were prepared in the usual manner. The derivatives were isolated by extraction of the reaction mixtures with methylene chloride (after having been made alkaline with sodium hydroxide). The semicarbazone (m.p. 93–94°) of a commercial sample of 5-diethylamino-2-pentanone[17] was identical to the semicarbazone (m.p. 93.5–94.5°) of the ketone obtained from the reaction of γ-diethylaminobutyric acid and acetic anhydride; mixture m.p. 92–94°.

The semicarbazone of 5-(4-morpholino)-hexan-2-one had a m.p. 135–137° after recrystallization from methylene chloride–petroleum ether.

Anal. Calcd. for $C_{22}H_{22}N_4O_2$: C, 54.52; H, 9.15; N, 23.13. Found: C, 54.99; H, 9.39; N, 22.50.

B. **Methiodide.**—A methiodide of 5-(1-piperidino)-2-pentanone was prepared by refluxing a solution of the ketone in acetone and methyl iodide for 2 hours. After recrystallization from acetone ether the derivative had m.p. 70–72°.

Anal. Calcd. for $C_{11}H_{22}NOI$: C, 42.45; H, 7.13; N, 4.50; I, 40.78. Found: C, 42.61; H, 6.93; N, 4.52; I, 40.90.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRANDEIS UNIVERSITY, WALTHAM 54, MASS.]

Preparation and Kinetics of Decomposition of a Bicyclic Azo Compound. A Novel Reduction[1]

BY SAUL G. COHEN, ROBERT ZAND AND COLIN STEEL

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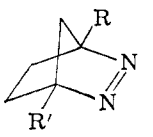
The decomposition of the azo compound 2,3-diazabicyclo[2,2,1]-2-heptene (I) has been studied in the gas phase from 131.5° to 180.8°. The reaction shows first-order kinetics, k_1 $7.2 \times 10^{14} e^{-37,300/RT}$, $\Delta S^{\ddagger}$ 8.7 E.U. The data are compared with those for acyclic aliphatic azo compounds. Attempts to prepare the $\Delta^{5,6}$-unsaturated analog of I from the adduct of diethyl azodicarboxylate to cyclopentadiene led to a novel reduction reaction and formation of 1. Reaction of 1,4-diphenyl-1,3-cyclopentadiene with diethyl azodicarboxylate is described.

As part of our study of the effects of structure on the ease of decomposition of azo compounds, it appeared of interest to prepare and examine the kinetics of decomposition of a bicyclic azo compound of type I. We are reporting at this time

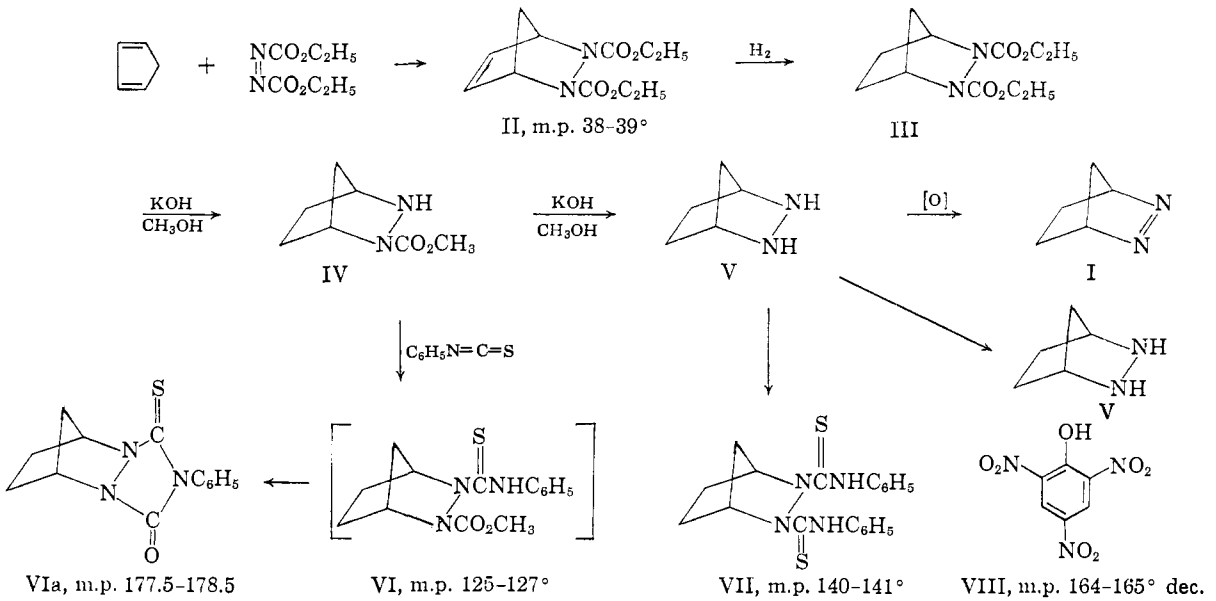


I

on some synthetic work directed toward such compounds and a related unsaturated $\Delta^{5,6}$-compound, and on the kinetics of decomposition of compound I, R = R′ = H, 2,3-diazabicyclo[2,2,1]-2-heptene.

(1) We are pleased to acknowledge generous support of this work by the National Science Foundation, Grant G.4244.

