Time, min.	IO_4^- cons.,[a] equiv.	HCO_2H lib.,[a] equiv.
5	1.74	
60	1.81	0.04
360	1.82	.15
1440	1.82	.17

[a] Standardization runs were conducted with mannitol and with I. In each case the oxidation was almost complete in 5 minutes and essentially complete in 1 hour. In no case was more than 90% of the theoretical value obtained.

Ring structure	2, 6	3, 6	4, 6
Equiv. IO_4^- required	2	2	2
Equiv. HCO_2H expected	1	0	1

NEWARK, DELAWARE

[CONTRIBUTION FROM THE R. B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Reactions of Maleic Anhydride with Hydrazine Hydrate[1]

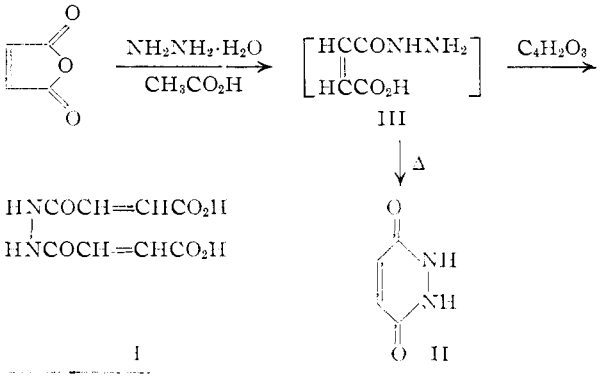
BY HENRY FEUER, EMIL H. WHITE AND JOHN E. WYMAN[2]

RECEIVED FEBRUARY 21, 1958

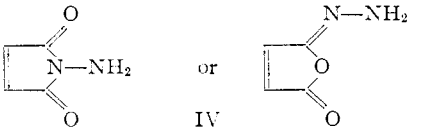
Depending on the conditions employed, maleic anhydride and hydrazine hydrate react to give 1,2-dimaleic acid hydrazine (I), maleic hydrazide, (1,2-dihydro-3,6-pyridazinedione) (II) and a yellow colored complex mixture which contains a small amount of I. Compound I was converted by hydrogenation to the known 1,2-disuccinic acid hydrazine and by refluxing in water to II.

In 1951, we reported the reactions of succinic anhydride with hydrazine hydrate.[3] Since then, we have investigated the reactions of maleic anhydride with hydrazine hydrate, and have found that they differ in some respects from those of succinic anhydride. The differences, however, can be accounted for by the facile ring closures that occur in the maleic acid series.

When hydrazine hydrate is added to two moles of maleic anhydride dissolved in acetic acid, 1,2-dimaleic acid hydrazine (I) is formed in good yield. Hydrogenation of I yields the known 1,2-disuccinic acid hydrazine.[3] When an equimolar mixture of maleic anhydride and hydrazine hydrate is heated in acetic acid, an excellent yield of maleic hydrazide[4] (II) is obtained. Maleic monohydrazide (III) is a likely intermediate in the formation of both I and II.



A similar procedure for the synthesis of II was reported recently by Hinterbauer.[5] The author reported the formation of a yellow intermediate which he considered to be N-aminomaleimide (IV).[6] We have repeated his directions and have found instead that under the conditions used (hydrazine hydrate added to the anhydride), the yellow intermediate is the linear hydrazide I. At higher temperatures, I is converted into II and maleic acid, a reaction that occurs even in a water solution (*vide infra*). The structure of IV was not established by Curtius[6] and we have not obtained it in any of our reactions.



When maleic anhydride and hydrazine hydrate are mixed in ether or in alcohol solvents, a canary yellow precipitate forms; this reaction was first reported by Curtius.[6] Our evidence indicates that the solid is a mixture of products. The infrared spectrum of a sample in a potassium bromide pellet had a moderately strong band centered at 5.90 μ (characteristic of –CON– groups) and an intense broad band at 6.40 μ ($-CO_2^-$ group). Most of the solid was soluble in water; the insoluble part was largely the linear hydrazide I. Some of the solid could be recrystallized with difficulty from methanol, and its elemental analysis agreed with maleic monohydrazide (III). When the solid was refluxed in methanol with maleic anhydride, two compounds were obtained, the linear hydrazide I and maleic hydrazide (II).

