including an historical review of *trans*-dypnone chemistry, May 1958; (c) Ph.D. dissertation, May 1960; University of Virginia.

(3) Important preparative references for *trans*-dypnone are: (a) N. O. Calloway and L. D. Green, *J. Am. Chem. Soc.*, **59**, 809 (1937); (b) W. Wayne and H. Adkins, *Org. Syntheses*, **Coll. Vol. III**, 367 (1955); (c) J. L. Guthrie and N. Rabjohn, *J. Org. Chem.*, **22**, 176 (1957); (d) A. R. Bader, U. S. Patent **2,769,842**, 1956 [*Chem. Abstr.*, **52**, 439 (1958)].

(4) (a) C. L. Browne, Dissertation, University of Virginia, May 1954; (b) W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **77**, 5137 (1955).

(5) R. E. Lutz and R. H. Jordan, *J. Am. Chem. Soc.*, **72**, 4090 (1950).

(6) H. Stobbe and L. Bremer, *J. prakt. Chem.*, (2) **123**, 1 (1929).

cis-Dypnone (II). Early unsuccessful preparative attempts[6] by irradiation of *trans*-dypnone had been followed by irradiation-conversion of the *trans*-semicarbazone into a mixture of stereoisomers from which isolation of the *cis* semicarbazone was claimed.[7] The more recent irradiation-inversion of *trans*-dypnone at high dilution[4] has now been developed into a practical preparation[3] of the pure *cis* isomer which has been characterized as follows: by reduction to β-phenylbutyrophenone[8]; by its *cis*-chalcone-like ultraviolet absorption spectrum including a long wave length band at 288 mμ which excludes the possible β-methylene structural isomer; and by conversion into distinctive derivatives, the oxime, semicarbazone, and 2,4-dinitrophenylhydrazone.

Upon irradiation of a $5 \times 10^{-5}M$ ethanol solution the absorption of *trans*-dypnone changed rapidly within five minutes and a new curve was obtained approximately paralleling but about 10% lower than that of pure *cis*-dypnone, a curve which showed survival of little or no *trans* isomer. At the higher concentrations used in preparations, twenty hours of irradiation was required to produce a moderately steady state giving rise to an absorption curve which indicated the formation mainly of *cis*-dypnone and little or no surviving *trans* isomer, but which indicated occurrence also of a significant degree of polymerization to products of high benzoyl-type absorptivity. The practically complete elimination of *trans*-dypnone in the preparative experiments was confirmed by conversion of a typical reaction mixture into pure *cis*-semicarbazone in 88% yield.

Rearrangement of *cis*-dypnone back to the *trans* isomer was followed spectrophotometrically in $5 \times 10^{-5}M$ 95% ethanol solution; it took place rapidly and practically completely within an hour at room temperature in the presence of 10% by volume of concentrated hydrochloric acid, but it occurred much more slowly under the action of potassium hydroxide. Occasionally samples of *cis*-dypnone spontaneously reverted partly or completely to *trans*-dypnone upon distillation or long standing, presumably under adventitious catalysis. The *cis*-to-*trans* inversion also took place under benzoyl peroxidic catalysis during unsuccessful attempts to brominate the *cis* isomer by means of *N*-bromosuccinimide at −10° in carbon tetrachloride. These experiments demonstrate that the *trans* is the lower-energy form and is able readily to absorb light energy with practically complete inversion into the higher-energy *cis* form.

cis-p,p′-Dibromodypnone was formed quickly and practically completely, like II, upon irradiation of $5 \times 10^{-5}M$ solutions of the *trans* isomer (known[9]). In more concentrated solutions the inversion was slow and incomplete, but fractional crystallization of the resulting mixtures gave pure *cis* isomer which was characterized by its absorption spectrum. The absorption spectrum of the *trans* isomer showed a relatively strong *trans*-chalcone-like band at 304 mμ, (ε 23,800 with a slight shoulder on the shorter wave length slope at *ca.* 273 mμ, ε 17,000). The spectrum of the *cis* isomer on the other hand had no distinct longer-wave length peak but showed a broad shoulder of more gentle slope defined by 280–300 mμ, ε 16,000–10,500, and a fairly sharp maximum at 260 mμ, ε 19,000 (these are comparable with the two distinct maxima for *cis*-dypnone itself of 257 and 284 mμ, ε 13,400 and 11,600).

