

TABLE I
PRODUCTS FORMED IN THE DECOMPOSITION OF NAA IN AROMATIC
SOLVENTS IN THE PRESENCE AND ABSENCE OF IODINE

Run	Substrate	Concentration ^a		Yield, % ^b	
		[NAA]	[I ₂]	C ₆ H ₆ I	C ₆ H ₆ Ar
1	Toluene	2.15	5.06	81.5	None
2		2.06	2.36	79.1	<i>c</i>
3		2.07	1.18	70.7	<i>c</i>
4		2.10	0	None	86.0
5	Chlorobenzene	2.07	4.93	81.6	<i>c</i>
6		2.08	2.51	79.9	<i>c</i>
7		2.25	1.1	71.0	<i>c</i>
8		2.1	0	None	84.3
9	Benzene	2.05	0	None	83.0
10		2.28	5.05	85.4	<i>c</i>
11		2.21	2.52	79.2	<i>c</i>
12		2.2	1.2	69.8	<i>c</i>
13		1.21	2.5	83.6	<i>c</i>
14		2.07	0	None	87.9

^a In moles/l. $\times 10^3$. Substrate was usually 100 ml. except in run 13 where it was 200 ml. ^b Based on NAA. Iodobenzene yield determined by gas chromatography on 20% Aplezon L on Chromosorb P at 200°, 10-ft. column, using 1-bromo-4-chlorobenzene as an internal standard. Biaryls were determined on a 10-ft. GE-SF-96 column at 165° using *p*-chloroaniline as the internal standard. ^c Not determined.

NAA arylation, they give no positive indication as to what the mechanism really is. Attempts to determine the fate of the acetoxy radical in the iodine-scavenged reactions were fruitless, the only product we were ever able to detect (by gas chromatography) being acetic acid. It is of interest, however, that in runs 3, 7, and 12 where the NAA:I₂ molar ratio was close to one-half and where, therefore, not enough iodine was present to combine with both the phenyl radical and whatever other radical (if any) is formed in the NAA decomposition, the phenyl radicals were still scavenged quite efficiently, iodobenzene being formed in about 70% yield (as compared to 83–85% in runs where iodine was in excess). These experiments suggest that whatever else is formed in the NAA decomposition combines with iodine either much less readily than phenyl radical does or else combines in such fashion as to regenerate iodine readily.

Regrettably our work leaves the mechanism of the NAA reaction still insufficiently understood. Speculations are possible but appear unwise at the present time.

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Photochemical Cycloaddition as a Device for General Annulation

Sir:

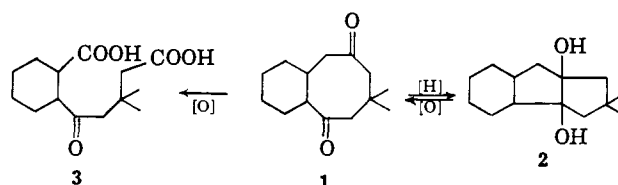
Intermolecular photochemical cycloaddition to isolated ethylenic linkages, aside from the more venerable instance of dimerization, has recently attracted attention, and it has been demonstrated to be of synthetic utility.^{1–8} With few exceptions,^{1,4} however, the ini-

- (1) P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963).
- (2) P. de Mayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963).
- (3) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 485 (1964).
- (4) E. J. Corey and S. Nozoe, *ibid.*, **86**, 1652 (1964).
- (5) J. A. Barltrop and R. Robson, *Tetrahedron Letters*, 597 (1963).
- (6) G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963).
- (7) P. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962).

tially generated ring formed by such cycloaddition has remained intact, a feature apparently limiting the scope and versatility of the reaction.

We now wish to show that, in fact, photochemical cycloaddition provides an important means for the synthesis of a variety of ring systems both single and fused. A number of specific examples follow.

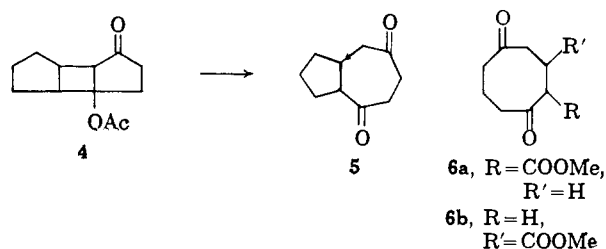
Irradiation⁹ of dimedone in cyclohexene-ether (1:3) solution converted it to 1, m.p. 96–97.5°,¹⁰ and 2, m.p. 79–81°. The dione 1, the initial product formed



by the retroaldol opening of the cyclobutane adduct, was reduced to 2 by irradiation in cyclohexene or by zinc and acetic acid; sodium metaperiodate cleavage regenerated 1. The structure of 1 was established by oxidation (potassium permanganate-acetone) to 3, m.p. 154–156°, and further oxidation (nitric acid) to *trans*-cyclohexane-1,2-dicarboxylic acid and *as*-dimethylsuccinic acid. Dione 1 was also obtained by replacing dimedone, in the irradiation, by its enol acetate, and hydrolysing the resultant adduct, m.p. 103–105°.

