ml of norbornadiene, and 1 l. of cyclohexane (or acetonitrile) at reflux under nitrogen was added gradually (2 hr) a solution of 0.5 mol of the requisite haloacyl halide in 50 ml of cyclohexane (or acetonitrile). The mixture was refluxed for an additional 1 hr, allowed to stand overnight at room temperature, filtered through Celite, concentrated under vacuum, and distilled. The distillate was freed from halogenated impurities generally present by placing in ten volumes of hexane and treating gradually with one volume of 1,5-diazabicyclo[4.3.0]non-5-ene. After standing for 1 hr, the upper layer was decanted, washed four times with water, dried over anhydrous sodium sulfate, and distilled. The isopropyl derivative was more sensitive and required washing with 10% aqueous NaOH and subsequent chromatography on Florisil. Properties of these products are presented in Table I.

Registry No.—**2**, 34922-27-5; **3**, 34922-28-6; *syn*-**6**, 34922-29-7; *anti*-**6**, 34934-85-5; *syn*-**7**, 34934-86-6; *anti*-**7**, 34934-87-7; *syn*-**8**, 34922-30-0; *anti*-**8**, 34922-31-1; *syn*-**9**, 34934-88-8; *anti*-**9**, 34934-89-9; *syn*-**11**, 34922-32-2; *anti*-**11**, 34922-33-3.

Tautomerism of a Secondary Azo Compound Accompanying Thermal Decomposition[1]

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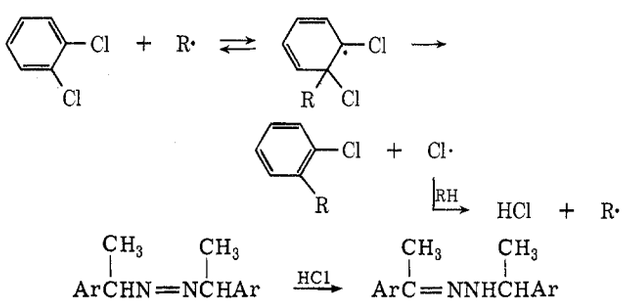
While studying[2] the thermal decomposition of some symmetrical secondary aralkyl azo compounds in solution, we found that in chlorinated solvents and with halogen-substituted azo compound, in addition to radical decomposition products, variable amounts of the starting material were diverted to a material that ultimately yielded the ketone of the initial moieties of the azo compound. α-Phenylazoethane (**1a**), when decomposed in a wide series of solvents (Table I), gave close to 100% yield of radical products (by glpc analysis). In *o*-dichlorobenzene, however, only 80% of the starting azo compound was accounted for when analysis was performed upon opening the sealed ampoule. After the ampoule had stood open for approximately 1 day a peak corresponding to acetophenone appeared. This peak grew with time and after 2 weeks finally accounted for all the α-phenethyl moieties in the starting material. A similar result was found for azo compound **1b** (*p*-chlorophenylazoethane) in benzene.

Addition of pyridine to an *o*-dichlorobenzene solution of **1a** prevented the side reactions; upon thermolysis only normal azo decomposition products were noted. Similarly, **1b** yielded almost theoretical radical products, and no ketone, upon addition of pyridine to the decomposition solution. Addition of dry 0.01 *M* HCl to fresh benzene solutions of **1a** and **1b** resulted in rapid rearrangement of the azo compounds to hydrazones as seen by nmr (*vide infra*). Under the conditions of these studies the hydrazones were stable in the sealed ampoules. Upon opening to air, a rapid oxidation occurred which produced one molecule of ketone for each azo compound originally added. After the ampoules had stood for about 1 week a second molecule of ketone was found, at this point accounting for all the starting material. These data are summarized in Table I. It is interesting to note that the radical–radical reaction rate constant ratio (k_d/k_c) remains constant for both compounds independent of the side reaction leading to ketone.