The *cis-p,p′*-dibromo isomer was shown spectrophotometrically at $5 \times 10^{-5}M$ in 95% ethanol to be labile, like II, by its catalyzed reversion to the stable *trans* isomer, quickly and almost completely within a half hour by 10% by volume of concentrated hydrochloric acid, and more slowly by potassium hydroxide. In the reaction with potassium hydroxide the development of moderate and transitory *trans*-type absorptivity at 306 mμ was followed by slow disappearance of the *trans* band and development of predominantly *p*-bromoacetophenone-type absorptivity which indicated formation of cleavage and condensation products. The *cis*-to-*trans* inversion under acid catalysis was much more rapid than that of the parent dypnone itself, and this greater lability in the *p,p′*-dibromo series must account for the failure to obtain a distinctive *cis*-dinitrophenylhydrazone as had been done with *cis*-dypnone itself.

Attempts to make a *cis* isomer of the orange colored *trans-p,p′*-di(dimethylamino)dypnone by irradiation of $5 \times 10^{-5}M$ ethanol solutions caused no change in the ultraviolet absorption curve, and there was no indication of even partial conversion into a *cis* isomer. This failure to isomerize may be explained in terms of effective stabilizing conjugation between the donor nitrogen and the acceptor carbonyl-oxygen coupled with high lability in the hypothetical *cis* form in which conjugation would be seriously disrupted by steric interferences.

Ultraviolet absorptions. *cis-p,p′*-Dibromodypnone has its ultraviolet absorption maximum at a much shorter wave length than does the *trans* isomer (270 *vs.* 306 mμ). This represents a lowering of 36 mμ which is significantly greater than the 12-mμ difference for the parent *cis-trans* dypnone pair (I-II, 284 *vs.* 296 mμ). The relatively small difference between the wave lengths of absorption of the two *trans* compounds is about what would be expected on the assumption that these molecules are relatively similar in respect to near-planarity. The quite large differences between both absorption wave lengths and ε values for the two *cis*

---

[7] F. J. Wilson and R. M. Macaulay, *J. Chem. Soc.*, **125**, 841 (1924).

[8] C. Harries and F. Gollnitz, *Ann.*, **330**, 185 (1904).

[9] R. E. Lyle *et al.*, *J. Am. Chem. Soc.*, **75**, 5959 (1953).

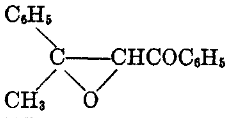
isomers, on the other hand, reflect the relatively great deviation from over-all planarity of the *cis* types with their sandwiched β-phenyl groups; and this difference may be explained in terms of conformational adjustment of the system so as relatively to increase conjugative independence of the styryl and benzoyl chromophores in the *p,p'*-dibromo compound.

The *cis* and *trans* dypnone semicarbazones show a considerable configurational effect on the dypnone absorption characteristics, in degree but not in kind, an effect which is quite unlike the difference in kind between the absorptions of the *cis* and *trans* dypnones themselves. The *trans*-semicarbazone (ϵ 21,700 at 266 mμ) and the *cis* isomer (ϵ 15,300 at 263 mμ) show prominent shoulders on the curves at *ca.* 285 mμ. It therefore appears that the semicarbazone group in both stereoisomers has considerable but far from complete conjugative independence of the styrene system and more independence in the *cis* than in the *trans* isomer.

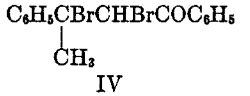
The *cis* and *trans* 2,4-dinitrophenylhydrazone pair represents an extreme in showing almost identical ultraviolet absorption spectra with λ_{max} at *ca.* 250 and 386 mμ, values which are close to those of styrene (259 mμ)[10] and acetophenone-2,4-dinitrophenylhydrazone (380 mμ).[11] It therefore appears that these two chromophores are conjugatively almost completely independent in the dypnone dinitrophenylhydrazone system.

Mono-ring-substituted dypnones. Attempts to prepare these by condensations of equimolar mixtures of acetophenone and a *p*-substituted acetophenone, using aluminum chloride as the condensing agent,[3a] were unsuccessful. No crystalline compounds were obtained using *p*-bromo or *p*-methoxyacetophenones; and when *p*-dimethylaminoacetophenone was used a small yield of *p,p'*-di(dimethylamino)dypnone was obtained. In all three cases *trans*-dypnone itself was formed in considerable amounts. These findings were disappointing because predominance of the mono-substituted dypnones might have been expected in analogy with thermodynamic equilibrium control in benzoin condensations where mainly one of the two unsymmetrically substituted benzoins is formed from a mixture of two benzaldehydes carrying widely different *para* substituents.[12]

Epoxidation of *cis*-dypnone by means of alkaline hydrogen peroxide, as with the *trans* isomer,[13] gave a mixture of *cis* and *trans* epoxides, III, which showed similar ultraviolet absorptivities at 250 mμ.[13c] The lower ϵ values of the *cis* isomer (13,000 *vs.* 16,800) reflect its necessarily more strained arrangement.



