an explanation for the failure of the Hammett parallelism in the present case might reside in an investigation of the temperature coefficients of rate of the addition and dehydration sub-steps postulated by Jencks[16] for semicarbazone formation and oxime formation.

# The Chemistry of Diazaquinones. 3,6-Pyridazinedione and 1,4-Phthalazinedione

BY THOMAS J. KEALY

The unstable diazaquinones 3,6-pyridazinedione, 4,5-difluoro-3,6-pyridazinedione and 1,4-phthalazinedione have been prepared by the low temperature oxidation of alkali metal salts of the corresponding hydrazides using *t*-butyl hypochlorite. The decomposition of the diazaquinones has been investigated. The diazaquinones react instantly with dienes at −77° and therefore are among the most reactive of the dienophiles. Use of the diazaquinones in the Diels–Alder reaction has made some otherwise difficultly accessible ring systems readily available.

Cyclic azo compounds have been used to advantage in the synthesis of ring compounds of various sizes by the elimination of nitrogen.[1,2] Some diacyl diimides (RCON=NCOR) and diaroyl diimides afford 1,2-diketones as the principal product when decomposed under certain conditions.[3,4] However, relatively little is known of cyclic systems containing the diacyl diimide grouping. Of particular interest to us was the preparation of compounds of type I since azo compounds in

I
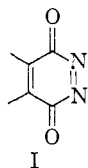
general afford radicals on decomposition[5] and those one might expect from compounds of this type seemed especially appealing.

We chose as the route to such compounds the low-temperature oxidation of the corresponding cyclic hydrazides. *t*-Butyl hypochlorite was found to be particularly effective for this oxidation since it is soluble in various organic solvents at low temperatures and does not give large amounts of inorganic products. Using this reagent with alkali metal salts of the corresponding hydrazides we have prepared 3,6-pyridazinedione (II), 4,5-di-

II   III   IV
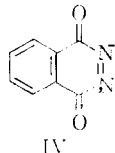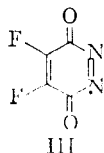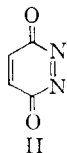
fluoro-3,6-pyridazinedione (III) and 1,4-phthalazinedione (IV), for which we propose the generic term, diazaquinones. Clement[6] has re-

cently reported the preparation of unstable acetonitrile solutions of IV by the oxidation of phthalhydrazide at 0° using lead tetraacetate, and has characterized the butadiene adduct of IV.

The preparations were conveniently carried out in acetone at −50 to −77°, according to eq. 1, to obtain emerald-green solutions of the diazaquin-

$$\text{(1)}$$
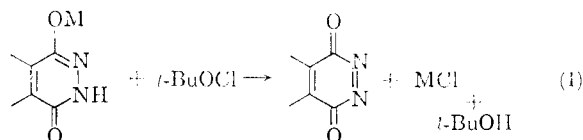
ones. The insoluble salts were removed by filtration at −77° under nitrogen. The diazaquinones are very unstable and highly reactive, and, although both II and IV are precipitated from acetone solutions upon the addition of highly chlorinated solvents, only IV has been isolated. No attempts were made to isolate III. Although IV has been isolated as a crystalline green solid, it frequently decomposed suddenly during the isolation procedures. In acetone solution at −77°, however, the diazaquinones are stable at least overnight and probably longer.

Decomposition of Diazaquinones.—Slow warming of diazaquinone solutions to room temperature results in a gradual fading of the green color well below 0°. 3,6-Pyridazinedione decomposes rapidly in solution near −30°, and the difluoro derivative III decomposes rapidly above −20°, the solution becoming colorless by 0°. 1,4-Phthalazinedione, which appears to be the most stable of the three, retains only a pale lime-green color on reaching room temperature in solution.

In the case of 3,6-pyridazinedione, warming of the solution results in nitrogen evolution and the formation of 1,4,6,9-tetraketopyridazino(1,2-a)-pyridazine (V) as the principal product (43% yield). This yellow compound was identified by hydrolysis

$$\text{(2)}$$

V

(1) For a review, see C. G. Overberger, *Record Chem. Progr.*, **21**, 21 (1960).

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

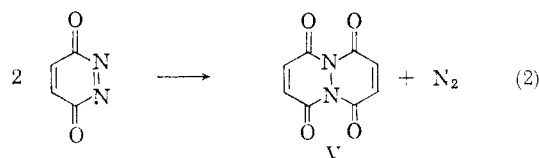(3) H. H. Inhoffen, H. Pommer and F. Bohlmann, *ibid.*, **81**, 507 (1948).

(4) L. Horner and W. Naumann, *Ann.*, **587**, 93 (1954).

(5) On the question of the formation of free acyl and aroyl radicals by decomposition of the corresponding diimides, see ref. 4 and R. Cramer, *J. Am. Chem. Soc.*, **79**, 6215 (1957).

(6) R. A. Clement, *J. Org. Chem.*, **25**, 1724 (1960).

in boiling water to give maleic hydrazide (86% yield) and maleic acid. A mode of decomposition similar to that of eq. 2 was observed by Stollé[7] with certain azo compounds derived from urazoles and was postulated by Cramer[5] in the decomposition of dipropionyldiimide. However, the decomposition of diacyl and diaroyl diimides usually follows a different course.[3,4,8,9]

The rapid hydrolysis of V in boiling water is noteworthy since the corresponding tetrahydro derivative[10] is stable to water. This synthesis of V is also of interest in view of the reported failure to obtain V by methods successful in the preparation of the tetrahydro derivative.[11] The ready hydrolysis of V may account for much of this difficulty. That V represents a strained ring system can also be inferred from the position of the carbonyl stretching frequency in the infrared; see Table II.

When acetone solutions of 1,4-phthalazinedione were brought to room temperature, much less gas evolution occurred than in the case of II, and poly-1,4-phthalazinedione $(IV)_n$ was obtained in 60% yield as an acetone-insoluble white solid. This product, which could not be purified without decomposition, was also obtained in the lead tetraacetate oxidation of phthalhydrazide.[6] To our knowledge polymers of diacyl or diaroyl diimides have not been reported previously. Thermal decomposition of $(IV)_n$ gave 5,6,11,12-tetraketophthalazino[2,3-b]phthalazine[12] (VI) in 66% yield.

$$(IV)_n \xrightarrow[\text{or}]{\Delta} \text{[structure]} + N_2$$

VI
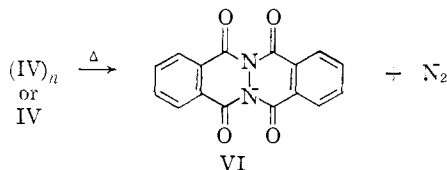
Compound VI was also obtained directly from solid 1,4-phthalazinedione by heating on a steam-bath or when the diazaquinone decomposed exothermically during isolation.