Synthetic Work.—Compound I was prepared by the sequence of reactions described in the literature[2]: addition of diethyl azodicarboxylate to cyclopentadiene, forming II, which we find to be a solid, m.p. 38–39°; catalytic hydrogenation to III; saponification to the mono-ester IV, and to the hydrazo compound V. Oxidation of hydrazo compound V to azo compound I proceeds very readily, and apparently was effected inadvertently in one of our experiments by air in the presence of cuprous chloride instead of by cupric chloride as directed,[2] the cuprous chloride complex



II, m.p. 38–39° III

IV V I

VIa, m.p. 177.5–178.5 VI, m.p. 125–127° VII, m.p. 140–141° VIII, m.p. 164–165° dec.

of the azo compound being formed in both cases. The oxidation also was effected readily by mercuric oxide,[3] a preferred reagent for this purpose.

(2) O. Diels, J. H. Blom and W. Koll, *Ann.*, **443**, 243 (1925).

(3) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 2457 (1955).

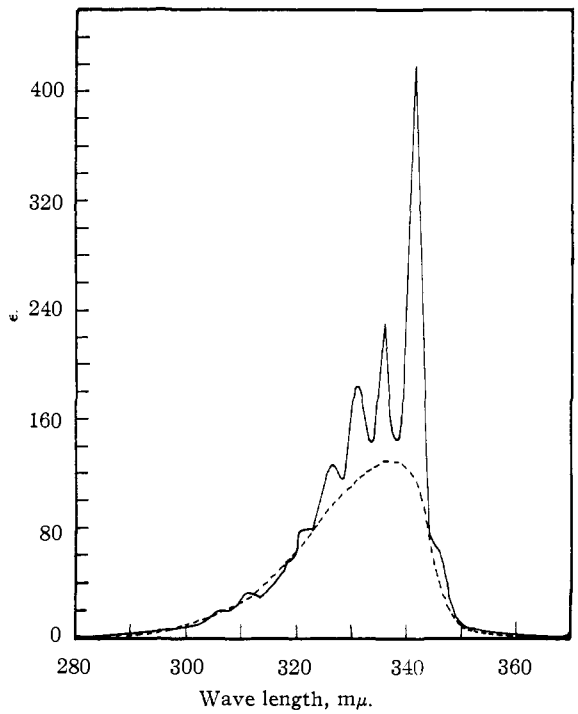
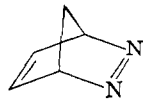


Fig. 1.—Ultraviolet absorption spectrum of compound I: solid line, in isoöctane; broken line, in 95% ethanol.

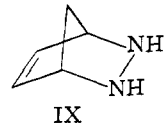
The intermediates IV and V were newly characterized in this work since we wished to study the saponification of the unsaturated adduct II and possibly prepare the unsaturated azo compound Ia. 2-Carbomethoxy-2,3-diazabicyclo[2,2,1]heptane (IV), on treatment with phenyl isothiocyanate, apparently led first to the phenyl thiosemicarbazide derivative VI and then to the novel derivative of 3-thiourazole VIa. This sequence of half-hydrolysis, formation of the thiosemicarbazide and cyclization to the thiourazole was also seen in the cyclic compounds obtained by addition of the azo-ester to substituted butadienes.[4] The hydrazine V was characterized both as the bisphenylthiocarbamate derivative VII and as the picrate VIII.



Ia

The absorption spectrum of compound I in isoöctane is interesting (Fig. 1) showing a number of sharp regularly spaced peaks: 3415 Å., ϵ 420; 3360, ϵ 231; 3310, ϵ 184; 3260, ϵ 128; 3210, ϵ 78; 3165, ϵ 42. The differences in frequencies between these peaks are similar, about 462 cm.$^{-1}$, indicating that a molecular vibration may be coupled with the electronic excitation and that this vibration might be detected at 21.6 μ. The absorption spectrum in ethanol did not show this splitting and led to a smooth curve, λ_{max} 3365 Å., ϵ 130. The absorption peak at 3415 Å. in isoöctane was used for following the kinetics of decomposition. It should be noted that the position of this maximum is similar to that of acyclic *trans*-azo compounds rather than that of a cyclic *cis*-azo compound.[5]

Compound Ia, the unsaturated analog of I, was of interest since its decomposition might lead directly to two stable molecules, cyclopentadiene and nitrogen, and thus be much more rapid than that of the saturated analog I which leads to bicyclo[0,1,2]pentane,[6] presumably *via* a biradical. Saponification of the unsaturated adduct II was examined both at room temperature and under reflux in the presence of two moles of alkali in an attempt to isolate the analog of IV, and in the presence of excess alkali to lead to the unsaturated hydrazo compound IX. However, in all cases only derivatives of the saturated hydrazo compound V—both the picrate VIII (19% yield) and the phenyl thiocarbamate derivative VII (25% yield)—and the saturated azo compound I itself (20% yield), were obtained as pure compounds. The yields, calculation of which is based on the compounds being formed in effect from bimolecular disproportionation reactions, are low and it cannot be ruled out that the desired unsaturated compounds were not present, but we were unable to isolate them. In addition, 35% of the total amount of cyclopentadiene originally present in the adduct II was isolated from a distillate of the hydrolysate as the bis-adduct to *p*-benzoquinone. Similar treatment of the adduct II, boiling with methanol and distillation of the solvent, but without potassium hydroxide being present to effect hydrolysis, led to no cyclopentadiene that could be detected by quinone, and thus gave no evidence for reversal of the initial Diels–Alder reaction as source of the cyclopentadiene. However, in the presence of alkali a slight initial reversal of the Diels–Alder reaction might be made more extensive by saponification of the diethyl azodicarboxylate. This would lead to potentially effective reducing agents, diimide HN=NH or its anion HN=N$^-$. Hydrolysis of the adduct II would lead to the unsaturated hydrazo compound IX which could