III. *cis* and *trans*

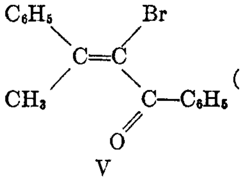


$$C_6H_5\underset{\displaystyle CH_3}{C}BrCHBrCOC_6H_5$$

IV
(one form only)

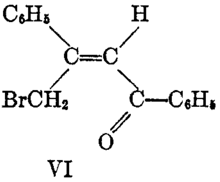
A single *dypnone dibromide* (IV)[14] (crystalline) was obtained by addition of bromine to either *cis* or *trans*-dypnone, only when the reaction was carried out in ether at −80°. A diastereoisomer was not isolated. The possibility of the alternative β,γ-dibromo structure, brought into question by some of its reactions, was excluded by the relatively long wave length of the benzoyl group absorption band, 257.5 mμ, which is close to those of the benzoyl bands of *threo*- and *erythro*-chalcone dibromides (253 mμ)[15] and of the *dl* and *meso*-1,2-dibenzoylethylene dibromides (261 mμ),[15] and which is distinctively higher than the range of 241–244 mμ for the benzoyl bands of phenyl ketones with a free α-methylene group, *e.g.*, 1,2-dibenzoylethane and -propane.[16]

α-Bromodypnone (V) was obtained in 67% yield upon dehydrohalogenation of dypnone dibromide IV by alcoholic potassium hydroxide at −10°. It showed the expected broad absorption range of a completely substituted chalcone, diminishing gradually in ϵ from 13,500 at λ_{max} 240 mμ through ϵ 11,000, 7330 and 4660 at 260, 270, and 280 mμ, respectively.



V

(configurations presumed)



VI

trans-γ-Bromodypnone, VI,[13a–c] obtained by the action of *N*-bromosuccinimide on *trans*-dypnone, is obtained similarly from *cis*-dypnone. It was shown that when benzoyl peroxide was added to catalyze the reaction, isomerization of *cis*- to *trans*-dypnone occurred at a temperature below that required for bromination; and undoubtedly therefore in the successful brominations stereoinversion of *cis*-dypnone occurs first.

---

(10) H. A. Laitinen, F. A. Miller, and T. D. Parks, *J. Am. Chem. Soc.*, **69**, 2710 (1947).

(11) R. Huisgen and W. Ropp, *Ber.*, **85**, 830 (1952).

(12) (a) W. S. Ide and J. S. Buck, *Org. Reactions*, **4**, 269 (1948); (b) J. S. Buck and W. S. Ide, *J. Am. Chem. Soc.*, **53**, 2350, 2789 (1931); (c) R. E. Lutz and J. W. Baker, *J. Org. Chem.*, **21**, 49 (1956).

(13) (a) H. H. Wasserman, N. E. Aubrey, and H. E. Zimmerman, *J. Am. Chem. Soc.*, **75**, 96 (1953); (b) H. H. Wasserman and N. E. Aubrey, *J. Am. Chem. Soc.*, **77**, 590 (1955); (c) C. L. Stevens, R. J. Church, and V. J. Traynelis, *J. Org. Chem.*, **19**, 522 (1954); (d) H. O. House and R. S. Ro, *J. Am. Chem. Soc.*, **80**, 2428 (1958); (e) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Org. Chem.*, **81**, 108 (1959).

(14) Reported but not characterized. M. Delacre, (a) Beilstein, *Handbuch der Org. Chem.*, 4th Ed., 485 (1925) [*Bull. Acad. Roy. Belgique* (3) **20**, 466 (1890)]; (b) *Ber.*, **27** (4), 338 (1894).

(15) R. E. Lutz, D. F. Hinkley, and R. H. Jordan, *J. Am. Chem. Soc.*, **73**, 4647 (1951).

(16) L. Kuhn, R. E. Lutz, and C. R. Bauer, *J. Am. Chem. Soc.*, **72**, 5058 (1950).

trans-γ-Bromodypnone showed a strong *trans*-chalcone-like ultraviolet absorption band at 297.5 mμ, ϵ 15,200, with a prominent shoulder at 268 mμ, ϵ 11,000,[13a] and it therefore must have the *trans* configuration VI.[11a] Irradiation[13c] of 5 × $10^{-5}M$ ethanol solutions caused rapid elimination of the longer wave length maximum and produced a steady state maximum at 245 mμ, ϵ 14,600 (like the $\lambda_{\max}$ of dibenzoylethane[16]), with ϵ diminishing sharply and practically to zero at 280 mμ. This showed that little if any *trans* isomer survived; and it showed that the product did not contain much if any *cis* isomer and arose from secondary condensations with retention of the benzoyl group.