The diazaquinones are very susceptible to attack by water and in the preparation and handling of their solutions it is desirable to exclude atmospheric moisture as much as possible. There is generally sufficient water in reagent grade acetone to, in theory, decompose all or nearly all of the diazaquinone present. However, under these circumstances, attack by water is only of minor importance in the decomposition of II and IV. On the other hand, the decomposition of III appears to proceed exclusively via attack by water.

The reaction of the diazaquinones with water appears to proceed according to eq. 3. Evidence for this stoichiometry was obtained from the decomposition of 1,4-phthalazinedione in which the products isolated accounted for 75% of the total phthalhydrazide salt charged (presumably the remainder did not react). Of the products isolated,
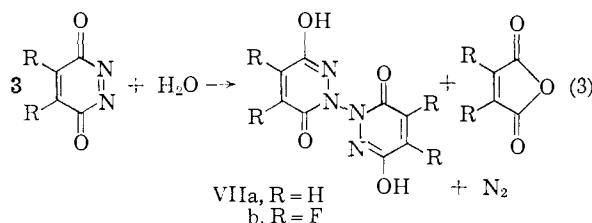
(7) R. Stollé, Chem. Ber., 45, 273 (1912).
(8) R. Stollé and W. Reichert, J. prakt. Chem., 123, 82 (1929).
(9) J. E. Leffler and W. B. Bond, J. Am. Chem. Soc., 78, 335 (1956).
(10) H. Feuer and J. E. Wyman, Chemistry & Industry, 577 (1956).
(11) H. Feuer, E. H. White and J. E. Wyman, J. Am. Chem. Soc., 80, 3790 (1958); H. Feuer and H. Rubinstein, J. Org. Chem., 24, 811 (1959).
(12) H. D. K. Drew and H. H. Hatt, J. Chem. Soc., 16 (1937).

VIIa, R = H
b, R = F

the polymer $(IV)_n$ accounted for 79% of the reacted hydrazide salt; the bishydrazide VIIc accounted for 13% and phthalic anhydride accounted for 8% the quantities of the latter products being in rough agreement with eq. 3. On the other hand,
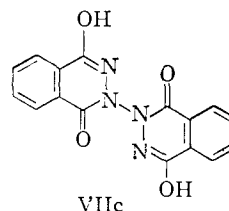
VIIc

in the presence of a large excess of water, 1,4-phthalazinedione afforded no polymer and instead VIIc was obtained in 85% yield according to eq. 3. In the absence of added water 3,6-pyridazinedione gave VIIa in only 6% yield. However, the crude decomposition product obtained from 4,5-difluoro-3,6-pyridazinedione was comprised largely of the bishydrazide VIIb as determined by infrared analysis. Some difluoromaleic acid could also be detected in the product. No evidence was found for the presence of a product analogous to V in this case.

The identification of the bishydrazides VIIa-c rests on the similarity of their solubilities, and their ultraviolet and infrared spectra to those of the corresponding hydrazides. Also, the neutralization equivalents of the bishydrazides were in agreement with the proposed structures.[13]

Poly-1,4-phthalazinedione $(IV)_n$ also affords VIIc when dissolved in hot aqueous dimethylformamide.

The diacyl and diaroyl diimides react with water in a different manner. According to Stollé[7] the reaction is represented by eq. 4.

$$2RCON{=}NCOR + H_2O \longrightarrow$$
$$(RCO)_2N{-}NHCOR + RCOOH + N_2 \quad (4)$$

Reactions with Dienes.—Perhaps the most remarkable property of the diazaquinones is their exceptional reactivity toward dienes. This was noted by Clement[6] in the case of IV, who found that the polymerization of IV could be completely

(13) The alternative structures for VIIa-c
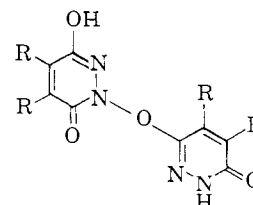
would be monobasic acids and therefore not in agreement with the observed neutralization equivalents; see H. Feuer and H. Rubinstein, J. Am. Chem. Soc., 80, 5874 (1958).

suppressed by forming IV at 0° in the presence of butadiene. We have found that the diazaquinones react rapidly with dienes at −77° which certainly places them in the class of the most reactive of dienophiles. In the case of II, particularly, the reaction with dienes occurs instantaneously on mixing as determined by discharge of the green color.

The usual course of the reaction is the formation of a Diels–Alder adduct by the addition of the diene to the —N=N— bond. In the case of 3,6-pyridazinedione the stable adducts VIIIa,b, IXa,-b and X were obtained from butadiene, 2,3-dimethylbutadiene, cyclopentadiene, cyclohexadiene and coumalic acid, respectively. Adducts obtained from III and IV are described in the Experimental section.
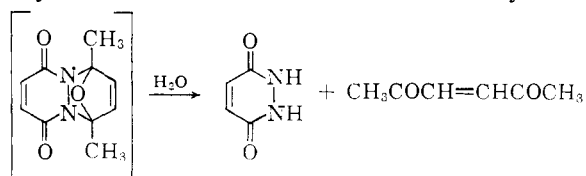

VIIIa, R = H
b, R = CH₃

IXa, n = 1
b, n = 2

X
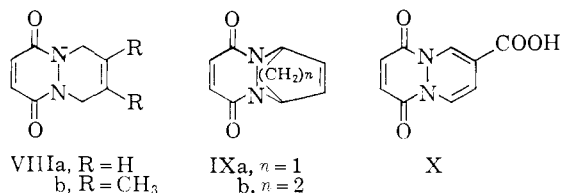
The yields of adducts VIIIa,b and IXa,b were 46–58% while X was obtained in only 15% yield, apparently due to the insolubility of coumalic acid in the solvent. It is certain that in the former cases these do not represent optimum yields since the 3,6-pyridazinedione solutions were prepared under different conditions of time and temperature. The best conditions found for the conversion of maleic hydrazide to 3,6-pyridazinedione were oxidation of the potassium salt at −77° in acetone for 2–3 hours and completion of the reaction at −50 to −55° for 1 hour. This procedure gives 80–85% conversions to 3,6-pyridazinedione.

The structure of the butadiene adduct VIIIa was proved by reduction to the known compounds 1,2-succinoylhexahydropyridazine and 2-butyl-6-hydroxy-3(2H)-pyridazinone.
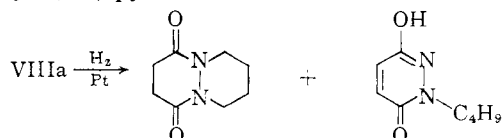

Furan and 2,5-dimethylfuran reacted rapidly with II, but Diels–Alder adducts were not isolated although they may have been formed initially. The product from furan immediately precipitated from solution, but decomposed exothermically when it was isolated. It appears that the adduct from 2,5-dimethylfuran and II is extremely sensitive to water and underwent hydrolysis during isolation to give maleic hydrazide and 1,2-diacetylethylene. Adducts from furans and dialkyl azo-


dicarboxylates have been reported[14]; they have only fair stability and frequently are non-crystalline.