Treatment of the aqueous solution of the yellow precipitate with benzaldehyde yielded benzalazine

$$C_6H_5CH{=}N{-}N{=}CHC_6H_5$$
V

(1) (a) From the Ph.D. thesis of John E. Wyman, Purdue University, 1956; (b) presented before the Division of Organic Chemistry at the Miami Meeting of the American Chemical Society, April, 1957.

(2) Purdue Research Foundation Fellow, 1954–1955, Monsanto Chemical Co. Fellow, 1955–1956.

(3) H. Feuer, G. B. Bachman and E. H. White, THIS JOURNAL, **73**, 4716 (1951).

(4) This compound has also been prepared by the reaction of maleic anhydride with mineral acid salts of hydrazine: (a) R. H. Mizzoni and P. E. Spoerri, THIS JOURNAL, **73**, 1873 (1951); (b) W. D. Harris and D. L. Schoene, U. S. Patent 2,575,954, Nov. 20 (1951); (c) Yu. A. Baskakov and N. N. Melnikov, *J. Gen. Chem. of U.S.S.R.*, **24**, 1216 (1954).

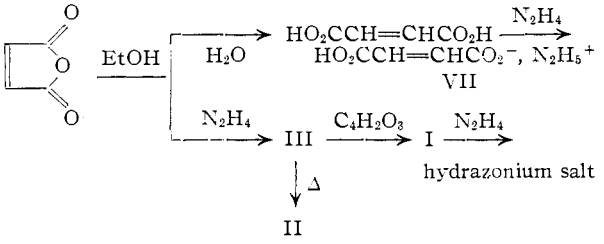
(5) H. Hinterbauer, Austrian Patent 176,563, Nov. 10, 1953; *C. A.*, **48**, 10785 (1954).

(6) T. Curtius and H. H. Foesterling, *J. prakt. Chem.*, **51**, 371 (1895).

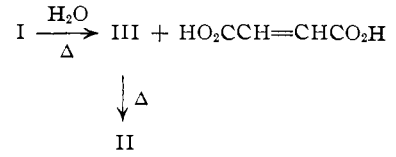
(V) and the monobenzalhydrazide of maleic acid[7]

$$C_6H_5CH{=}NNHCOCH{=}CHCO_2H$$
VI

(VI). Compound V results from the reaction of benzaldehyde with the various hydrazonium salts present (*e.g.*, VII), and VI derives from the reaction of benzaldehyde with III. The reaction of maleic anhydride with hydrazine hydrate in ether or in alcohol differs from the reaction in acetic acid in that hydroxide ion is probably involved in the former reactions.



The dehydrations and ring closures which occur readily in this series are illustrated by the following reactions. An aqueous solution of I, after 30 min. at 100°, yields II (quantitatively) and maleic acid. Also, the hydrazonium salt VII is converted by polyphosphoric acid (quantitatively) into II. Surprisingly, I is recovered unchanged on heating in polyphosphoric acid[8] indicating that a hydrolysis step is involved in the transformation of I to II.



Experimental

1,2-Dimaleic Acid Hydrazine (I).—A solution of 5.95 g. (0.1 mole) of 85% hydrazine hydrate in 25 ml. of glacial acetic acid was prepared by adding slowly with stirring the cooled acid to the hydrazine which was surrounded by ice. The solution was then added with stirring in ten minutes to a solution of 20 g. (0.2 mole) of maleic anhydride in 100 ml. of glacial acetic acid keeping the temperature below 30°. After the mixture was allowed to stand at about 30° for three hours, the solid (96% yield) was filtered and recrystallized twice from ethanol to give **1,2-dimaleic acid hydrazine**, yellow crystals, m.p. 185–187° dec.