EXPERIMENTAL[17]

trans-Dypnone (I) was prepared in 54% yields by the method of Calloway and Green;[3a] b.p. 167–177°/1 mm.;[18] $n_{\mathrm{D}}^{21.5}$ 1.6338;[17g] $d_4^{23.2}$ 1.108;[19] molar refraction, 71.72. Absorption: $\lambda_{\max}$[17d] 296 mμ, ϵ 18,000, with shoulder at 258 mμ, ϵ 10,200.

After irradiation of a 5 × $10^{-5}M$ chloroform solution containing iodine (3 hr.) the $\lambda_{\max}$ 264 mμ, ϵ 9,640 indicated drastic change but not to the *cis* isomer.

trans-Dypnone semicarbazone[7] was prepared in 84% yield; m.p. 150–151°; absorption: $\lambda_{\max}$ isooctane 161 mμ, ϵ 22,400, shoulder at 285 mμ, ϵ 17,200, μ, 3.13w, 5.91s, 6.33s, 6.71m, 6.92s, 7.10m, 7.60w, 7.69w, 8.71w, 9.00w, 9.31w, 9.48w, 9.78w, 10.03w, 10.89w, 11.45w, 12.55w.

trans-Dypnone oxime[20,21] was prepared in 23% yield; m.p. 130°; absorption: $\lambda_{\max}$[17d] 250 mμ, ϵ 22,800; μ 3.24w, 6.09m, 6.32w, 6.69m, 6.90s, 7.25m, 7.51m, 7.71m, 8.00w, 8.59w, 9.15w, 9.34w, 9.70w, 9.98w, 10.21s, 10.68s, 10.73s, 11.56s, 11.88w, 12.64w.

trans-Dypnone 2,4-dinitrophenylhydrazone was prepared in the usual way,[21] yield 86%, and was recrystallized from ethanol–ethyl acetate mixture; m.p. 173–174°.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 5.51. Found: C, 65.52; H, 4.49.

Absorption: $\lambda_{\max}$, mμ, 250, 388; ϵ 23,300, 30,000; $\lambda_{\min}$ 322 mμ, ϵ 5,200; μ, 3.04w, 3.24w, 6.20s, 6.30s, 6.62s, 6.96w, 7.52s, 7.67s, 7.91m, 8.21w, 8.84s, 8.99m, 9.12m, 9.49w, 9.82w, 10.93w, 12.00w, 12.82w.

cis-Dypnone (II). A solution of 5 g. of *trans*-dypnone per 100 ml. of 95% ethanol was sunlight irradiated. The progress of the reaction was followed by spectrophotometric analysis of aliquots and was complete in 24 hr. Evaporation of the solvent and distillation of the residual oil under reduced pressure usually gave pure *cis*-dypnone although occasionally some reversion to *trans* occurred during the process or afterward upon long standing; small foreruns and polymeric residues were obtained. Pure *cis*-dypnone usually was stable for considerable periods of time but was stored at −25° and always analyzed spectrophotometrically before use. The yields of pure *cis*-dypnone were *ca.* 78%; yellow oil; b.p. 132–135°/1 mm.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.30; H, 5.91.

Absorption: $\lambda_{\max}$ 232, 257.5, 288 mμ, ϵ 11,500, 13,500 and 11,500; μ 3.10s, 5.95s, 6.39s, 6.72w, 6.89s, 7.42w, 7.86w, 8.90 bm, 9.33m, 9.70w, 9.98w, 10.89w, 11.35w, 12.18m. $n_{\mathrm{D}}^{21.5}$ 1.6277; $d_4^{23.2}$ 1.0725; molar refraction 73.52.

Isooctane, diethyl ether, or benzene was also used successfully as solvent for irradiation-inversion. USP grade chloroform gave erratic results, however; in one run inversion occurred, in another it did not[6]; in both cases polymerization was extensive.

When 5 × $10^{-5}M$ 95% ethanol solutions of *cis* and *trans*-dypnones were irradiated by means of a mercury vapor arc in a quartz system delivering a high relative intensity at 257 mμ, it was shown spectrophotometrically, by lack of change with the *cis*, and complete change of *trans*- to the *cis*-type absorption pattern, that the favorable direction of rearrangement was still *trans*-to-*cis*.

In another experiment at 5 × $10^{-5}M$ in chloroform containing enough iodine to impart persistent color throughout the experiment, followed spectroanalytically, it was found that *cis*-dypnone was not affected, whereas *trans*-dypnone was, with shift of $\lambda_{\max}$ to 260–265 mμ, ϵ 15,900.

Stereoinversion. (a) *By acid catalysis.* A 5 × $10^{-5}M$ solution of *cis*-dypnone in 1–10 by volume concentrated hydrochloric acid–95% ethanol after 2 hr. was shown by spectroanalysis before and after to have undergone complete *cis*-to-*trans* inversion. The reaction was almost complete after 1 hr.