3,6-Pyridazinedione and 6,6-dimethylfulvene gave an adduct in 46% yield which underwent a gradual rearrangement in the solid state to an isomeric product. The infrared spectrum of the adduct as first isolated appeared to be consistent with that expected for the Diels–Alder adduct XI (strong 6.1 μ carbonyl, no evidence of hydrogen bonding in the 3.5 μ region of the spectrum). However, after several days, the product had an infrared spectrum which contained new bands and those due to the original component were weaker. Analysis of the crude product (richer by then in the new component) without purification gave values in rough agreement with a 1:1 adduct. The new component was isolated as an insoluble white solid on treating the enriched product with hot acetone. The infrared spectrum of the new component was not consistent with that expected for a Diels–Alder adduct, but was very similar to the spectra of the hydrazides and bishydrazides in the 3–7 μ region. Thus, the two components were not exo–endo isomers and it was concluded that the new component was probably a substituted hydrazide (XII). Dissolution of either the crude Diels–Alder product,

XII
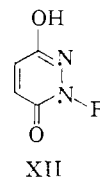
or a sample comprised almost exclusively of XII, in boiling ethanol gave an orange solution. Concentration and cooling of the solution gave an orange, crystalline 1:1 adduct which had an infrared spectrum different from that of either of the other products. Furthermore, this third product was not present initially in either XI or XII. The color and the infrared and ultraviolet spectra of the orange product suggest that it contains a hydrazide and a fulvene moiety; the structure 2-(6,6-dimethylfulven-1-yl)-6-hydroxy-3(2H)-pyridazinone (XIII) is proposed. On the basis of the available evidence it appears that the following transformations occurred
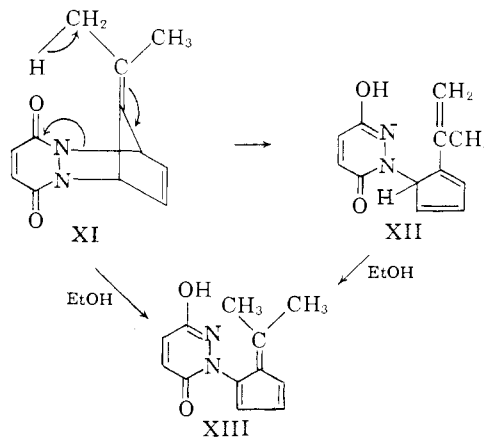
(14) K. Alder, H. Niklas, R. Aumüller and B. Olsen, Ann., 585, 81 (1954); C. W. Huffman, U. S. Patent 2,957,874, October 25, 1960; Yu. K. Yur'ev and N. S. Zefirov, J. Gen. Chem. (USSR), 29, 2916 (1959),

No data are available on whether the rearrangement XI → XII is inter- or intramolecular; however, an intramolecular rearrangement of this type is clearly not possible for endo-XI. The relief of strain and the increase in conjugation would appear to be the driving force for the rearrangement. The transformation XII → XIII is viewed as an allylic shift of hydrogen.[15]

Although N-methyl pyrrole does not undergo the Diels–Alder reaction, it was of interest to determine if such a reaction could be obtained in the presence of a very reactive dienophile at low temperature. The addition of a cold acetone solution of N-methylpyrrole to a solution of 3,6-pyridazinedione at −77° resulted in a very rapid reaction and the precipitation of a yellow solid, isolated in 80% yield, for which structure XIV is proposed. This structural assignment is based on the fact that the product is very insoluble, which

XIV
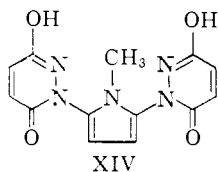
is characteristic of the hydrazides, and on the infrared and ultraviolet spectra of the adduct and its neutralization equivalent which were consistent with structure XIV. This assignment is also consistent with the usual mode of reaction of pyrroles with dienophiles.[16] The reaction of N-methylpyrrole with 3,6-pyridazinedione (II) occurs as rapidly as Diels–Alder reactions of II; XIV is obtained as an instantaneous precipitate even when a solution containing a large excess of N-methylpyrrole is added all at once to a solution of II.

Experimental[17]

Preparation and Decomposition of 3,6-Pyridazinedione in Solution.—The potassium salt of maleic hydrazide was prepared by dissolving 112 g. (1 mole) of maleic hydrazide[18] in a warm solution of 66 g. (1 mole) of ca. 85% potassium hydroxide in 400 ml. of water. The solution was evaporated to dryness under vacuum and the solid was ground to a fine powder and dried in a vacuum oven at 100° for 48 hours to obtain 134 g. of the potassium salt. The sodium salt was prepared in a similar manner using equimolar quantities of base and hydrazide.

To a flask equipped with a low-temperature thermometer, a calcium chloride drying tube and a magnetic stirring bar, and containing a solution of 44 g. (0.40 mole) of t-butyl hypochlorite[19] in 1 l. of reagent grade acetone at −77°

(15) Although the position of the ring methylene hydrogen in XII appears fixed, the known mobility of the methylene hydrogen in cyclopentadiene derivatives would suggest that XII may be better represented as i.

i
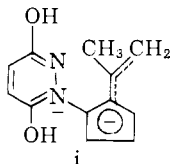
(16) M. C. Kloetzel, "Organic Reactions," Vol. IV, Edited by R. Adams, John Wiley and Sons, Inc., New York, N. Y.. 1948, p. 38.

(17) Melting points are uncorrected. Infrared spectra were measured on a Perkin–Elmer model 21 spectrophotometer; ultraviolet spectra were measured on a Cary model 14 spectrophotometer.

(18) U. S. Rubber Co., Naugatuck. Conn.

(19) H. M. Teeter and E. W. Bell. Org. Syntheses, **32**, 20 (1952).

was added 60 g. (0.40 mole) of the potassium salt of maleic hydrazide. After 3.5 hours at −77° the emerald green reaction mixture was filtered under nitrogen at −77° through a coarse sintered glass filter funnel equipped with a solid carbon dioxide cooling jacket into a filter flask maintained at −77°. The insoluble solid obtained in the filtration (40.8 g., solid A) was a mixture of potassium chloride and unreacted hydrazide salt, and corresponded to a conversion of ca. 63% (the theoretical weight of potassium chloride is 29.8 g.). The green filtrate containing the 3,6-pyridazinedione was allowed to warm to room temperature resulting in decomposition of the diazaquinone. The product was worked up with that obtained in the following experiment.