IX

lead in several ways to the observed products, cyclopentadiene and the saturated hydrazo compound V. It might reduce unreacted adduct II, being itself converted to the unsaturated azo compound Ia, which would decompose; it might disproportionate with a second molecule of IX; or, which seems unlikely, it might in part undergo intramolecular disproportionation leading directly to azo compound I. Alternatively, compound IX may itself decompose to cyclopentadiene and diimide, and the latter might reduce any of azo compound I which may have formed, or adduct II, or compound IX itself. It may be noted that

(4) M. G. Kouzmin, "A New Method of Synthesis of Cyclobutanes, Catalytic Decomposition of Tetrahydropyridazines," Ph.D. Thesis, State University of Moscow, U.S.S.R., 1959.

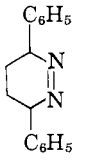
(5) S. G. Cohen, S. Hsiao, E. Saklad and C. H. Wang, *J. Am. Chem. Soc.*, **79**, 4400 (1957).

(6) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

the formation of saturated products in this reaction is consistent with the formation[7] of N,N'-dibenzoylhydrazine, $C_6H_5CONHNHCOC_6H_5$, during the hydrolysis of dibenzoyldiimide, $C_6H_5CON{=}NCOC_6H_5$.

Before it had been established that the azo compounds obtained from II and from III were identical, they were subjected to catalytic hydrogenation, each absorbing slightly less than two moles of hydrogen and leading to 1,3-diaminocyclopentane, characterized as 1,3-bis-(phenylthioureyl)-cyclopentane.

During the course of this work we also attempted to prepare 1,4-diphenyl-2,3-diazabicyclo[2,2,1]2-heptene (Ib, R = R' = C_6H_5) since we had earlier prepared and studied the decomposition of an acyclic analog,[8] 1-azo-bis-1-phenylethane, $C_6H_5CHN{=}NCHC_6H_5$, and had also prepared a cyclic analog 1,4-diphenyl-2,3-diaza-2-cyclohexene.[5]



Treatment of 1,4-diphenyl-1,3-cyclopentadiene with the azo-ester in benzene led to recovery of much of the diene and, in low yield, to a product with elementary analysis satisfactory for a compound derived from one mole of diene and two of azo-ester. A similar reaction carried out in cyclohexane led to recovered diene, some product of reduction of the azo-ester, diethyl hydrazodicarboxylate, and a product which may be a 1-1 adduct. Attempts to catalyze[9] the addition with acetic acid and other acids failed. However, 1,4-diphenyl-1,3-cyclopentadiene may tautomerize to a diene which may undergo 1,4-addition to form an adduct which will not have both phenyl groups at the bridge-heads as desired. Also diethyl azodicarboxylate undergoes ready addition reactions with nucleophilic reagents,[10] including aromatic nuclei and active methylene compounds, and the latter may also add by a free radical mechanism. Therefore this work was discontinued. It may be that the reactions of 1,4-diphenyl-1,3-cyclopentadiene which we observed were at least in part additions to the azo-ester *via* the active methylene group.

Kinetics of Decomposition of I.—The decomposition was studied in the vapor phase at 131.5°, 142.3°, 164.1° and 180.8° as described in the Experimental part. At each temperature 0.1-ml. samples of 0.45 m./l. of I in isoöctane (*ca.* 4% solutions) were heated in 30-ml. ampoules, the total internal pressure being approximately one atmosphere. At 164.1° a number of variations were examined. In one set a more dilute solution of I in isoöctane (0.012 m./l., *ca.* 0.1 % solution) was studied. In another, isoöctane was replaced by toluene as the solvent. In a third set the ampoules were packed with pieces of glass tubing to ascertain whether there was any surface effect. In a fourth set the volume of the sample heated was varied from 0.01 ml. to 0.10 ml. to examine the effect of total pressure. At each temperature in the standard runs 7 to 10 points were taken; the reactions were followed for 2.8 half-lives at 131.5° and for more than 4 half-lives at the higher temperatures. In the toluene and packing variations 4 points were taken over 3.5 half-lives. In the study of pressure variation 7 points were taken at about the same time, after 2 half-lives. The decompositions showed excellent first-order kinetics and there were no significant effects due to concentration of I in the solvent, or to the presence of toluene, a possible chain inhibitor, or to surface area or pressure. Half-lives were 35.3 hours at 131.5°, 10.6 hours at 142.3°, 69.6 minutes at 164.1°, and 13.8 minutes at 180.8°. Plots of ln ($O.D._0$/$O.D._x$) *vs.* time were linear and are given in Fig. 2; from the slopes the rate constants were calculated. A least squares analysis of the primary data led to the same rate constants. A plot of log k *vs.* $1/T$ was linear, and from it was calculated the activation energy; the entropy of activation and the pre-exponential factor A were calculated in the usual way. The data are summarized in Table I. The kinetic data in this work seem to us to be quite accurate; the reactions were carried out in the high pressure region in a static system and were followed essentially to completion, and a wide temperature range was studied. The rate constants probably were accurate to 2% and the energies and entropies of activation as indicated.