(b) *By basic catalysis.* A 1–10 by volume triethylamine–95% ethanol solution of *cis*-dypnone (1 week) underwent slow change to new products showing $\lambda_{\max}$ 289 mμ, ϵ 14,200; but a solution in 1–10 by volume 10% sodium hydroxide–95% ethanol underwent absorptivity change indicating close to complete *cis*-to-*trans* inversion in 30 min. and complete inversion in 2 hr.

(c) *By peroxide catalysis.* In an attempt to brominate *cis*-dypnone by *N*-bromosuccinimide in carbon tetrachloride at −10°, catalyzed by added benzoyl peroxide, an oil was recovered (90%) and identified by infrared spectrum as nearly pure *trans*-dypnone.

cis-Dypnone oxime, prepared in the usual way,[21] was recrystallized from methanol; yield 19%, m.p. 119–120°.

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37. Found: C, 80.64; H, 6.67.

Reduction of *cis*-dypnone by 2% sodium amalgam in absolute ethanol containing glacial acetic acid, as did *trans*-dypnone,[8] gave β-phenylbutyrophenone of m.p. 72–74° (11%), which showed no mixture melting point depression with a sample made from *trans*-dypnone.

cis-Dypnone semicarbazone,[7] prepared like the *trans* isomer[7] but directly from the new *cis*-dypnone, was obtained in 88% yield; recrystallized from 95% ethanol, m.p. 174–176°. (lit. m.p. 175–176°).[7]

Anal. Calcd. for $C_{17}H_{17}N_3O$: C, 73.20; H, 6.12. Found: C, 73.52; H, 6.38.

Absorption: $\lambda_{\max}$ (isooctane) 262 mμ, ϵ 15,400, shoulder, 285 mμ, ϵ 13,600.

Partial conversion of *trans*-dypnone semicarbazone into the *cis* isomer by irradiation of a chloroform solution has been claimed.[7] Our attempts to duplicate this led to difficultly separable mixtures and noncrystalline material from which we did not isolate pure *cis* isomer. Irradiation for shorter periods of time of a 5 × $10^{-5}M$ isooctane solution and com-

---

(17) (a) Melting points are corrected; the thermometer used was calibrated by melting point determinations on National Bureau of Standard's samples; (b) Beckmann Model DU or (c) Perkin-Elmer Model 4000A "Spectracord" spectrophotometers were used for ultraviolet absorption spectra; (d) solutions were at 4 × $10^{-5}M$, in 95% ethanol unless otherwise specified. Infrared absorption bands, expressed as w = weak, m = medium, s = strong, and b = broad, were determined using Perkin-Elmer, (e) "infracord" or (f) model 21 spectrophotometer, in potassium bromide pellet unless otherwise specified; (g) for refractive indices an Abbe refractometer was used. (h) microanalyses were by the Mrs. Ludwig Zirngibl, James Logan, Robert T. Ellis, and Thomas Jensen.

(18) For literature data on boiling points at different pressures see Table II, page 14 of ref. 2b.

(19) M. Konowalow and Finogejew, *Chem. Zentr., I,* 521 (1903) [*J. Russ. Phys. Chem. Gesell.,* **34,** 944 (1903)].

(20) F. Henrich and A. Wirth, *Ber.,* **37,** 731 (1904).

(21) *Cf.* R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds,* 4th Ed., John Wiley and Sons, Inc., New York, N. Y. (1958).

parison of the ε 17,100 at λ_{max} 266 mμ with those of pure *cis* and *trans* isomers indicated *ca.* 60–70% conversion to *cis,* but because the ε value at the longer wave length shoulder on the absorption curve of ε 16,000 at 285 mμ indicated a smaller change toward pure *cis,* and because of continuing slow changes upon further irradiation, no conclusions were drawn. Our samples of the *cis*-semicarbazone were all made from *cis*-dypnone and corresponded in melting point to that reported.[7] Both *cis* and *trans* semicarbazones upon acid hydrolysis[7] gave only *trans*-dypnone, as would be expected in view of the facility of the acid-catalyzed *cis*-to-*trans* rearrangements described above.

cis-Dypnone 2,4-dinitrophenylhydrazone, prepared in the usual way[21] in 79% yield, was recrystallized from ethanol–ethyl acetate mixture; m.p. 219.5–220°.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51. Found: C, 65.58; H, 4.38.

Absorptions: λ_{max}, 385 mμ, ε 28,300; shoulder, 250 mμ, ε 22,500; λ_{min} 319 mμ, ε 4300; μ, 3.11w, 6.19s, 6.30s, 6.61s, 6.96m, 7.09s, 7.55s, 7.68s, 8.21m, 8.82s, 9.00m, 9.42w, 10.95w, 12.09m, 12.96m.

