analogs of 2-N-ethyleniminoquinoxaline, e.g. 2-chloro-3-N-aziridinoquinoxaline (III), with a view to investigating the effect of the quinoxaline system as an adjunct to the aziridine system as well as an adjunct to homologous alkylenimino systems which are chemically stable under conditions which permit the aziridine system to serve in its alkylating role.

To this end 2,3-dichloroquinoxaline (I)[4] and 2-chloro-3-methylquinoxaline (II)[5] were prepared and used as primary starting materials for condensation with appropriate alkylenimines. The two active chlorines of I permitted the introduction of either one such substituent (III–VII) or two (similar or different) substituents (XII–XXV). Data are assembled in Table I.

In addition a quinoxaline carrying a nitrogen-mustard function was prepared by condensing 2-hydroxy-3-methylquinoxaline[6] with *p*-[*N,N-bis*-(2-chloroethyl)amino]benzaldehyde[7] to give 2-hydroxy - 3 - *p* - [*N,N* - *bis* - (2 - chloroethyl)amino]-styrylquinoxaline (XXVI).

It should be noted that for unaccountable reasons most of the aziridine-substituted compounds proved difficult to purify and invariably contained traces of water which could not be removed satisfactorily.

EXPERIMENTAL

The following general procedure served for the preparation of all but one of the compounds reported.

The appropriate alkylenimine was added to a mixture of the appropriate chloroquinoxaline and triethylamine (using ether as solvent for III, IV, and V and filtering off the triethylamine hydrochloride, evaporating ether from the filtrate, and adding water to the residue). The reaction mixture was stirred with water and the solid filtered off and recrystallized. In one case (IX) the product was extracted into ether and in two (XXIV and XXV) into chloroform; and after drying, filtering and removal of the organic solvent the residue was crystallized. External cooling during imine addition was necessary for XVI and XX. Data are summarized in Table 1.

2-Hydroxy-3-p-[*-N,N-bis(2-chloroethyl)amino*]*styrylquinoxaline* (XXVI). A mixture of 3 g. of 2-hydroxy-3-methylquinoxaline[6] and 4.5 g. of *p*-[*N,N-bis*-(2-chloroethyl)amino]-benzaldehyde[7] in 20 ml. of benzene containing 10 ml. of acetic anhydride was heated under reflux for 14 hr. The reaction mixture was evaporated under reduced pressure, and the dark gum was boiled with benzene and filtered hot. The shiny crimson residue crystallized from ethyl acetate as small needles, m.p. 215°: 3.1 g. (42%). If benzene is not used in the initial stage, intractable tars are obtained.

Anal. Calcd. for $C_{20}H_{19}ON_3Cl_2$: C, 61.85; H, 4.89; N, 10.82. Found: C, 61.43; H, 5.19; N, 10.75.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICH.

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The Geometrical Isomers of 1,5-Diphenylpentadiene-3-one

J. G. DINWIDDIE, JR., H. M. WHITE, AND W. J. DAY

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Although 1,5-diphenylpentadiene-3-one (dibenzalacetone) has been known for many years, the geometrical isomerism of this compound has not been investigated. This note describes the preparation and characterization of the three possible isomers. The physical and spectral properties are reported and isomerization studies are described.

The preparation of 1,5-diphenylpentadiyne-3-one has been reported by Chauvelier.[1] This method was utilized except that 1,5-diphenylpentadiyne-3-ol was oxidized to 1,5-diphenylpentadiyne-3-one with manganese dioxide rather than with chromic acid. The chromic acid oxidation as described by Chauvelier gave benzoic acid as the only isolable product in our laboratory. The manganese dioxide oxidation gave almost quantitative yields of 1,5-diphenylpentadiyne-3-one in large runs.

Nightingale and Wadsworth[2] have reported the preparation of 1,5-diphenylpent-1-en-4-yn-3-one by the reaction of sodium phenylacetylene and cinnamic anhydride. Our crude yields approached those reported, but we obtained pure yields of only 5% by this method. The reaction of phenylacetylene-magnesium bromide with cinnamaldehyde gave 1,5-diphenylpent-1-en-4-yn-3-ol in 55% yield. The alcohol was oxidized to 1,5-diphenylpent-1-en-4-yn-3-one with Kiliani's reagent[3] or with manganese dioxide.

Hydrogenation of 1,5-diphenylpentadiyne-3-one and 1,5-diphenylpent-1-en-4-yn-3-one over Lindlar catalyst gave the *cis-cis* (I) and *cis-trans* (II) isomers, respectively. The *trans-trans* compound (III) was prepared by the method described in *Organic Syntheses*.[4] The properties of the three isomers are summarized in Table I.

TABLE I

PROPERTIES OF THE ISOMERS OF 1,5-DIPHENYLPENTADIENE-3-ONE

Isomer	M.P.	B.P.	λ_{max}	ϵ_{max}
cis-cis (I)	—	130/0.02 mm	287 mμ	11,000
cis-trans (II)	60	—	295 mμ	20,000
trans-trans (III)	111	—	330 mμ	34,300

The infrared absorption of the isomers confirms the structures that have been assigned. Both II

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and III absorb strongly at 10.3 mμ while I does not. Absorption at this wave length is indicative of a *trans*-substituted double bond.[5] Absorption at 13.15 mμ, which is characteristic of the *cis*-substituted double bond,[5] is present in the spectra of I and II but absent in that of III.