When **1a** was decomposed at 118° in benzene in a degassed and vacuum-sealed nmr tube for 24 hr (*ca.* 8 half-lives), the nmr peaks for the diphenylbutanes (*meso* and *dl*) as well as those for ethylbenzene and for styrene were evident. Glpc analysis showed only these products in close to quantitative yield. A similar experiment using dichlorobenzene as solvent showed, in addition to the peaks noted for the benzene solution, a doublet at τ 8.56, an equal-sized singlet at τ 8.25, and a small quartet at τ 5.5, readily assignable to the corresponding hydrazone. When this nmr tube was opened to air and allowed to stand overnight, the three peaks attributed to hydrazone disappeared and were replaced by a singlet at τ 8.5 (identical with acetophenone). The *p*-chloroazo compound, **1b**, showed analogous behavior in benzene. In degassed ampoules at room temperature all the secondary aralkyl azo compounds that we have examined in a wide range of solvents including the chlorinated benzenes are indefinitely stable to decomposition and rearrangement.

It is clear that we are observing an acid-catalyzed (by the pyridine experiment) rearrangement of the azo compound to hydrazone accompanying the radical decomposition, and subsequent formation of ketone from hydrazone in two steps, one fast and one slow. We conclude that the acid-catalyzed rearrangement accompanies the radical decomposition, a likely path being



The reversible addition of a radical to the aromatic nucleus probably occurs in benzene as well, but when chlorine is attached to the ring, the reverse reaction must compete with the loss of a stable chlorine atom. A very small amount of this process would produce sufficient acid to catalyze the rearrangement.

Immediately after opening, analysis in all cases showed no trace of acetophenone. The decomposed solution of **1a** in dichlorobenzene was examined by glpc after opening and exposure to anaerobic water in one experiment, and to dry oxygen in another. The oxygenated sample showed 1 mol of acetophenone per mole of hydrazone within 15 min, but the aqueous sample showed only small traces of acetophenone. It thus seems that the first mole of acetophenone arises from the reaction of hydrazone with oxygen. Several in-

(1) Taken in part from the Ph.D. dissertation of R. C. C., University of California, Riverside, 1971. Support by the Air Force Rocket Propulsion Laboratory (R. C. C.) and the Intramural Fund of the University of California is gratefully acknowledged.

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TABLE I

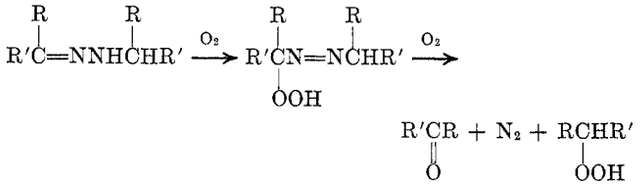
RATE CONSTANT RATIOS AND PRODUCT BALANCES FROM THE DECOMPOSITIONS OF COMPOUNDS 1a AND 1b[a]

Azo compound ArCHN=NCHAr (CH3, CH3)	Solvent	No. of samples[b]	k_d/k_c[c]	Yield[d] of combination + disproportionation products, %	Yield of ketone, %
Ar = C_6H_5 (1a)	C_6H_6	8	0.097 ± 0.002	95 ± 2	0
1a	o-$C_6H_4Cl_2$	16	0.090 ± 0.006	80 ± 3	21–54[e]
1a	C_6H_6/C_6H_5N	2	*f*	*f*	0[g]
Ar = p-ClC_6H_4 (1b)	C_6H_6	8	0.176 ± 0.009	50 ± 2	48.6 ± 2.2[h]
1b	C_6H_6/C_6H_5N	4	0.182 ± 0.008	96.9 ± 2.4	0

[a] From decomposition of the appropriate azo compounds at 118° in sealed ampoules degassed three times. [b] Each sample analyzed in duplicate by glpc. [c] Relative rates of disproportionation to combination as moles α-arylethane/mole 2,3-diarylbutane. [d] From standard plots using 0.1 *M* biphenyl as internal standard. [e] The yield is given as a range since it increases with time up to the value 54%, after which time it remains constant. [f] No values given since pyridine obscured the disproportionation product peak in the glpc trace. [g] Acetophenone was added and the solution rechecked to prove pyridine was not obscuring that peak also, which it was not. [h] The only analysis on this solution was 4 days after opening.

vestigators[3–5] have shown that hydrazones are readily autoxidized to azo hydroperoxides.