Anal. Calcd. for $C_8H_8O_6N_2$: C, 42.11; H, 3.53; N, 12.28; neut. equiv., 114. Found: C, 42.20, 42.35; H, 3.78, 3.79; N, 12.40, 12.56; neut. equiv., 116.

When the directions in the patent[6] for the preparation of the supposed "N-aminomaleimide" were followed by treating equimolar amounts of hydrazine hydrate and maleic anhydride below 40°, a 91% yield of I and no other product was obtained.

Hydrogenation of 1,2-Dimaleic Acid Hydrazine (I). (a) **In Absolute Ethanol Slurry.**—A slurry of 22.8 g. (0.1 mole) of 1,2-dimaleic acid hydrazine, 0.2 g. of platinum oxide, and 150 ml. of absolute ethanol was shaken in a Parr pressure reaction apparatus at an initial hydrogen pressure of 46.5 lb. Hydrogen uptake ceased at 34 lb. (71.4% of the theoretical amount). The slurry was diluted with 300 ml. of water, warmed briefly to dissolve unreacted I, filtered and dried, affording 15.3 g. (92% based on the starting material which had reacted) of product. Recrystallization from hot water gave **1,2-disuccinic acid hydrazine**, m.p. 219–221° (lit. val.[8] 222.5°). A mixed melting point determination with an authentic sample showed no depression.

(b) **In 50% Aqueous Ethanol.**—A solution of 0.32 g. (0.0014 mole) of I in 100 ml. of 50% aqueous ethanol was hydrogenated in the presence of 0.2 g. of platinum oxide at 49 lb. initial hydrogen pressure. Evaporation of the solvent after filtering the solution afforded 0.28 g. (90%) of **1,2-disuccinic acid hydrazine**, m.p. 219–220°.

Reaction of Maleic Anhydride and Hydrazine Hydrate in Alcohol.—To a solution of 39.6 g. (0.4 mole) of maleic anhydride in 300 ml. of absolute ethanol was added a solution of 20 g. (0.4 mole) of hydrazine hydrate in 100 ml. of absolute ethanol with external cooling to maintain a temperature of 30–40°. The mixture was allowed to stand at room temperature for four hours, and then filtered. The solid (45.6 g.) consisted of a mixture of white granules and a yellow powder. A small amount of this mixture was soluble in hot methanol and gave a crystalline product, m.p. >260° dec. Its composition was that of maleic monohydrazide (III).

Anal. Calcd. for $C_4H_6O_3N_2$: C, 36.93; H, 4.65; N, 21.53; neut. equiv., 130. Found: C, 37.05; H, 4.59; N, 21.25; neut. equiv., 128.

A 5-g. portion of the above mixture was dissolved in water by stirring for ten minutes, then 5 g. of benzaldehyde was added and the two phase system was stirred for 50 minutes and filtered. An additional 8 g. of benzaldehyde was added to the filtrate, stirring was continued for a half-hour, and the mixture was then filtered. The solid residues were combined and dried *in vacuo* overnight affording 5.5 g. of material. The dry solids were triturated with ether and filtered. The ether-insoluble residue amounting to 1.9 g., m.p. 186.5–188.5°, was identified as the monobenzalhydrazide of maleic acid. Three recrystallizations from acetone raised the melting point to 192–193° (lit. val.[7] 183°).

Anal. Calcd. for $C_{11}H_{10}O_3N_2$: C, 60.54; H, 4.62; N, 12.84. Found: C, 60.47, 60.52; H, 4.46, 4.51; N, 12.61, 12.67.

The ether extract was evaporated to dryness, leaving 3.2 g. of benzalazine, m.p. 83–93°. A single recrystallization from absolute ethanol raised the melting point to 93°.

The benzaldehyde-treated solution of the original reaction mixture was extracted with ether (three times 50-ml. portions) and its *p*H was then adjusted to seven (Hydrion B paper) with dilute ammonium hydroxide. Addition of an aqueous solution of silver nitrate afforded a voluminous precipitate of a light yellow salt which decomposed rapidly. In a parallel experiment in which barium chloride was employed in place of silver nitrate a small amount of a white barium salt was obtained. This same behavior was shown by an aqueous solution of an authentic sample of 1,2-dimaleic acid hydrazine.