I was isomerized to a mixture of II and III on treatment with acid. The action of sunlight on I produced only III. The action of light or acid on III yielded only high molecular weight material.[6,7] There was no evidence of light-catalyzed isomerization of III.

EXPERIMENTAL[8]

1,5-Diphenylpentadiyne-3-one. A solution of 1,5-diphenylpentadiyne-3-ol (5.0 g.) in 50 ml. of acetone was added to a suspension of manganese dioxide (50.0 g.) in 450 ml. of petroleum ether (b.p. 30–60°), stirred vigorously for 3 hr., filtered, and the solvent removed on a steam bath leaving a light red oil which solidified in an ice bath. The solid was recrystallized from petroleum ether (b.p. 30–60°) as light yellow needles; 3.5 g. (70%), m.p. 64°.

cis-cis-1,5-Diphenylpentadiene-3-one. (*I*). To a solution of 1,5-diphenylpentadiyne-3-one (2.0 g.) in 50 ml. of methanol was added 0.5 g. of Lindlar catalyst. The suspension was stirred in an atmosphere of hydrogen until the calculated amount (2 moles) had been taken up, the catalyst removed by filtration and the solvent removed *in vacuo*. The resulting oil (2 g.) was washed with petroleum ether (b.p. 30–60°) and distilled to give 1.2 g. (60%) of light yellow oil, b.p. 130°/0.02 mm.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.03. Found: C, 87.06; H, 6.31.

Attempts to prepare the 2,4-dinitrophenylhydrazone of *cis-cis*-1,5-diphenylpentadiene-3-one, in all cases but one, resulted in the derivative of the *trans-trans* isomer melting at 181°. Under less vigorous conditions, a derivative was prepared which melted at 92°. On acid hydrolysis this material gave *trans-trans*-1,5-diphenylpentadiene-3-one.

1,5-Diphenylpent-1-en-4-yn-3-ol. Ethylmagnesium bromide was prepared by adding 100 ml. of ethyl bromide to 20.5 g. of magnesium turnings in 250 ml. of dry ether. Phenylacetylene (80 ml.) was added slowly and the solution stirred for 1 hr. after addition was complete. The solution was cooled to 0° and 21.5 g. of cinnamaldehyde was added dropwise over a period of 30 min. The reaction mixture was poured over 100 g. of ice and 25 g. of ammonium chloride, the ether layer washed with water, dried over calcium chloride, and the solvent removed on a steam bath. The residue solidified in an ice bath and was recrystallized from petroleum ether (b.p. 30–60°) as white needles; 23 g. (60%), m.p. 68°.

1,5-Diphenylpent-1-en-4-yn-3-one. Kiliani's reagent[3] was added dropwise to a solution of 1,5-diphenylpent-1-en-4-yn-3-ol (2.0 g.) in 50 ml. of acetone until the yellow color persisted. The solution was diluted with water and extracted with ether. The ether layer was washed several times with water, dried over anhydrous sodium sulfate, and the ether removed on a steam bath. The residue solidified in an ice bath and was recrystallized from petroleum ether (b.p. 30–60°) as light yellow needles; 1.8 g. (90%), m.p. 69°.

cis-trans-1,5-Diphenylpentadiene-3-one (II). To a solution of 2.0 g. of 1,5-diphenylpent-1-en-4-yn-3-one in 50 ml. of methanol was added 0.5 g. of Lindlar catalyst. The suspension was stirred in an atmosphere of hydrogen until the calculated amount (1 mole) had been taken up, the catalyst removed by filtration, and the solvent removed *in vacuo*. The residue solidified in an ice bath and was recrystallized from ethanol as light yellow needles; 1.0 g. (50%), m.p. 60°. The 2,4-dinitrophenylhydrazone was prepared in the usual manner and melted at 159°.

Anal. Calcd. for $C_{23}H_{18}N_4O_4$: N, 13.52. Found: N, 13.53.

Isomerization studies. cis-cis-1,5-Diphenylpentadiene-3-one (2.0 g.) was exposed to normal room light for 24 hr. *trans-trans*-1,5-Diphenylpentadiene-3-one (2.0 g.) was obtained as the only product. The *cis-cis* isomer showed no change in a month's time in the absence of light. *cis-trans*-1,5-Diphenylpentadiene-3-one remained unchanged after several days exposure to normal room light.

Concentrated hydrochloric acid (1 ml.) was added to a solution of *cis-cis*-1,5-diphenylpentadiene-3-one (0.5 g.) in 25 ml. of methanol and the solution heated on a steam bath for 5 min. The solution was diluted with water and extracted with ether. The ether layer was washed with dilute sodium bicarbonate then with water. The ether layer was dried over calcium chloride and the ether removed on a steam bath. The residue was recrystallized from petroleum ether (b.p. 30–60°) yielding approximately equal amounts of the *cis-trans* and the *trans-trans* isomers.

Department of Chemistry and Geology
Clemson College
Clemson, S. C.

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16-Hydroxylated Steroids. XXII.[1] The Preparation of the 16-Methyl Ether of Triamcinolone[2]

Milton Heller, Stephen M. Stolar, and Seymour Bernstein

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The isolation of 2-methoxy-estrogens[3] as metabolites of known estrogens has encouraged us to study the influence of ether functions on biologically active steroids. In the corticoid field, 9α-methoxy and ethoxy groups,[4] 6β and 6α-methoxy groups,[5] and a 16β-methoxy grouping[6] have been introduced

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