A stirred suspension of 72 g. (0.48 mole) of the potassium salt of maleic hydrazide and 40 g. of solid A from the previous experiment (containing 0.145 mole of the hydrazide salt) in a solution of 62.3 g. (0.62 mole) of t-butyl hypochlorite in 1.5 l. of acetone was maintained at −77° for 2 hours and at −50 to −55° for 1 hour. The reaction mixture on filtration at −77° afforded 72 g. of insoluble salts, corresponding to a conversion of 84%, and a deep green filtrate. The stirred filtrate was allowed to warm to room temperature slowly and at a bath temperature of ca. −30° considerable gas evolution was noted as the color of the solution faded and a yellow solid precipitated. The suspension was concentrated under vacuum to a small volume and was filtered to obtain 33.6 g. of crude 1,4,6,9-tetraketopyridazino(1,2-a)pyridazine (V) and filtrate B. This solid product together with that of the previous experiment (11.4 g.) and 3 g. from another experiment was extracted with acetone in a Soxhlet apparatus to obtain 33.5 g. (ca. 43% yield) of the acetone-soluble, yellow product V. The acetone-insoluble bishydrazide VIIa (7.5 g., ca. 6% yield) was obtained from the Soxhlet thimble and was found by infrared analysis to be contaminated with a small amount of maleic hydrazide.

1,4,6,9-Tetraketopyridazino(1,2-a)pyridazine (V) was purified for analysis by several recrystallizations from acetone to obtain yellow needles which decomposed gradually above ca. 160° in a melting point capillary; m.p. 247° (Maquenne block).

Anal. Calcd. for $C_8H_4N_2O_4$: C, 50.01; H, 2.10; N, 14.58. Found: C, 50.18; H, 2.32; N, 14.16.

Filtrate B, obtained in the isolation of crude V, on standing for several weeks exposed to the atmosphere, deposited 11.7 g. of maleic hydrazide, and, on further standing, 7.4 g. of maleic acid which were identified by infrared analysis. It appears likely, in view of the insolubility of maleic hydrazide, that these products were formed by the gradual hydrolysis of residual V.

Heating an aqueous suspension of 1 g. of V in 10 ml. of water at reflux for several minutes resulted in dissolution of V followed by the precipitation of maleic hydrazide at the boiling point (0.50 g., 86% yield). After removal of the hydrazide by filtration, concentration of the filtrate to dryness afforded 0.53 g. of maleic acid (containing a small amount of hydrazide) which was identified by infrared analysis.

The bishydrazide, 2,2'-bis-(6-hydroxy-3(2H)-pyridazinone) (VIIa), was purified for analysis by dissolution in base followed by precipitation with acid; m.p. 229° dec.

Anal. Calcd. for $C_8H_6N_4O_4$: C, 43.25; H, 2.72; N, 25.22; neut. equiv., 111. Found: C, 43.14; H, 2.91; N, 25.01; neut. equiv., 112.5.

The infrared spectrum of VIIa was very similar to that of maleic hydrazide but could easily be distinguished from the latter by the absence of a band at 9.9μ in the spectrum of VIIa and by a shift in the frequency of the carbonyl band; see Table II.

Difluoromaleic Hydrazide.—To 60 ml. of glacial acetic acid cooled in an ice-bath was added dropwise 17.4 g. (0.348 mole) of 100% hydrazine hydrate. This solution was then added dropwise during 15 minutes to a solution of 46.5 g. (0.348 mole) of difluoromaleic anhydride[20] in 100 ml. of glacial acetic acid to give a white precipitate. The reaction mixture was heated to reflux causing dissolution of the solid and then precipitation of the hydrazide. After 1 hour at reflux the mixture was cooled and filtered. The hydrazide, after being washed with a little water, amounted to 33 g.

(20) M. S. Raasch, R. E. Miegel and J. E. Castle, *J. Am. Chem. Soc.*, **81**, 2678 (1959).

(64% yield) and was found to be of high purity. Concentration of the filtrate did not afford additional hydrazide. For analysis, a portion of the difluoromaleic hydrazide was recrystallized several times from glacial acetic acid; white needles, m.p. 258° dec.

Anal. Calcd. for $C_4H_2F_2N_2O_2$: C, 32.44; H, 1.36; N, 18.92; neut. equiv., 148. Found: C, 32.61; H, 1.65; N, 18.48, 18.79; neut. equiv., 146.

Preparation and Decomposition of 4,5-Difluoro-3,6-pyridazinedione in Solution.—For the preparation of this diazaquinone the sodium salt of the hydrazide is preferred with acetone as the reaction medium. A suspension of the sodium salt of difluoromaleic hydrazide (0.0233 mole) in a solution of 2.53 g. (0.0233 mole) of *t*-butyl hypochlorite in 125 ml. of reagent grade acetone was stirred and protected from atmospheric moisture during a reaction time of 2 hours at −50 to −55° and was then filtered at −77° under nitrogen to obtain a 4,5-difluoro-3,6-pyridazinedione solution. On warming the solution to room temperature a colorless turbid mixture was obtained. Evaporation of the suspension to dryness afforded 3.0 g. of white solid comprised of 2,2′-bis-(6-hydroxy-4,5-difluoro-3(2H)-pyridazinone) (VIIb), containing difluoromaleic acid as determined by infrared analysis. The bishydrazide was purified for analysis by several recrystallizations from acetone-chloroform; m.p. gradual above 225° with decomposition.

Anal. Calcd. for $C_8H_2F_4N_4O_4$: C, 32.65; H, 0.68; N, 19.05; neut. equiv., 147. Found: C, 33.06; H, 1.08; N, 19.56, 19.64; neut. equiv., 143.

Preparation and Decomposition of 1,4-Phthalazinedione in Solution. A. In the Absence of Added Water.—The sodium salt of phthalhydrazide was prepared by dissolving 32.4 g. (0.2 mole) of phthalhydrazide[12] in a boiling solution of 8 g. (0.2 mole) of sodium hydroxide in 200 ml. of water. The solution was evaporated to dryness under vacuum and the solid was dried under an infrared lamp to obtain 34 g. of sodium salt which was ground to a fine powder.

To a solution of 4.34 g. (0.04 mole) of *t*-butyl hypochlorite in 150 ml. of reagent grade acetone contained in a flask equipped with a calcium chloride drying tube, a low-temperature thermometer and a magnetic stirring bar, and cooled in an acetone–solid carbon dioxide-bath, was added 7.26 g. (0.04 mole) of the sodium salt of phthalhydrazide. After 2.5 hours at −50 to −55°, the emerald green reaction mixture was cooled to −77° and filtered under nitrogen to obtain a clear green solution of 1,4-phthalazinedione.

Warming of the diazaquinone solution resulted in the precipitation of a white solid which gradually developed a transient salmon color. Little gas evolution was noted. After standing overnight at room temperature, the pale yellow mixture was filtered to obtain 3.8 g. (60% yield) of white solid believed to be poly-1,4-phthalazinedione, $(IV)_n$.[21] The product was insoluble in most common organic solvents. A portion of the product was washed with water and acetone, and dried at 66° under vacuum over phosphorus pentoxide for analysis.