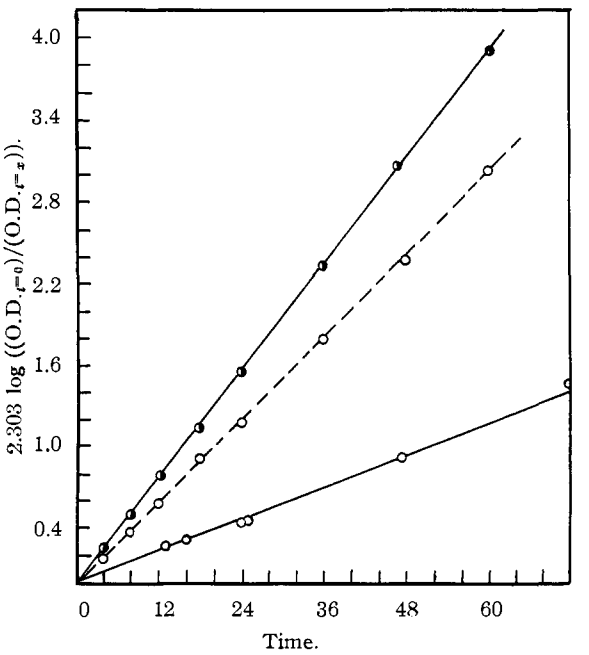


Fig. 2.—Kinetics of vapor phase decomposition of compound I: —O—O—, 131.5°, time in hours; - -O- -O- -, 180.8°, time in minutes; —◑—◑—, 142.3°, time in hours.

In compound I the azo linkage is fused into a rigid bicyclic structure in which it is incorporated,

(7) R. Stolle and A. Benrath, *J. prakt. Chem.*, **70**, 263 (1904).

(8) S. G. Cohen, S. J. Groszos and D. B. Sparrow, *J. Am. Chem. Soc.*, **72**, 3947 (1950).

(9) L. E. Gast, E. W. Bell and H. M. Teeter, *J. Am. Oil Chem. Soc.*, **33**, 278 (1956).

(10) R. Huisgen, F. Jacob, W. Siegel and A. Cadus, *Ann.*, **590**, 1 (1954).

TABLE I

DECOMPOSITION OF 2,3-DIAZABICYCLO[2,2,1]-2-HEPTENE (I)

T, °C.	131.5	142.3	164.1	180.8
$10^5 k$, sec.$^{-1}$	0.544[a]	1.82[a]	16.6[a]	83.5[a]
			16.4[b]	
			16.6[c]	
E_A, kcal. mole^{-1}				37.3 ± 0.3
$\Delta S^{\ddagger}$, cal. mole^{-1} deg.$^{-1}$				8.7 ± .4
log A				14.86 ± .1

[a] Isoöctane. [b] Toluene. [c] Surface area increased.

in the *cis* configuration, into six- and five-membered rings. The six-membered cyclic analog of 1-azo - bis - 1 - phenylethane, 1,4 - diphenyl - 2,3-diaza-2-cyclohexene, was found to decompose about 100 times as fast as the acyclic compound at 80°, the increased reactivity being ascribed to the *cis*-azo configuration.[5] The seven-membered cyclic analog similarly[11] decomposed more rapidly than the acyclic compound while, on the other hand, the eight-membered ring was more stable than the open chain compound.[12] In the present case, azo compound I may be compared to its acyclic analog azo-bis-2-propane, $(CH_3)_2CHN{=}NCH(CH_3)_2$, while the cyclic analog, 1,4-dimethyl-2,3-diaza-2-cyclohexene, has not been prepared. The decomposition of azo-bis-2-propane has been studied by Ramsperger[13] in the range 250–290°, and shows first-order kinetics, $k = 5.6 \times 10^{13} e^{-\frac{40,900}{RT}}$, $k_{250} = 4.4 \times 10^{-4}$ sec.$^{-1}$. Compound I decomposes at about the same rate at 175° as azo-bis-2-propane does at 250°. Extrapolation of the data for compound I to 250° leads to a value of $k_{250} = 1.9 \times 10^{-1}$ sec.$^{-1}$, about 430 times larger at this temperature than that of the acyclic compound. This *cis*-azo compound, in this case bicyclic, decomposes considerably more readily than the *trans* acyclic analog. It appears that a significant portion of the increased rate is due to a more favorable pre-exponential factor, while the major effect is due to the energy of activation being more favorable by 3.6 kcal. However, comparison of the reported[13] pre-exponential factor for azo-bis-2-propane, 5.6×10^{13}, with those for azomethane,[14] 5.0×10^{15}, and for azo-ethane,[15] 5.9×10^{15}, and for 2,2-azo-bis-isobutane,[16] 2.2×10^{15}, indicates that the value of A for azo-bis-2-propane may in fact be somewhat higher and that the kinetics of decomposition of this compound should be re-examined. The rate of decomposition of I may be larger than that of azo-bis-2-propane entirely because of more favorable energy of activation. The frequency factors, $\sim 10^{15}$, and the entropies of activation, 12–15 E.U., for the decomposition of aliphatic azo compounds may be high because of simultaneous rupture of two bonds[17a,b] and incipient formation of a nitrogen molecule and two radicals in the transition state. In the decomposition of the rigid bicyclic azo compound I, while two C–N bonds may well be breaking simultaneously, only two fragments are being formed and the biradical 1,3-cyclopentadiyl quickly leads to the observed product bicyclo-[0,1,2]pentane.[6] The frequency factor 7.2×10^{14} and entropy of activation of +8.7 E.U. which we observe are lower than when three fragments are formed, but high enough to be consistent with the simultaneous rupture of two C–N bonds and probably high enough to indicate that the biradical is formed and the reaction is not of the molecular or four-center type in which the new C–C bond is formed simultaneously with the rupture of the two C–N bonds.[18]