Preparation of cis and trans-dypnone oxides from cis-dypnone was carried out by the method used on *trans*-dypnone,[13a] namely, addition of 10 ml. of 30% hydrogen peroxide and 12 ml. of 8% sodium hydroxide in 100 ml. of methanol to 10 g. (0.045 mole) of *cis*-dypnone, and shaking for 45 min. Upon addition of a small amount of water and cooling, the product crystallized. Recrystallization from 300 ml. of ethanol gave 9% of pure *cis*-dypnone oxide melting at 160–162.5°.[13a–c]

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.34; H, 5.62.

Absorption maxima: 250 mμ, ε 13,200.[13a] μ, 5.98s, 6.30m, 6.71w, 6.94m, 7.18w, 7.29w, 7.55w, 7.65w (bifureated), 7.93w, 8.16s, 8.49w, 9.02w, 9.20w, 9.38w, 9.75w, 10.01w, 10.28s, 10.90w, 11.11m, 11.80m (bifureated).

The ethanol filtrate on dilution with water and cooling, slowly deposited less pure *cis*-oxide bringing the total yield to *ca.* 18–20%. More soluble fractions of *trans*-dypnone oxide were then obtained (*ca.* 46%) which upon recrystallization from absolute ethanol melted at 89–91.5°.[13a–c]

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.32; H, 5.87.

Absorption maxima: 250 mμ, ε 16,800[13a]; μ, 5.91s, 6.26m, 6.69w, 6.91s, 7.24s, 7.65w, 7.78m, 8.11s, 8.98w, 9.21m, 9.70w (trifurcated), 10.40s, 11.77m.

Dypnone dibromide (IV).[14] To a solution of 22.3 g. (0.1 mole) of *trans*-dypnone in 100 ml. of ether, cooled to −80° in a Dry-Ice–acetone bath, was added with stirring 16 g. (0.1 mole) of bromine, with continued stirring for several hours (the orange color disappeared). Evaporation under an air stream at −80° gave an oil which crystallized from ether and was recrystallized from 95% ethanol; yield 48%, m.p. 74.5–77° (yield from *cis*-dypnone, 34%).

Anal. Calcd. for $C_{16}H_{14}Br_2O$: C, 50.29; H, 3.69. Found: C, 50.23; H, 3.73.

Absorption maxima: 257.5 mμ, ε 14,100; μ, 2.90bw, 3.31w, 5.92s, 6.29m, 6.71w, 6.95s, 7.40m, 7.69w, 8.00w, 8.31m, 8.50w, 8.68w, 9.35w, 9.68w, 9.99w, 11.19w.

Using *cis*-dypnone as starting material a similar result was obtained (identification of product by infrared absorption spectrum).

Reaction run at 0° or −10° gave intractable products.

α-Bromodypnone (V). At a controlled reaction temperature of −10° a solution of 0.164 g. (0.0041 mole) of sodium hydroxide in 100 ml. of absolute ethanol was added dropwise under stirring to 100 ml. of absolute ethanol containing 1.57 g. (0.0041 mole) of dypnone dibromide (IV) over 1 hr. with continued stirring for another hour. This was followed by evaporation at −10°. An ether extract of the residual oil was dried over sodium sulfate (−25°) and concentrated (at −10°). The resulting solid was recrystallized from absolute ethanol; yield (pure) 67%; m.p. 89–91°.

Anal. Calcd. for $C_{16}H_{13}BrO$: C, 63.80; H, 4.35. Found: C, 63.32; H, 4.46.

Absorptions: λ_{max} 240 mμ, ε 13,500 (the slope over the body of the curve is defined by 260, 270, 280 mμ, ε 11,000, 7330, 4660, respectively): μ, 3.22w, 5.99s, 6.20w, (bifurcated), 6.70w, 6.91m, 7.63w, 7.80w, 8.03s, 8.50w, 10.00bw, 12.10m, 12.99m.

trans-γ-bromodypnone (VI), known,[13a–c] was made by interaction of equimolar amounts of *N*-bromosuccinimide and *trans*- or *cis*-dypnones in carbon tetrachloride under stirring and refluxing for 2.5 hr.; VI crystallized on cooling and standing at *ca.* −25° and on recrystallization from absolute ethanol melted at 66.5–67.5°;[13a,c] yield *ca.* 43% from *trans*- and 32% from *cis*-dypnone. The samples gave no mixture melting point depressions with authentic material[13a,c] and were identified by infrared spectra.

Anal. Calcd. for $C_{16}H_{13}BrO$: C, 63.80; H, 4.35. Found: C, 63.51; H, 4.47.

Absorption maxima: 297 mμ, ε 15,200[13c] shoulder, 268 mμ, ε 11,000; λ_{min}, 246 mμ, ε 8000); μ, 2.81w, 3.27w, 6.02s, 6.21s, 6.32m, 6.89m, 7.41m, 7.78w, 8.20s (bifurcated) 8.50w, 9.51m, 9.92w, 10.02w, 11.40m, 11.79w.