Anal. Calcd. for $C_{16}H_8N_4O_4$: C, 60.00; H, 2.52; N, 17.50. Found: C, 58.92; H, 3.12; N, 16.13, 16.38.

The infrared spectrum of the analytical sample was indistinguishable from that of the crude product. The polymer was insoluble in, and unaffected by, hot water over a short heating period, but it dissolved in cold aqueous sodium hydroxide with gas evolution. Dissolution of 1 g. of $(IV)_n$ in a little hot aqueous dimethylformamide followed by cooling afforded 0.25 g. of 3,3′-bis-(1-hydroxy-4(3H)-phthalazinone) (VIIc) which was identified by infrared analysis; see section B. The melting point of the polymer varied with the rate of heating. On slow heating in a melting point capillary, the polymer melted reproducibly at 195° with gas evolution and then solidified to a yellow solid identified as VI; *vide infra*. When placed in a melting point block preheated to *ca.* 150° or higher, the polymer decomposed suddenly to give the same yellow solid splattered on the walls of the capillary.

Concentration to dryness of the filtrate from the isolation of $(IV)_n$ afforded 1.1 g. of white solid. Sublimation of the solid at 110° under vacuum afforded 0.35 g. (6% yield) of phthalic anhydride as a white crystalline sublimate and a

residue of 0.65 g. (10% yield) of 3,3′-bis-(1-hydroxy-4(3H)-phthalazinone) (VIIc) which were identified by comparative infrared analysis; see section B.

B. In the Presence of Added Water.—The reaction of 18.4 g. (0.1 mole) of the sodium salt of phthalhydrazide and 10.8 g. (0.1 mole) of *t*-butyl hypochlorite in 400 ml. of acetone was carried out as in section A except that 8 ml. (0.44 mole) of water was also added. The filtered reaction mixture was allowed to warm and to stand overnight at room temperature. Concentration of the suspension thus obtained afforded 6.3 g. of 3,3′-bis-(1-hydroxy-4(3H)-phthalazinone) (VIIc). Concentration of the filtrate almost to dryness gave additional VIIc which was purified by dissolution in aqueous sodium hydroxide followed by precipitation with acid to obtain 2.8 g. of VIIc; total yield 9.1 g., 85%. Dissolution of the total product in aqueous sodium hydroxide followed by acidification of the solution with dilute hydrochloric acid afforded 8.3 g. of pure VIIc. An analytical sample of VIIc was prepared by two recrystallization from dimethyl sulfoxide to obtain an amorphous looking white solid which was washed with acetone and dried under vacuum.

Anal. Calcd. for $C_{16}H_{10}N_4O_4$: C, 59.63; H, 3.13; N, 17.39; neut. equiv., 161. Found: C, 59.48, 59.19; H, 3.46, 3.56; N, 17.11, 17.18; neut. equiv., 161.

The melting point of VIIc varied with the rate of heating; most samples decomposed sharply in the range 215–222°. The infrared spectrum of VIIc was similar to, but clearly distinguishable from, that of phthalhydrazide.

Isolation and Decomposition of Solid 1,4-Phthalazinedione (IV).—A solution of 1,4-phthalazinedione was prepared by the reaction of 4.6 g. (0.025 mole) of the sodium salt of phthalhydrazide with 2.7 g. (0.025 mole) of *t*-butyl hypochlorite in 50 ml. of acetone for 2 hours at −50 to −65°. During this time the reaction mixture was not protected from atmospheric moisture. The reaction mixture was cooled to −77° and filtered under nitrogen. A small amount of IV, as green needles, was noted in the filter cake indicating that insufficient solvent was used. Precooled trichloroethylene (30 ml.) was added to approximately one-half of the filtrate at −77° and caused the precipitation of IV. The suspension was filtered cold under nitrogen to obtain IV as a crystalline green solid.

Anal. Calcd. for $C_8H_4N_2O_2$: C, 60.00; H, 2.52; N, 17.50. Found: C, 60.21; H, 2.83; N, 16.20, 16.00.

The infrared spectrum (Nujol) of this sample showed carbonyl absorption at 5.85 μ, assigned to 1,4-phthalazinedione and also contained bands at 5.4, 5.65 μ and at longer wave length indicative of the presence of some phthalic anhydride impurity. On the basis of the nitrogen and infrared analysis, IV was isolated in 92% purity; the contaminant being phthalic anhydride. The infrared spectrum of the product indicated the absence of VIIc. In other experiments it was observed that, when water was not excluded as much as possible during the preparation and isolation of IV, the product was lighter in color and contained substantial amounts of both decomposition products phthalic anhydride and VIIc.

1,4-Phthalazinedione was also isolated by evaporation of its solutions under vacuum. A solution of IV was prepared by the reaction of 9.2 g. (0.05 mole) of the sodium salt of phthalhydrazide with 5.7 g. (0.053 mole) of *t*-butyl hypochlorite in 125 ml. of reagent grade acetone at −55 to −65° for 1.7 hours. During this time the reaction mixture was protected from atmospheric moisture by means of a calcium chloride tube. The reaction mixture was filtered at −77° and the filtrate evaporated at a pressure of <1 mm. and at a gradually increasing temperature during 8 hours. Compound IV was obtained as a crystalline green solid which contained small areas that had partially faded. After several minutes at room temperature, the product suddenly decomposed exothermically to give 3.5 g. of tan solid identified by infrared analysis as 5,6,11,12-tetraketo-phthalazino[2,3-b]phthalazine (VI), containing a small amount of phthalic anhydride. The phthalazino-phthal-azine(VI) was purified by recrystallization from dimethyl-formamide to obtain pale yellow crystals which did not have a sharp melting point but which decomposed gradually above 300°, particularly above 337°; reported[12] m.p. 350–360° dec. The combustion analysis of the product was consistent with this structure.

(21) The X-ray diffraction pattern of $(IV)_n$ indicated that the product was polymeric and contained a small amount of sodium chlorid impurity.

The thermal decomposition of poly-1,4-phthalazinedione also affords VI. A 1.0-g. sample of the polymer in an open flask was gradually heated in an oil-bath. At a bath temperature of 133° the solid suddenly decomposed. The product amounted to 0.6 g. (66% yield) of 5,6,11,12-tetraketophthalazino[2,3-b]phthalazine (VI) which was identified by comparative infrared analysis. A small amount of phthalic anhydride was also detectable in the infrared spectrum of the crude product.