Experimental[19]

2,3-Dicarboethoxy-2,3-diazabicyclo[2,2,1]-5-heptene (II).—Diethyl hydrazodicarboxylate was prepared from 59 g. (1 mole) of 85% hydrazine hydrate (Matheson), 217 g. (2 moles) of ethyl chlorocarbonate (Matheson) and 106 g. (1 mole) of sodium carbonate, according to the published procedure[20]; yield 145 g. (0.82 mole), 82%, m.p. 133–135° from water, reported[20], m.p. 134–135°. Diethyl azodicarboxylate was prepared by treatment of 40 g. (0.22 mole) of diethyl hydrazodicarboxylate in 80 ml. of concentrated nitric acid and 100 ml. of chloroform with 25 ml. of fuming nitric acid at 0° for 2.5 hours.[21] The acid layer was extracted with five 20-ml. portions of chloroform, the combined chloroform solution was washed well with water, sodium bicarbonate, and water, diluted with ether, dried and distilled; 35.4 g. (0.20 mole), 89% yield, b.p. 90–95° (5 mm.). Dicyclopentadiene (Eastman Kodak Co., Technical) was heated under a Vigreux column with a reflux head, and the fraction boiling at 41–44° was collected and used directly. Solutions of 58 g. (0.33 mole) of diethyl azodicarboxylate in 50 ml. of ether and 22 g. (0.33 mole) of cyclopentadiene in 50 ml. of ether were mixed and allowed to stand at room temperature for 24 hours. The product was distilled, leading to 72 g. (0.30 mole), 91% yield, of the adduct II, b.p. 131° (1 mm.), reported[2] b.p. 125° (0.8 mm.). This product solidified on long standing; m.p. 38–39°.

2,3-Dicarboethoxy-2,3-diazabicyclo[2,2,1]heptane (III).—A solution of 48 g. (0.20 mole) of the adduct II in 100 cc. of absolute ethanol was hydrogenated at 40 p.s.i. over 0.3 g. of 10% palladium-on-charcoal. The solution was filtered and distilled, leading to the hydrogenated adduct III, 46 g. (0.19 mole), 95% yield, b.p. 123° (0.2 mm.), reported[2] b.p. 123° (0.2 mm.).

2-Carbomethoxy-2,3-diazabicyclo[2,2,1]heptane (IV).—A solution of 53 g. (0.22 mole) of the hydrogenated adduct III and 13 g. (0.23 mole) of potassium hydroxide in 50 ml. of methanol was heated on the steam-bath under nitrogen for 3 hours. Precipitated potassium carbonate was filtered off and washed with methanol, the combined methanol solutions were concentrated and the residue was extracted with ether, dried and distilled, leading to IV, b.p. 125° (5 mm.), reported[2] b.p. 133° (9–10 mm.), 20 g. (0.13 mole), 59% yield. A sample of IV, 1.5 g. (0.010 mole) and 2.0 g. (0.015 mole) of phenyl isothiocyanate were mixed, heat being evolved, and kept at −10° for 16 hours leading to a product, 2.6 g., 90% yield, m.p. 125–127° from ethanol, and to a second product on crystallization from benzene, m.p. 177.5–178.5°, apparently a derivative of thiourazole (VIa).

Anal. Calcd. for $C_{15}H_{13}N_3OS$: C, 60.21; H, 5.31; N, 16.21; S, 11.98. Found: C, 59.98; H, 4.94; N, 16.05; S, 11.61.

2,3-Diazabicyclo[2,2,1]heptane (V).—A solution of 30 g. (0.13 mole) of the hydrogenated adduct III and 29 g. (0.52

(11) C. G. Overberger and J. G. Lombardino, *J. Am. Chem. Soc.*, **80**, 2317 (1958).

(12) C. G. Overberger and I. Tashlick, *ibid.*, **81**, 217 (1959).

(13) H. C. Ramsperger, *ibid.*, **50**, 714 (1928).

(14) C. Steel and A. F. Trotman-Dickinson, *J. Chem. Soc.*, 975 (1959).

(15) W. D. Clark, Ph.D. Dissertation, University of Oregon, Eugene, Oregon, June, 1959.

(16) J. B. Levy and B. K. W. Copeland, *J. Am. Chem. Soc.*, **82**, 5314 (1960). These authors misquote the value of A for azo-bis-2-propane as 5.6×10^{13}, and record a different value of azoethane, 5.87×10^{14}.