Among other bicyclic ring systems to which a new route may be of utility is that of the perhydroazulenes common to many sesquiterpenoids. This was achieved by irradiation of the enol acetate¹¹ of cyclopentane-1,3-dione in cyclopentene-cyclohexane (2:3). The adduct (4) obtained was converted by mild alkali into 5, $\nu_{\max}^{\text{CCL}_4}$ 1710 cm^{-1} .

Cycloaddition is not restricted to cycloalkanes, and with other substrates may serve as a useful route to cyclooctane derivatives. Thus, irradiation of cyclohexene-1,3-dione in methyl acrylate gave 6a, m.p. 89–91°, and 6b, m.p. 104–105°. The former on standing in chloroform was slowly converted to the corresponding enol.

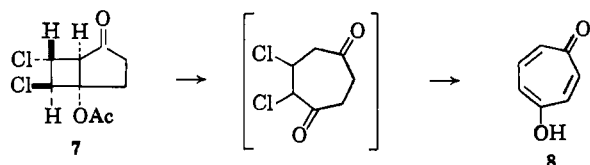


One evident feature of photochemical cycloaddition is that both substrate and addend may be modified to contain the number of potential units of unsaturation desired in the ultimate product, without the necessity of their subsequent and possibly difficult introduction. For instance, in tropolone syntheses, after construction of the ring the required aromaticity has been achieved,

- (8) For other general references see G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).
- (9) Irradiations were conducted using a 450W source in a Hanovia water-cooled immersion unit with a pyrex filter. Concentrations varied from 0.3–0.5%.
- (10) Adequate analyses have been obtained for all new compounds mentioned.
- (11) Prepared by the action of ketene on the dione.

frequently, by such means as bromination-dehydrobromination. The following synthesis of γ -tropolone illustrates the point at issue.

Irradiation of the enol acetate of cyclopentane-1,3-dione in ethylene dichloride led to the production of three stereoisomers. One of these, m.p. 90–91°, provisionally allocated from n.m.r. data the stereochemistry shown in 7, on standing at room temperature in methanol containing N,N-dimethylaniline (1%) was methanolized, in 36 hr., to the ketol which presumably underwent spontaneous dealdolization. Treatment of this, without isolation, with dilute aqueous sodium hydroxide¹² at room temperature for 3 hr. led to the elimination of the elements of hydrogen chloride and the formation of γ -tropolone (8).¹³ The yield, estimated spectroscopically, was 45%.



Acknowledgment.—This work was supported by the U. S. Army under Grant DA-ARO(D)-31-124-G399.

(12) Omission of the methanolysis step led to quite different reactions which are presently being investigated.

(13) Identified by ultraviolet spectra in neutral and alkaline solution and by melting point.

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The Mechanism of the Acid-Catalyzed Isomerization of *cis*-Stilbene

Sir:

Following our recent studies^{1,2} of the acid-catalyzed isomerization of *cis*-cinnamic acids, we have investigated the isomerization of *cis*-stilbene. *cis*-Stilbene is readily isomerized quantitatively to *trans*-stilbene in 50–60% sulfuric acid, as summarized in Table I. From 10 to

TABLE I
RATE OF ISOMERIZATION OF *cis*-STILBENE^a

Wt. %	H ₂ SO ₄		D ₂ SO ₄	
	H ₀ ^b	k, sec. ⁻¹	Wt. %	k, sec. ⁻¹
49.92	-3.40	1.28 × 10 ⁻⁶		
55.50	-4.02	7.35 × 10 ⁻⁶	52.58	1.99 × 10 ⁻⁶
57.62	-4.28	1.43 × 10 ⁻⁴	58.10	1.43 × 10 ⁻⁴
60.92	-4.69	5.12 × 10 ⁻⁴		
63.17	-4.95	1.10 × 10 ⁻³	62.77	6.94 × 10 ⁻⁴
66.06	-5.40	3.84 × 10 ⁻³	65.45	2.37 × 10 ⁻³

^a The reaction medium contained 5% added ethanol to impart sufficient solubility to the stilbenes; initial concentration of *cis*-stilbene 2 × 10⁻⁶ M; reaction followed by ultraviolet spectroscopy using 10 cm. cells; T 25.00°. ^b The H₀ values were measured. A full discussion of the H₀ scale in 5% ethanol will be presented in a complete paper.