1,4-Phthalazinedione may also be prepared in dimethyl ether, a solvent which is easily removed at low temperature under vacuum. The reaction of 4.6 g. (0.025 mole) of the sodium salt of phthalhydrazide with 2.7 g. (0.025 mole) of t-butyl hypochlorite in 50 ml. of dimethyl ether at −55 to −65° for 2.5 hours afforded a deep green reaction mixture containing some precipitated 1,4-phthalazinedione indicating that insufficient solvent was used. The reaction mixture was filtered at −77° under nitrogen and the solvent was evaporated from the filtrate at low pressure and temperature to obtain a solid green residue after 0.75 hour. In order to remove residual t-butyl alcohol, the solid was treated with 50 ml. of cold methylene chloride and the suspension was filtered at −77° under nitrogen. The filter cake was isolated from the filtrate by means of a stopcock and the solid was allowed to warm while being dried under vacuum. During this operation the 1,4-phthalazinedione decomposed (apparently due to a leak in the system which prevented the effective removal of solvent) to give 0.85 g. of VI which was identified by infrared analysis.

Solid 1,4-phthalazinedione when heated on a steam-bath suddenly decomposed to give VI. The diazaquinone also decomposed gradually on storage at room temperature to give a white solid comprised of phthalic anhydride and 3,3'-bis-(1-hydroxy-4(3H)-phthalazinone) (VIIc). It appears that the latter decomposition is the result of gradual attack by atmospheric moisture.

Diazaquinone Diels–Alder Adducts.—Diels–Alder adducts obtained from the diazaquinones are given in Table I. In most cases, the reactions were carried out by adding a precooled acetone solution of the diene to the diazaquinone solution at −77° resulting in instantaneous discharge of the green color. The adducts were usually isolated by filtration of the cold reaction mixtures.

Reduction of 1,2-Maleyl-1,2,3,6-tetrahydropyridazine (VIIIa).—A suspension of 1.64 g. of VIIIa in 100 ml. of ethanol containing a platinum oxide catalyst was shaken in a Parr apparatus for 3.5 hours under an initial hydrogen pressure of 27 lb., additional hydrogen being supplied as needed. The reaction mixture was filtered free of catalyst and the filtrate was evaporated to dryness to obtain a white solid having a wide melting point range. The solid was recrystallized from carbon tetrachloride to obtain large white needles (0.8 g., m.p. 167–169°) and a white powder (0.25 g., m.p. <160°) which were separated mechanically. Recrystallization of the needles from carbon tetrachloride afforded 0.4 g. of 1,2-succinoylhexahydropyridazine[22a,b] as white needles, m.p. 174–177°, having an infrared spectrum identical to that of the product, m.p. 174–177°, obtained by the method of Hinman and Landborg. Recrystallization of the powder from carbon tetrachloride afforded 0.15 g. of 2-butyl-6-hydroxy-3(2H)-pyridazinone[23] as microcrystals, m.p. 121.5–122°, reported m.p. 125–126°. The identity of this compound was established by analysis and also by its ultraviolet spectrum λ_{max}^{EtOH} 318 mμ, ϵ 3160) which agreed well with that reported[23]; λ_{max}^{EtOH} 318 mμ, ϵ 3310).

Reaction of 3,6-Pyridazinedione (II) with 2,5-Dimethylfuran.—A solution of II was prepared by the reaction of 6.7 g. (0.05 mole) of the sodium salt of maleic hydrazide and 5.4 g. (0.05 mole) of t-butyl hypochlorite in 100 ml. of acetone at −50° for 1.5 hours. To the filtered reaction mixture was added a cold solution of 4.8 g. (0.05 mole) of 2,5-dimethylfuran in 20 ml. of acetone with immediate discharge of the green color on mixing. After two hours at −77° some white crystals had separated. The suspension was filtered cold (exposed to the atmosphere) to obtain 4.8 g. of white solid which developed a tan color on standing. Sublimation of the solid afforded 1.9 g. (34% yield) of white crystalline sublimate, m.p. 75.5–77.5°, whose analysis,

(22) (a) H. Stetter and H. Spangenberger, *Chem. Ber.*, **91**, 1982 (1958); (b) R. L. Hinman and R. J. Landborg, *J. Org. Chem.*, **24**, 724 (1959).

(23) H. Feuer and R. Harmetz, *J. Am. Chem. Soc.*, **80**, 5877 (1958).

TABLE I

PREPARATION OF DIAZAQUINONES AND THEIR DIELS–ALDER ADDUCTS

Diaza-quinone	Diene, mole	Hydrazide salt, mole	t-BuOCl, mole	CH₃CO-CH₃, ml.	Time, hr.	Temp., °C.	Yield, %	M.p. and recrystn. solvent	Formula	Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Nitrogen, % Calcd. Found
II	Butadiene	Sodium, 0.1	0.1	200	1.5	−50	58	157–159 benzene	$C_8H_8N_2O_2$	58.53 58.45	4.91 5.38	17.07 16.92 / 16.84
II	2,3-Dimethylbutadiene, 0.15	Sodium,[a] 0.15	.15	300	1.5	−50	46	153–159 d.[b] acetone	$C_{10}H_{12}N_2O_2$	62.48 62.02	6.29 6.26	14.58 14.43 / 14.49
II	Cyclopentadiene, 0.15	Potassium,[c] 0.13	.15	200	1.5	−77	58	183–184 CHCl₃–acetone	$C_9H_8N_2O_2$	61.36 61.46	4.58 5.01	15.90 15.83 / 15.93
II	1,3-Cyclohexadiene, 0.047	Potassium,[c] 0.044	.05	125	2.5	−77	58	212–214.5 benzene	$C_{10}H_{10}N_2O_2$	63.15 63.59	5.30 5.36	14.73 14.87
II	Coumalic acid, 0.05	Potassium,[c] 0.052	.05	125	2.5	−77	15[d]	233 d.[e] water	$C_9H_6N_2O_4$	52.43 52.37	2.93 3.19	13.59 13.21
III	2,3-Dimethylbutadiene, 0.037	Sodium,[a] 0.025	.025	125	2	−50 to −55	63	222.5–224 d. ethanol–benzene	$C_{10}H_{10}F_2N_2O_2$	52.61 52.77	4.42 4.46	12.28 12.13 / 12.37
IV	Butadiene	Sodium, 0.05	.05	100	4 1.5	−70 to −77 −45 to −65	f	263–268 d. acetone–CHCl₃	$C_{12}H_{10}N_2O_2$	67.28 67.29	4.71 4.96	13.08 13.29
IV	2,3-Dimethylbutadiene, 0.025	Sodium, 0.05	.056	150	1.5	−60 to −77	~50	200[e] acetone	$C_{14}H_{14}N_2O_2$	69.40 69.49	5.83 5.82	11.56 11.48

[a] Salt was not oven dried. [b] Melted on a Maquenne block at 161°. [c] Ref. 25. [d] The reactants were mixed at −77° and stirred for 2 hours. After standing overnight at room temperature, the suspension was filtered and the solid was dissolved in aq. sodium carbonate. Acidification of the solution with gl. acetic acid gave the crude product as red-orange crystals. [e] On a Maquenne block. [f] The addition of 500 ml. of cold chloroform to the diazaquinone solution caused the precipitation of IV, which was removed by filtration. The addition of butadiene to the filtrate afforded 2.1 g. of adduct; reported[6] m.p. 272–275° dec.

infrared spectrum and melting point were consistent with those for 1,2-diacetylethylene; reported[24] m.p. 75–76°. The residue from the sublimation (2.4 g., 43% yield) was identified as maleic hydrazide by infrared analysis.