(17) (a) S. G. Cohen and C. H. Wang, *ibid.*, **77**, 3628 (1955); (b) C. Steel, *J. Chem. Phys.*, **31**, 899 (1959).

(18) B. G. Gowenlock, *Quart. Rev.*, **14**, 133 (1960).

(19) Melting points are uncorrected. Analyses are by Dr. S. M. Nagy, Massachusetts Institute of Technology.

(20) N. Rabjohn, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 375.

(21) A. Rodgman and G. F. Wright, *J. Org. Chem.*, **18**, 468 (1953).

mole) of potassium hydroxide in 150 ml. of methanol was heated on the steam-bath under nitrogen for 2.5 hours. Precipitated potassium carbonate was filtered off, the filtrate was heated for 0.5 hour, cooled and concentrated in vacuum, more solid precipitating. The residue was extracted well with ether, the washings were dried and concentrated in vacuum, leading to an oil, presumably the hydrazine V, 6.2 g. (0.063 mole), 48% yield.

Compound V (2 g., 0.02 mole) was treated with 5.7 g. (0.042 mole) of phenyl isothiocyanate, heat being evolved. This was refrigerated overnight, leading to VII which was washed with hexane and ethanol; 6.0 g., 80% yield, m.p. 140–141° after crystallization from ethanol and from benzene.

Anal. Calcd. for $C_{19}H_{20}N_4S_2$: C, 61.92; H, 5.47; N, 15.20; S, 17.40. Found: C, 62.36; H, 5.68; N, 15.19; S, 17.28.

A sample of compound V (0.5 g., 0.0050 mole) in 5 ml. of ether was treated with 10 ml. of a saturated solution of picric acid in ether, leading to the picrate, 1.23 g. (0.0038 mole), 75% yield, m.p. 164–165° dec. from ethanol.

Anal. Calcd. for $C_{11}H_{18}N_8O_7$: C, 40.37; H, 4.00; N, 21.40. Found: C, 40.82; H, 4.16; N, 21.28.

2,3-Diazabicyclo[2,2,1]-2-heptene (I).—The hydrazo compound V, 6.2 g. (0.063 mole), was dissolved in 75 ml. of distilled water and stirred for 3 hours with 6.3 g. (0.063 mole) of cuprous chloride, leading to the cuprous chloride complex of the azo compound I; 9.1 g. (0.047 mole), 74% yield. The complex (16 g., 0.082 mole) was dispersed in 25 ml. of water, treated with 4.0 g. of sodium hydroxide in 10 ml. of water and extracted continuously with ether for 24 hours. The ether was dried and concentrated leading to a residue which crystallized when cooled; 6.22 g. (0.065 mole), 79% yield, m.p. 99–100° from *n*-hexane, reported[2] m.p. 99–99.5°.

Anal. Calcd. for $C_5H_8N_2$: C, 62.47; H, 8.39; N, 29.14. Found: C, 62.3; H, 8.2; N, 29.0.

A solution of 24 g. (0.1 mole) of the adduct II in 50 ml. of methanol was treated with a solution of 23 g. (0.4 mole) of potassium hydroxide in 70 ml. of methanol on the steam-bath under nitrogen for 1 hour. The solution was cooled and filtered, the potassium carbonate was washed well with methanol, and the methanol was distilled from the combined filtrates through a 30-cm. column packed with glass helices, 175 ml. of methanol being collected. The residue was triturated with several portions of ether. The ether extracts were filtered, dried and filtered again; total volume 350 ml.

Benzoquinone (*ca.* 1 g.) was added to 75 ml. of the methanol distillate and the solution was allowed to stand at room temperature. Crystals formed slowly, several crops being collected; total yield 1.8 g. (0.0075 mole) of the adduct two moles of cyclopentadiene to quinone, m.p. 155–156° from methanol, reported[22] m.p. 157°. The yield corresponds to 0.035 mole of cyclopentadiene in the total methanol distillate, 35% yield.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.17; H, 6.57.

An aliquot of the ether extracts, 5 ml., was treated with 8 ml. of a saturated ether solution of picric acid, leading to the picrate of V; 0.090 g. (0.276 mmole), m.p. 163–164° from ethanol, mixed m.p. with an authentic sample unchanged. The yield corresponds to 0.0193 mole of V, 19% yield. Another aliquot, 30 ml., of the ether extracts was treated with 1 g. (0.0074 mole) of phenyl isothiocyanate and allowed to stand for 2 days. The ether was removed in vacuum, the residue was washed with hexane and dried; 0.80 g. (0.0021 mole) of the bis-phenylthiocarbamate of V, m.p. 140–141° after being chromatographed on alumina and crystallized from benzene. The mixed melting point with an authentic sample was unchanged. The yield corresponds to 0.025 mole of V, 25% yield.

The remainder (90%) of the ether extract was concentrated, leading to an oil, 3.4 g. (0.034 mole, 34%, calculated as the hydrazine V). A portion of this (1 g., 0.01 mole) was treated with 3 g. (0.022 mole) of phenyl isothiocyanate at room temperature for 24 hours; this was taken up in benzene and diluted with hexane, leading to the bis-phenylthiocarbamate of V, m.p. 137–139° from benzene, mixed m.p. 138–141°, 0.81 g. (0.0022 mole), 22% yield from the residue, 17% yield from the adduct II. A second portion of the residue (1 g., 0.01 mole) was dissolved in 20 ml. of hexane and oxidized with excess mercuric oxide, filtered and concentrated leading to the azo compound I, m.p. and mixed m.p. 98–100°, 0.25 g. (0.0026 mole), 26% yield from the residue, 20% yield from the adduct II.