The azo hydroperoxide could decompose to ketone, nitrogen, and a secondary alkyl hydroperoxide *via* a homolytic scission and reaction with oxygen. The resultant phenylalkyl hydroperoxide would slowly decompose to a second mole of ketone, with ample precedent.[6]



Chloroazo compound **1b** had been found by Cohen, *et al.*,[7] to yield only about 60% of the theoretical amount of N_2, and Peterson and Ross[8] also obtained approximately 60% of the theoretical N_2 in their study of induced decomposition of azo compound **1a** in the presence of chloranil. Both groups postulated hydrazone formation.

In both these and the study reported here the abnormal decomposition was found when a reactant or solvent contained chlorine. Ioffe and Stopskii[9] have determined that the hydrazone is the more stable tautomer for a series of alkyl azo compounds, in agreement with the observations here. Care must be exercised in analyzing the results of studies of free radicals in halogenated aromatic solvents.

Experimental Section

A more detailed description of synthesis, solvent purification, analytical equipment, techniques, and experimental errors has been presented elsewhere.[2] Benzene, *o*-dichlorobenzene, and pyridine were dried and carefully distilled.

The azo decompositions were performed in sealed ampoules after three freeze–thaw degassings at 10^{-6} mm. Half-lives of the azo compounds studied were approximately 3 hr[7] at 118° and typical reaction times were 24–48 hr (8–16 half-lives).

For the nmr studies, three nmr tubes connected to 10/30 standard taper joints were degassed, sealed, and thermolyzed as above. Tube A contained 49.1 mg of **1a** and 0.5 ml of benzene, tube B 50 mg of **1a** and 0.5 ml of *o*-dichlorobenzene, and tube C 65 mg of **1b** and 0.5 ml of benzene.

Registry No.—**1a**, 5661-68-7; **1b**, 32234-17-6.

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Transannular Alkylations of Cyclooctanones

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Intramolecular alkylation reactions have recently enjoyed considerable popularity as a method for the synthesis of complex polycyclic compounds.[2] In the present report we examine three suitably substituted cyclooctanones for which transannular effects might be expected to play an important role.

Derivatives of 4-hydroxycyclooctanone (**1**) were examined first. In this instance base treatment should promote enolate formation by proton removal at either side of the carbonyl group with roughly equal facility. The conformational constraints of the carbocyclic system might be expected to enhance the formation of a cyclopentane ring at the expense of the normally favored three-membered ring.[3] In fact, treatment of tosylate **2** with NaH–DMSO, KO-*t*-Bu in ether, or potassium carbonate in DMF all gave bicyclo[5.1.0]cyclooctan-2-one (**3**) cleanly. None of the isomeric ketone **4** was detected. Heating alcohol **1** with dicyclohexylcarbodiimide[4] led to **3** in a more direct synthetic approach.

The acetolysis of certain sulfonate esters has been described as proceeding by participation of a preformed enol derived from a neighboring ketone group.[5] A similar process could occur with **2**. Treatment of **2**

(1) (a) Alfred P. Sloan Fellow, 1968–1970; John Simon Guggenheim Fellow, 1970–1971. (b) NSF Undergraduate Summer Research Participant, 1970–1971. (c) NSF Undergraduate Summer Research Participant, 1967.
(2 See, for example, C. H. Heathcock, *J. Amer. Chem. Soc.*, **88**, 4110 (1966); **89**, 4133 (1967); J. E. McMurry, *ibid.*, **90**, 6821 (1968); H. W. Whitlock, *ibid.*, **84**, 3412 (1962).
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