Reaction of 3,6-Pyridazinedione with Furan.—The addition of a cold acetone solution of furan to an acetone solution of II at −77° caused the immediate precipitation of a cream colored solid. The isolated solid decomposed after a few minutes with considerable heat evolution to give a carbonaceous product. A small amount of solid remaining in the filter funnel did not undergo this sudden exothermic decomposition (but may have otherwise decomposed) and without further purification gave analytical values reasonably close to those expected for a 1:1 3,6-pyridazinedione-furan adduct. The infrared spectrum of this solid showed evidence of hydrogen bonding in the 3 μ region and contained a carbonyl band at 5.97μ and thus was not consistent with that expected for a Diels–Alder adduct of II.

Anal. Calcd. for $C_8H_6N_2O_3$: C, 53.93; H, 3.40; N, 15.73. Found: C, 52.15; H, 4.10; N, 14.78.

2,5-Bis-(6-hydroxy-3(2H)-pyridazinone-2-yl)-N-methylpyrrole (XIV).—3,6-Pyridazinedione was prepared by the reaction of 17 g. (0.1 mole)[25] of the potassium salt of maleic hydrazide with 10.8 g. (0.1 mole) of *t*-butyl hypochlorite in 300 ml. of acetone at −77° for 3.5 hours and at −50° for 1 hour. The reaction mixture was filtered at −77° under nitrogen and to the magnetically stirred filtrate at −77° was added dropwise a cold solution of 4.0 g. (0.05 mole) of N-methylpyrrole in 25 ml. of acetone. When the addition was complete (5–10 minutes), the green color of the reaction mixture was entirely discharged to give a yellow suspension. The cold reaction mixture was filtered to obtain 12.05 g. (80% yield) of 2,5-bis-(6-hydroxy-3(2H)-pyridazinone-2-yl)-N-methylpyrrole (XIV). The adduct was purified by dissolution in aqueous sodium hydroxide followed by precipitation with glacial acetic acid to obtain 9.8 g. of XIV as pale yellow microcrystals which darkened but did not melt up to 315°. For analysis, the product was purified several times by this procedure.

Anal. Calcd. for $C_{13}H_{11}N_5O_4$: C, 51.83; H, 3.68; N, 23.25; neut. equiv., 151. Found: C, 51.65; H, 3.96; N, 22.75, 22.85; neut. equiv., 154 (potentiometric).

2-(6,6-Dimethylfulven-1-yl)-6-hydroxy-3(2H)-pyridazinone (XIII).—A solution of II was prepared by the reaction of 6.7 g. (0.05 mole) of the sodium salt of maleic hydrazide with 5.4 g. (0.05 mole) of *t*-butyl hypochlorite in 100 ml. of acetone at −50° for 1.5 hours. The reaction mixture was filtered at −77° and to the filtrate was added a cold solution of 5.3 g. (0.05 mole) of 6,6-dimethylfulvene[26] in 20 ml. of acetone. The green color of the diazaquinone solution was discharged immediately upon mixing the two solutions. After standing overnight at −77°, the reaction mixture was filtered to obtain 5.0 g. (46% yield based on the 1:1 adduct) of pale yellow solid XI, which did not have a definite melting point but decomposed gradually above 200°. A 2.3-g. portion of the crude product was dissolved in boiling ethanol and the solution was concentrated to a small volume with the development of an orange color. On cooling the solution, 1.1 g. (*ca.* 50% conversion) of 2-(6,6-dimethylfulven-1-yl)-6-hydroxy-3(2H)-pyridazinone (XIII) was obtained as orange crystals, m.p. 213–215° dec. The infrared spectra of XIII and the crude product established that XIII was not present in the product initially and therefore was formed during the attempted recrystallization. Recrystallization of XIII from alcohol gave orange prisms, m.p. 218° dec.

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.91, 66.88; H, 5.84, 5.67; N, 12.55, 12.80.

The infrared spectrum of crude product XI as first isolated contained a carbonyl band at 6.1μ as the strongest band in the spectrum in good agreement with the spectra of other Diels–Alder adducts of II. However, on standing 4 days XI had an infrared spectrum which contained new bands and when the product was then boiled with acetone some white insoluble solid could be isolated whose infrared

(24) G. O. Schenck, *Chem. Ber.*, **77**, 661 (1944).

(25) The salt inadvertently contained *ca.* 12% by weight of maleic hydrazide because insufficient potassium hydroxide was used in the preparation. The molar amount of salt is correct and yields are based on the quantity of salt present.

(26) J. Thiele, *Chem. Ber.*, **33**, 666 (1900).

TABLE II

SPECTRA OF DIAZAQUINONE PRODUCTS AND PRECURSORS

Compound Diels–Alder adducts	λ_{max}^{EtOH}, mμ	ε	λ_{max}^{KBr} (carbonyl), μ
VIIIa	337	2,050	6.1
	215	13,900	
VIIIb	338	2,800	6.1
	216	13,840	
IXa	340	3,020	6.0, 6.05
	215	15,800	
IXb	345	3,440	6.15
	217	15,200	
X			6.15 > 5.8 > 5.93
A[a]	304	4,730	6.1
	245(sh)	7,460	
	237	10,750	
	215	42,600	
B[b]			6.1 > 5.85[c]
Hydrazides			
VIIa	318	5,560	5.95, 6.0(sh)[a]
C[e]	318	3,160	6.0[d]
XIII	325[f]	3,175	6.05, 6.1[d]
	273	15,780	
XIV	337[g]	6,325	6.0[d]
	210	28,900	
VII[c]	295	11,900	5.97, 6.03[d]
	261	8,700	
	254	9,025	
	229	30,300	
	210	87,000	
D[h]			6.2 > 5.85[c]
VIIb			6.05 > 5.9[c]
E[i]			6.05 (medium)[d]
F[j]			6.02 (strong)[d]
Other products			
V	357[k]	3,150	5.75 > 5.9[l]
	230	12,200	
VI	332[k]	6,140	5.75 > 5.70 > 5.90 > 6.0
	304	6,430	
	253(sh)	18,700	
	229	48,800	
IV			5.85
(IV)ₙ	290	5,120	5.78, 5.82[m]
	263(sh)	4,480	
	252(sh)	5,120	
	235(sh)	17,000	
	227(sh)	20,200	