Addition of 3.7 g. of the original mixture dissolved in water to a solution of 2.9 g. of maleic anhydride in methanol refluxing for 15 minutes and evaporating to a slurry gave, after filtering, 3.5 g. of 1,2-dimaleic acid hydrazine (I), m.p. 183–187°. Evaporation of the filtrate to dryness left 1.1 g. of a solid which after washing with ethanol was identified as maleic hydrazide (II). The infrared spectra of compounds I and II were found to be identical with those of authentic samples.

Maleic Hydrazide (II). (a) **From Maleic Anhydride and Hydrazine Hydrate.**—In a 2-l. three-necked round-bottom flask fitted with a heating mantle, a motor driven Hershberg stirrer, a dropping funnel and a Friedrichs condenser were placed 1 l. of glacial acetic acid and 161.7 g. (1.65 moles) of maleic anhydride. The mixture was stirred and heated to reflux during which time the maleic anhydride dissolved. Heating was then discontinued and 75 g. (1.5 moles) of hydrazine hydrate (100%) was added in ten minutes. A yellow precipitate appeared initially which redissolved. After complete addition of the hydrazine hydrate, refluxing and stirring were continued for a half-hour during which time a granular white precipitate of II formed. The solution was then allowed to come to room temperature and was cooled to 18° in an ice-bath. The solid was collected by suction filtration, washed with small portions of ethanol and ether, and air-dried yielding 100 g. of colorless II. The filtrate was concentrated by distilling off about 800 ml. of solvent, then 200 ml. of water was added and the solution cooled to 15° in an ice-bath. The solid was again

(7) C. Caronna, *Gazz. chim. ital.*, **77**, 427 (1947).

(8) The saturated analog of I, 1,2-disuccinic acid hydrazine was readily converted to bicyclic disuccinhydrazide on heating in polyphosphoric acid (H. Feuer and J. E. Wyman, *Chemistry & Industry*, 577 (1956)).

collected by suction filtration, washed with 100 ml. of ice-water, a small amount of ethanol, then ether, and dried at 100°. The second crop amounted to 22 g. The filtrate was diluted with 400 ml. of water and concentrated to a volume of 100 ml. Cooling, filtering, and washing as before gave a third crop, 20 g. The total yield of maleic hydrazide melting over 300° was 144 g. (83%).

(b) **From 1,2-Dimaleic Acid Hydrazine.**—In a 125-ml. erlenmeyer flask was placed a solution of 11.4 g. (0.05 mole) of 1,2-dimaleic acid hydrazine in 75 ml. of water and it was boiled for 30 minutes. The solution was then cooled to 5° and filtered, affording 5.2 g. (93%) of maleic hydrazide, m.p. 300° dec.

The filtrate was evaporated *in vacuo* at 28° affording 6.14 g. of maleic acid, m.p. 127–130°. Assuming that the 0.4 g. of maleic hydrazide which is unaccounted for is contained in the maleic acid residue, the recovery of maleic acid amounted to 100%.

(c) **From Monohydrazonium Maleate.**—In a 100-ml. round-bottom flask was placed a solution of 23.2 g. (0.2 mole) of maleic acid in 25 ml. of water, and 5.0 g. (0.1 mole) of hydrazine hydrate was slowly added with cooling to keep the temperature below 40°. The mixture was then evaporated to dryness *in vacuo* at 25°, and a total of 100 g. of polyphosphoric acid was added to the salt cake. A vigorous exothermic reaction occurred immediately and the slurry yielded a clear colorless solution in two minutes. The solution was heated at 102° for 12 hours, then it was decomposed by pouring it into 300 ml. of ice-water. After stirring to promote crystallization, the slurry was filtered and dried, affording 11.3 g. (100%) of **maleic hydrazide,** m.p. 300° dec.