Repeating the sunlight irradiation of VI in a $5 \times 10^{-}M^{5}$ 95% ethanol solution to photoequilibrium (0.5 hr.) brought λ_{max} to 250 mμ, ε 12,200. At higher concentration (3 g./100 ml.) 33 hr. of irradiation was required but no crystalline product was isolated. VI was recovered (76%) after treatment with absolute ethanolic silver nitrate (at −10°). Treatment with ethanol–water–silver nitrate–ammonium hydroxide at −10° precipitated silver and noncrystalline product.

trans-p,p'-Dibromodypnone,[9] obtained in 74% yield by the Calloway-Green procedure[3a] (without distillation), was recrystallized from absolute ethanol; m.p. 105–106° (lit.[9] m.p. 104°).

Anal. Calcd. for $C_{16}H_{12}Br_2O$: C, 50.56; H, 3.18. Found: C, 50.85; H, 3.44.

Absorption: λ_{max}, mμ, 226, 305, ε 13,780, 23,950, slight shoulder, 273 mμ, ε 15,500; λ_{min} 248 mμ, ε 8200; μ, 3.30w, 6.01s, 6.25s, 6.71s, 6.99w, 7.14m, 7.39w, 7.82s, 8.19bw, 8.50m, 9.34s, 9.54m, 9.90s, 10.56w, 11.64w, 12.23s.

trans-p,p'-Dibromodypnone 2,4-dinitrophenylhydrazone, prepared in the usual way,[21] (81% yield) was recrystallized from 95% ethanol–ethyl acetate mixture; m.p. 232.5–233.5°.

Anal. Calcd. for $C_{22}H_{16}Br_2N_4O_4$: C, 47.16; H, 2.88. Found: C, 46.84; H, 3.10.

Absorption: mμ, 257.5, 389; ε 24,200, 27,600; μ,[17e] 2.85w, 3.05w, 3.20w, 6.20s (bifurcated), 6.62s (bifurcated), 7.09m, 7.50s, 7.65s, 8.20w, 8.80s, 9.00w, 9.30w (bifurcated) 9.70w, 9.93s.

trans-p,p'-Dibromodypnone oxime was prepared in the usual way[21]; yield 31%, recrystallized from absolute ethanol, m.p. 134–135°.

Anal. Calcd. for $C_{16}H_{13}Br_2NO$: C, 48.63; H, 3.32. Found: C, 48.39; H, 2.86.

Irradiation of trans-di-p,p'-dibromodypnone at $5 \times 10^{-5}M$ in 95% ethanol in a quartz cell, by sunlight or mercury arc delivering 257 mμ, brought about quick and practically complete inversion to the *cis* isomer, as shown by changes in absorptivity. Irradiation for 32 hr. of a chloroform solution containing a persistent amount of iodine brought about change of λ_{max} to 245 mμ, ε 20,000, showing destruction of the dypnone system.

cis-p,p'-Dibromodypnone. Photometric analysis of a solution of 4 g. of the *trans* compound in 400 ml. of 95% ethanol after exposure to sunlight for 45 hr. showed that photoequilibrium reached was considerably short of the complete conversion obtained at $5 \times 10^{-5}M$. Upon standing at *ca.* −25° yellow crystals separated and on recrystallization from 95% ethanol gave *cis* isomer (12%), m.p. 115–115.5°. It gave a mixture melting point depression with the *trans* isomer.

Anal. Calcd. for $C_{16}H_{12}Br_2O$: C, 50.56; H, 3.18. Found: C, 50.82; H, 3.24.

Absorption: λ_{max} 268 mμ, ε 18,900; λ_{min} 243 mμ, ε 12,000. Infrared μ, 3.30m, 6.00s, 6.20m, 6.30s, 6.71m, 6.95w, 7.17m, 8.02s, 8.34w, 8.51w, 9.23m, 9.33s, 9.90s, 10.20w.

Acid-catalyzed inversion to the trans isomer of a 5 × $10^{-5}M$ solution of the *cis* isomer in 1–10 by volume mixture of concentrated hydrochloric acid and 95% ethanol was followed spectrophotometrically. The λ_{max} changed rapidly, in 30 min. approaching and in 2 hr. coming to a steady state at 307 mμ, ε 22,400.

trans-p,p'-Di(dimethylamino)dypnone was prepared like *trans*-dypnone (above), but the product crystallized upon removal of solvent; recrystallized from 95% ethanol (16%), m.p. 156–158°.

Anal. Calcd. for $C_{20}H_{24}N_2O$: C, 77.88; H, 7.87. Found: C, 78.13; H, 7.74.