A solution of 17 g. (0.7 mole) of the adduct II in 100 ml. of methanol was boiled under reflux for 1.25 hours and allowed to stand at room temperature overnight. A 15-ml. portion of this solution was treated with 0.5 g. of benzoquinone, no precipitate forming after 2 weeks. Methanol was distilled from the remainder of the solution through a 30-cm. column, and the distillate was treated with 0.5 g. of quinone, no precipitate forming after 2 weeks.

Hydrogenation of Azo Compound I. (1) **Compound I Prepared from Hydrogenated Adduct III.**—(a) Platinum oxide (0.0120 g.) was pre-reduced in 10 ml. of ethanol, 0.1013 g. (0.00106 mole) of I was added and the hydrogenation was followed, 48.7 ml. of hydrogen being absorbed, 92% of 52.5 ml. calculated for 2 moles. (b) A solution of 0.27 g. (0.0028 mole) of I in 20 ml. of *n*-hexane was hydrogenated over 0.050 g. of platinum oxide, 150 ml. (0.0060 mole) of hydrogen being absorbed in 0.5 hour. The solution was filtered and treated with 1 g. (0.0081 mole) of phenyl isothiocyanate, an immediate precipitate forming. Benzene (10 ml.) was added, the solution was boiled for 5 minutes and cooled, leading to 1,3-bis-phenylthioureylcyclopentane, 0.5 g. (0.00135 mole), 48% yield, m.p. 181–182° from ethanol.

(2) **Compound I Prepared Directly from Adduct II.**—(a) Platinum oxide, 0.0098 g., was pre-reduced in 10 ml. of ethanol, 0.045 g. (0.00047 mole) of I was added and the hydrogenation was followed, 19.6 ml. of hydrogen being absorbed, 84% of 23.3 ml., calculated for 2 moles. (b) A solution of 0.25 g. (0.0026 mole) of I in 20 ml. of *n*-hexane was hydrogenated over 0.050 g. of platinum oxide, 91 ml. (0.0037 mole) of hydrogen being absorbed. Treatment with 0.73 g. (0.0054 mole) of phenyl isothiocyanate led to the same derivative as above; 0.50 g. (0.00135 mole), 57% yield, m.p. and mixed m.p. 181–182°.

Anal. Calcd. for $C_{19}H_{22}N_4S_2$: C, 61.58; H, 5.98; N, 15.12; S, 17.31. Found: C, 61.23; H, 5.79; N, 15.32; S, 17.41.

1,4-Diphenyl-1,3-cyclopentadiene.—(1) **β-Benzoylpropionic acid** was prepared by reaction of succinic anhydride (68 g., 0.68 mole, Eastman Kodak Co.) with benzene in the presence of aluminum chloride (200 g., 1.5 moles) in accordance with directions in the literature[23]; 67 g. (0.38 mole), 55% yield, m.p. 117–118°, reported m.p. 116°. (2) **Ethyl-β-benzoylpropionate** was prepared by esterification of 44.5 g. (0.25 mole) of β-benzoylpropionic acid; 44.2 g. (0.21 mole) 86% yield, b.p. 180–182° (16 mm.), reported[24] b.p. 183–184° (22 mm.). (3) Dry sodium ethoxide was prepared from 11.5 g. (0.5 mole) of sodium and 29.5 ml. of absolute ethanol in 250 ml. of dry benzene. To this was added 51.5 g. (0.25 mole) of ethyl β-benzoylpropionate, and, after the sodium ethoxide had dissolved, 32.5 g. (0.25 mole) of acetophenone, and the solution was kept at 42° for 24 hours. The solution was worked up[25] and the product was crystallized from benzene–petroleum ether; 14.5 g. (0.066 mole), 27% yield, m.p. 158–158.5°. The absorption spectrum was taken in dioxane, λ_{max} 239 mμ, ε 12,600; 357 mμ, ε 21,000.

Reaction of 1,4-Diphenyl-1,3-cyclopentadiene with Diethyl Azodicarboxylate.—(1) A solution of 10 g. (0.046 mole) of the diene and 10 g. (0.057 mole) of the azo-ester in 15 ml. of benzene was boiled under reflux for 24 hours and cooled. Starting diene crystallized and was collected (5.55 g., 55% yield) and the filtrate was refrigerated. A second precipitate was collected, washed with carbon tetrachloride and crystallized twice from chloroform–ether and once from ethyl acetate; 1.22 g. (0.0022 mole), 10% yield, m.p. 187–188.5° dec.

Anal. Calcd. for $C_{29}H_{34}O_8N_4$: C, 61.48; H, 6.05; N, 9.89. Found: C, 61.54; H, 6.22; N, 9.35.

The absorption spectrum was taken in dioxane, λ_{max} 241 mμ, ε 1,760; 339 mμ, ε 1,581. (2) A solution of 2.18 g. (0.01 mole) of the diene and 4 g. (0.023 mole) of the azo-ester in 28 ml. of cyclohexane was boiled under reflux for 5

(22) W. Albrecht, *Ann.*, **348**, 31 (1906).