[a] A is 1,4-dihydropyridazino[1,2-b]phthalazine-6,11-dione (from IV and butadiene). [b] B is 2,3-difluoro-7,8-dimethyl-6,9-dihydropyridazino[1,2-a]pyridazine-1,4-dione (from III and 2,3-dimethylbutadiene). [c] These bands have not been assigned. [d] Carbonyl weaker than double bond absorption. [e] C is 2-butyl-6-hydroxy-3(2H)pyridazinone. [f] 6,6-Dimethylfulvene $\lambda_{max}^{i-octane}$ 270 mμ, ε 8,500. [g] N-Methylpyrrole λ_{max}^{EtOH} 215 mμ, 7,150. [h] D is difluoromaleic hydrazide. [i] E is maleic hydrazide. [j] F is phthalhydrazide. [k] $\lambda_{max}^{CH_3CN}$ [l] Tetrahydro-1,4,6,9-tetraketopyridazino[1,2-a]pyridazine, λ_{max}^{KBr} 5.75 μ. [m] λ_{max}^{Nujol}.

spectrum showed weak absorption at 6.0 μ and no band at 6.1 μ. In addition, the infrared spectrum of the new component (XII) showed evidence of strong hydrogen bonding in the 3μ region and over-all was very similar to that of XIII. Analysis of the crude initial product comprised by then of both XI and XII, without purification gave values in approximate agreement with a 1:1 product derived from II and 6,6-dimethylfulvene.

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 64.01; H, 5.90; N, 12.28.

In another experiment, the crude product as first iso-

lated was composed of XII and a lesser amount of XI. This product on standing for several weeks became enriched in XII and bands due to XI were then barely detectable in the infrared spectrum. Dissolution of this enriched product in refluxing ethanol followed by concentration and cooling of the solution afforded XIII in *ca.* 30% yield.


The Carbanion Mechanism for *cis*-Elimination Reactions

BY JACK HINE[1] AND O. BERTRAND RAMSAY

The kinetics of the sodium hydroxide-catalyzed deuterium exchange of *cis*-2-methoxycyclohexyl *p*-tolyl sulfone and the dehydrofluorination of *cis*-2-fluorocyclohexyl *p*-tolyl sulfone have been studied. The Taft substituent constant (σ^*) for the *p*-toluenesulfonoxymethyl group has been determined by measurements of the acidity of *p*-toluenesulfonoxyacetic acid. By use of a Taft equation correlation it is shown that, contrary to a previous estimate, the reaction of *trans*-2-*p*-toluenesulfonylcyclohexyl *p*-toluenesulfonate with sodium hydroxide (a *cis* elimination) is *not* too fast for carbanion formation to be a plausible intermediate step.

In previous papers from this Laboratory, our knowledge of β-elimination reactions that proceed *via* intermediate carbanions has been reviewed and additional reactions of this type have been described.[2,3] The present paper describes evidence that the *cis*-elimination reactions of certain β-substituted sulfones described in an important series of papers by Bordwell, Pearson and their co-workers[4-7] also proceed *via* intermediate carbanions.

In both the cyclohexane and cyclopentane series the *cis* isomers of the 2-*p*-toluenesulfonyl 1-*p*-toluenesulfonates react with base to yield the α,β-unsaturated sulfone (by *trans* elimination) much faster than the *trans* isomers do (by *cis* elimination).[4,5] The rate of *cis* elimination by the base
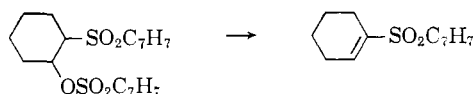
piperidine was found (in the cyclohexane series) to be unaffected by the addition of piperidine hydrochloride.[5] From these observations it seems clear that the *trans* eliminations are concerted reactions and that even the *cis* eliminations do not involve the *reversible* formation of intermediate carbanions. To rule out the possibility of the formation of an intermediate carbanion that is almost invariably transformed to the final product, a reactivity argument, the strongest type of evidence that could be brought in at this point, was then used. The rate at which hydroxide ions form α,β-unsaturated sulfone from *trans*-2-*p*-toluenesulfonylcyclohexyl *p*-toluenesulfonate is about 84,500 times the rate at which hydroxide ions form carbanions (as measured by the rate of deuterium exchange) from 1-deuteriocyclohexyl *p*-tolyl sulfone.[7] Assuming that the inductive effect of a *p*-toluenesulfonoxy (tosyloxy) group is about the same as that of a chlorine atom, it was argued, from data on the

effects of α-chloro substituents on the rates of carbanion formation of acetone and nitroethane, that a β-tosyloxy substituent (and a deuterium kinetic isotope effect) could not increase the rate of carbanion formation by more than 100-fold and certainly not by so much as the 84,500-fold increase that must be postulated if the carbanion mechanism is operative for the *cis* elimination.[7] Therefore the *cis* elimination was held to be a concerted rather than a stepwise process.

We noticed that another method of estimating the effect of a β-tosyloxy group on the rate of carbanion formation gives much different results. From the ionization constants of acetic and chloroacetic acids[8] (for the moment we are approximating the inductive effect of tosyloxy as that of chlorine) the chloro substituent is seen to increase the acidity of a hydrogen three atoms away by $10^{1.9}$. Since inductive substituent effects usually increase by around 2.8-fold (when expressed logarithmically) for every atom the substituent is moved closer to the reaction center,[9] a β-chloro substituent might increase the acidity of a hydrogen atom by $10^{5.3}$. In a rate process in which an unstable reactive intermediate is formed the transition state should resemble the intermediate closely, and therefore the effect of substituents on the rate constant should be almost as large as on the equilibrium constant.[10] According to this argument the formation of unsaturated sulfone from the 2-tosylcyclohexyl tosylate is *not* unreasonably fast for a reaction involving rate-controlling carbanion formation.

In order to resolve this disagreement between two methods of predicting the rate constant to be expected for carbanion formation from 2-tosylcyclohexyl tosylate, we decided to determine the rate of carbanion formation of a *p*-tolyl cyclohexyl sulfone in which the cyclohexyl group contained a β-substituent that was electron-withdrawing but that was not so easily lost as an anion as to make base-catalyzed deuterium exchange at the α-position unobservable. Then by determining the Taft substituent constant for the tosyloxy group

(1) Alfred P. Sloan Foundation Fellow. 1956–1960.

(2) J. Hine and L. A. Kaplan, *J. Am. Chem. Soc.*, **82**, 2915 (1960).

(3) J. Hine, R. Wiesboeck and O. B. Ramsay, *ibid.*, **83**, 1222 (1961).

(4) F. G. Bordwell and R. J. Kern. *ibid.*, **77**, 1141 (1955).

(5) J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3468, 3473 (1956).

(6) F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957).

(7) J. Weinstock, J. L. Bernardi and R. G. Pearson, *ibid.*, **80**, 4961 (1958).

(8) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939).

(9) R. W. Taft, Jr., in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 592.

(10) *Cf.* J. E. Leffler, *Science*, **117**, 340 (1953); G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).