Absorption: λ_{max}, 250, 362.5 mμ, ε 18,210, 24.880; infrared, μ, 3.41w, 6.75s, 6.38s, 6.59s, 6.98m, 7.30s, 7.76w, 8.11m, 8.30w, 8.60s (bifurcation), 8.87bm, 9.51m, 10.60w, 11.11w, 12.21s.

After irradiation of a 5 × $10^{-5}M$ solution in 95% ethanol for three 0.5-hr. periods, spectrophotometric analysis indicated decomposition; no *cis* isomer could be obtained when operating on a larger scale.

trans-p,p'-Di(dimethylamino)dypnone oxime was prepared in the usual way[21] and was recrystallized from absolute ethanol; yield 34%, m.p. 149–150°.

Anal. Calcd. for $C_{20}H_{26}N_3O$: C, 74.27; H, 7.79. Found: C, 73.98; H, 7.66.

Acknowledgment is gratefully made to Phillip Zoretic for checking some of the data.

CHARLOTTESVILLE, VA.

[COMMUNICATION NO. 2208 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK CO.]

cis and *trans* Isomers of 2-Styrylpyridine

J. L. R. WILLIAMS, S. K. WEBSTER, AND J. A. VAN ALLAN

Received July 6, 1961

Further work on the photodimerization of 2-styrylpyridine, its methiodide, and hydrochloride has revealed that the normally isolated forms of such 2-styrylpyridines are in the *trans* configuration. Ultraviolet irradiation in the solid state of the methiodide or the hydrochloride causes dimerization while analogous irradiation in solution gives both isomerization to the *cis* configuration and dimerization. Irradiation of the free base under nitrogen in benzene solution produces only *cis*-2-styrylpyridine.

It was previously reported[1] that solid-state irradiation of 2-styrylpyridine methiodide (Ia) gave a dimeric salt (II) which was pyrolytically converted into the isomeric dimers (IIIa and IIIb), with the elimination of methyl iodide. An irradiation time of eighty hours with a 450-watt ultraviolet source at a distance of ten inches was required to convert 25 g. of Ia to II.[1] Recently, this reaction has been carried out more efficiently. 2-Styrylpyridine methiodide (Ia) was ball-milled in benzene to provide a suspension in which 50 g. of Ia was converted quantitatively to the dimer II by six hours of irradiation time, using a 550-watt source. In contrast, when Ia was irradiated in water with sunlight, a rapid shift occurred in λ_{max} from 340 mμ (ε 28,000) to 325 mμ (ε 14,600). This shift represented the photoisomerization of *trans*-2-styrylpyridine methiodide (Ia) to the corresponding *cis* configuration (Ib). Subsequently, dimer II was formed at a slower rate. Fractional crystallization of the photoproducts showed the reaction mixture to contain dimer II, 64.5%, and *cis*-2-styrylpyridine methiodide (Ib), 28%. Upon rapid heating, Ib melted at 180–183°, but resolidified when held at 195–200° for several minutes. The solid (Ia) then remelted at 225–230°. During storage for several months, the melting point of Ib changed from 180–183° to 193–196°, indicating a gradual conversion to the *trans* form.

In the previous paper,[1] powdered 2-styrylpyridine (IVa) (λ_{max} 309) was irradiated in air to produce only a 2.6% yield of dimer IIIa; the remaining materials were products of photooxidation. Since that time, it has been found that irradiation of *trans*-2-styrylpyridine (IVa) (λ_{max} 309) in a nitrogen atmosphere gave 58.3% conversion to *cis*-2-styrylpyridine, λ_{max} 290. No dimer IIIa was obtained. If, however, *trans*-2-styrylpyridine hydrochloride (V) was irradiated as a benzene dispersion, dimer IIIa was obtained in 85% yield. Alternatively, when V was irradiated in aqueous solution, approximately equal quantities of dimer IIIa hydrochloride and *cis*-2-styrylpyridine (IVb) hydrochloride were produced. The *cis* configuration (IVb) is assigned to this other modification of IVa, since IVb possesses absorption characteristics at a shorter wave length than *trans*-IVa. *trans*-IVa has λ_{max} 309 mμ (ε 28,000), while *cis*-IVb has λ_{max} 290 mμ (ε 11,400). *cis*-IVb can be converted quantitatively to *trans*-IVa by heating in *p*-cymene with a trace of 15% palladium on charcoal catalyst. Under the same conditions, in the absence of catalyst, no conversion occurs. Both IVa and IVb hydrogenate under the same conditions, absorbing one mole equivalent of hydrogen. Quaternization of IVb with methyl *p*-toluenesulfonate, followed by treatment of the re-

---

(1) J. L. R. Williams, *J. Org. Chem.*, **25**, 1839 (1960).