(23) L. H. Somerville and C. F. H. Allen, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 81.

(24) R. Meyer and K. Togel, *Ann.*, **347**, 88 (1906).

(25) N. L. Drake and J. R. Adams, *J. Am. Chem. Soc.*, **61**, 1326 (1939).

hours under nitrogen, and cooled, leading to recovered diene, 0.45 g. (21% yield), m.p. 152–154°, mixed m.p. 153–158°. A second fraction was diethyl hydrazodicarboxylate, 0.75 g. (19% yield), m.p. 129–131° from alcohol, mixed m.p. 129–132°. A third fraction appeared to be adduct, 0.96 g. (0.0025 mole), 25% yield, m.p. 139–140° from chloroform–petroleum ether. The absorption spectrum was taken in dioxane; λ_{max} 259 mμ, ϵ 15,840.

Anal. Calcd. for $C_{23}H_{24}O_4N_2$: C, 70.39; H, 6.16; N, 7.14. Found: C, 70.44; H, 6.08; N, 6.64.

Kinetics of Decomposition of I.—A sample of I, *ca.* 0.2 g., was weighed accurately and dissolved in isoöctane in a 5-ml. volumetric flask. Samples of the solution, 0.100 ml., were carefully pipetted into ampoules approximately 30 ml. in volume and immediately frozen in liquid nitrogen. The ampoules were placed on a vacuum manifold, degassed by freezing and thawing at 10^{-6} mm., and sealed. They were placed in a constant temperature silicone oil-bath at the indicated temperatures for measured periods of time, removed from the bath and cooled in liquid nitrogen. The ampoules were opened, sufficient solvent was added to bring the volume of liquid to 5 ml., the solution was mixed and the absorption spectrum of the solution was obtained on a model 21 Cary spectrophotometer. The optical density at 3415 Å. was noted and a first-order rate constant was calculated for each point from the equation $\ln (O.D.)_0/(O.D.)_t = kt$.

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Intramolecular H-Bonds. I. A Spectroscopic Study of the Hydrogen Bond between Hydroxyl and Nitrogen

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A survey of simple compounds containing similar intramolecular OH···O and OH···N bonds indicates that, contrary to currently held views, the latter system forms the stronger H-bond. A detailed infrared spectroscopic study of internal five- and six-membered rings involving bonding of phenolic hydroxyl to azomethine nitrogen also supports the above conclusion. It is demonstrated that when the OH···N=C bond is incorporated in a π-electron system, the strength of the bond parallels that of the carboxylic acid dimers and the enolized β-diketones. Some observations regarding the C=N stretching frequency of the phenolic Schiff bases are presented.

Introduction.—The overwhelming majority of investigations of hydrogen bonds which involve hydroxyl as the proton donor group are also concerned with oxygen as the proton acceptor atom, and comparatively few spectroscopic studies are available concerning H-bonding of hydroxyl to nitrogen as the acceptor atom. This can be seen readily from an examination of the two most comprehensive reference texts on infrared spectroscopy, Bellamy,[1a] and Jones and Sandorfy,[1b] both of which have extensive sections on OH···O and NH···N bonds with but casual mention of bonds involving OH···N.[2a]

A similar situation exists in the study of the strength of H-bonds by crystallographic methods. Donahue,[3] in a review of hydrogen bonds in organic crystals, dismisses the OH···N bond with the statement that only two examples were known (in 1950), and that this is due mainly to the preferential formation of OH···O bonds. He further states that there is apparently no significant difference between NH···O and OH···N bonds. On the basis of Donahue's[3] review, a linear relationship between bond distance and the OH stretching frequency for OH···O bonds was derived by Rundle and Parasol[4] and this was followed by a similar treatment by Lord and Merrifield.[5] Further empirical relations were extended to NH···O and NH···N bonds as well as OH···O[6] and, with the accumulation of crystallographic X-ray data, a more extensive treatment by Nakamoto, Margoshes and Rundle[7] included a short section on OH···N bonds. However, no comment was made as to the relative strength of the OH···N bond, and it was further noted by these authors that four of the five compounds examined (in contrast to the 26 compounds containing OH···O bonds) were oximes and that the molecular crystal structure was ambiguous.[7]

An indication that the strength of the OH···N bond may have been greatly underestimated may be inferred from a recent discussion on the structure of formamidoxime[8] in which the estimated frequency of the OH···N bond is placed at 3260 cm.$^{-1}$, a value significantly lower than the mean frequency of 3350 cm.$^{-1}$ as given by Sutherland[9] for OH···O bonds. Further, the spectroscopic evidence of Baker, Davies and Gaunt[10] specifically supports the greater strength of intermolecular OH···N over OH···O bonds. These authors, in seeking evidence for alcohol–amine association in the base-catalyzed reaction of phenyl isocyanate with alcohols, studied the effect of the addition of triethylamine on the hydroxyl stretching band of methanol in both di-*n*-butyl ether and in benzene. Though their choice of solvents has adversely affected the quality of the resulting spectra, their conclusion that "the energy of the amine interaction with the hydroxyl group is of the same order

(1) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1958; (b) R. N. Jones and C. Sandorfy, in "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956.

(2) (a) The recent appearance of a text devoted exclusively to a study of hydrogen bonding[2b] does not significantly affect the validity of the above statement. (b) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

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