90% completion the reaction followed excellent first-order kinetics in any individual run. Correlation of the rate data with H₀ shows linearity with slope 1.25. More instructive is the fact that there is an induction period, a slight delay in the formation of *trans*-stilbene,

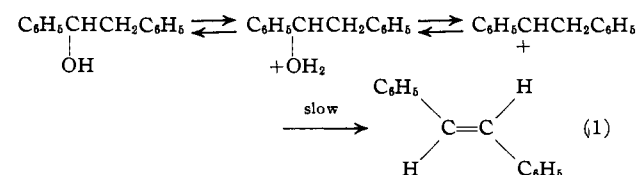
(1) D. S. Noyce and H. S. Avarbock, *J. Am. Chem. Soc.*, **84**, 1644 (1962).

(2) D. S. Noyce, H. S. Avarbock, and W. L. Reed, *ibid.*, **84**, 1647 (1962).

indicating that an intermediate is formed during the course of the isomerization. The length of this induction period may be computed exactly from the rate of dehydration of 1,2-diphenylethanol under the same experimental conditions.

In 50% sulfuric acid, the dehydration of 1,2-diphenylethanol is 7.0 times faster than the isomerization of *cis*-stilbene; the product is exclusively *trans*-stilbene. Under similar conditions, racemization of optically active 1,2-diphenylethanol occurs some 58 times more rapidly than dehydration. The rate of dehydration of 1,2-diarylethanol is extremely sensitive to variation of substituents in the aromatic rings. As a case in point, the rate of dehydration of 1-*p*-anisyl-2-phenylethanol is 1070 times that of 1,2-diphenylethanol under comparable conditions. The rate data for 1-aryl-2-phenylethanol (five compounds) correlate with σ^+ , $\rho = -3.77$, correlation coefficient 0.999. Examination of the fate of 1,2-diphenylethanol-2-*d*₁ reveals that the introduction of deuterium reduces the rate of dehydration by almost a factor of two, $k_H/k_D = 1.83$. However, the product composition is 78.7% *trans*-stilbene- α -*d*₁ and 21.3% *trans*-stilbene.

Thus, the rate-limiting process is the final elimination of a proton from the carbonium ion formed in small steady-state concentration, as depicted in eq. 1. These



observations on the mechanism of the acid-catalyzed dehydration of 1,2-diphenylethanol clearly imply that the rate-limiting step in the isomerization of *cis*-stilbene is the initial protonation of the olefinic system.³ Confirmation of this view comes from a consideration of the solvent kinetic isotope effect.

When the isomerization of *cis*-stilbene is carried out in deuteriosulfuric acid (*cf.* Table I), the rate of isomerization is substantially reduced. The ratio k_{H_2O}/k_{D_2O} is 2.4 at 55% sulfuric acid; it increases to 3.0 at 65% sulfuric acid (comparisons made on a mole fraction basis).

Similar results were obtained with substituted stilbenes. Most striking is the solvent isotope effect in the case of *cis*-4,4'-dimethoxystilbene (*cf.* Table II).

TABLE II
SOLVENT ISOTOPE EFFECTS IN THE ACID-CATALYZED ISOMERIZATION OF SUBSTITUTED *cis*-STILBENES

<i>cis</i> -Stilbene	H ₂ SO ₄ , %	k _{H₂O} , sec. ⁻¹	k _{D₂O} , sec. ⁻¹ ^a	k _{H₂O} /k _{D₂O}
—H	55.3	6.91 × 10 ⁻⁶	2.88 × 10 ⁻⁶	2.4
4-CH ₃	55.3	5.50 × 10 ⁻⁴	1.95 × 10 ⁻⁴	2.8
4-OCH ₃	55.3	1.23 × 10 ^{-2b}	2.95 × 10 ⁻³	4.2
4,4'-(OCH ₃) ₂	55.3	4.68 × 10 ^{-2b}	7.76 × 10 ^{-3b}	6.0

^a Interpolated to N_{SO₄} = 0.1954. ^b Extrapolated from data at lower acidities.

This variation in solvent isotope effect strongly suggests that the degree of carbon-hydrogen bond formation at the transition state is varying in a predictable manner with changes in the structure of the stilbene. As the stability of the resultant carbonium ion is increased, the extent to which carbon-hydrogen bond formation has been completed is lessened. Thus C-H

(3) *Cf.* ref. 2, p. 1649.