(d) **From Hydrazine Hydrate and Maleic Acid.**—In a 125-ml. erlenmeyer flask were placed 5.0 g. (0.1 mole) of hydrazine hydrate and 30 ml. of water. A total of 23.2 g. (0.2 mole) of maleic acid was added in one portion and the mixture was warmed to hasten solution. The resulting solution was boiled until a slurry formed, then it was cooled and filtered, washed with water and dried, affording 7.5 g. of maleic hydrazide. Evaporation of the filtrate to a slurry and filtering gave an additional 4.7 g. of material which after trituration with ether and recrystallization from water yielded 1.3 g. of maleic hydrazide and 1.0 g. of maleic acid. The filtrate was then evaporated to dryness and recrystallized from ether affording 8.8 g. of maleic acid, m.p. 128–130°. The total yield of maleic hydrazide was 8.8 g. (80%) and the total recovery of maleic acid was 9.8 g. (76%).

Acknowledgment.—We are indebted to the Office of Naval Research and to the Purdue Research Foundation for the financial support of this work.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Reaction of Free Radicals with Non-benzenoid Aromatic Hydrocarbons. I. 6-Phenylfulvenes and Benzofulvenes

BY JOHN L. KICE AND FRED M. PARHAM

RECEIVED JANUARY 23, 1958

The reaction of free radicals with 6-phenylfulvenes and benzofulvenes has been investigated both by reactivity studies using the kinetic method previously employed for the dibenzofulvenes, and by a product study of the reaction of diphenylfulvene with 2-cyano-2-propyl radicals. The results demonstrate that in all cases radical attack occurs at one of the fulvene ring positions and indicate that for the phenylfulvenes such attack occurs at least predominantly at the 2-position while for diphenylbenzofulvene attack apparently occurs at the 3-position. The behavior of the radicals resulting in the two cases differs considerably, that from diphenylfulvene being quite unreactive toward any further reaction other than termination while that from diphenylbenzofulvene shows behavior intermediate between a styryl and a fluorenyl radical. No evidence was found for any substituted fulvenes as radical–fulvene reaction products, a finding consistent with the presumed low degree of aromaticity of the fulvenes.

In recent years there has been considerably increased interest in the chemistry of the non-benzenoid aromatic hydrocarbons.[1] However, to the best of our knowledge there have been no studies of the reactions of these compounds with free radicals. In view of the extensive data on radical reactivity available for benzenoid hydrocarbons[2] and for simple olefins and dienes,[3] similar studies on the non-benzenoid aromatics would seem to be of some interest.

In the present paper we wish to report our initial efforts in this area. These have been concerned with the reaction of free radicals with 6-phenyl-substituted fulvenes and benzofulvenes, especially 6,6-diphenylfulvene (I).

(1) W. Baker and J. F. W. McOmie, "Progress in Organic Chemistry," Vol. 3, Academic Press, Inc., New York, N. Y., 1955, pp. 44–80.

(2) (a) M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955); (b) E. C. Kooyman and E. Farenhorst, *Nature*, **169**, 153 (1952); *Trans. Faraday Soc.*, **49**, 58 (1953); (c) J. R. Dunn and W. A. Waters, *J. Chem. Soc.*, 580 (1954); (d) J. Smid and M. Szwarc, THIS JOURNAL, **78**, 3322 (1956).

(3) (a) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); (b) F. Leavitt, M. Levy, M. Szwarc and V. Stannett, THIS JOURNAL, **78**, 5493 (1955); (c) M. Szwarc and A. Rajbenbach, *ibid.*, **79**, 6343 (1957); (d) R. P. Buckley and M. Szwarc, *ibid.*, **78**, 5696 (1956); (e) R. P. Buckley, F. Leavitt and M. Szwarc, *ibid.*, **78**, 5557 (1956).

Initial qualitative indications that diphenylfulvene is quite reactive toward free radicals were provided by the observations that decomposition of excess azobisisobutyronitrile in degassed benzene solutions of the fulvene led to a disappearance of the fulvene color and that addition of small amounts of the fulvene caused a pronounced retardation of the rate of polymerization of methyl methacrylate.

Reaction of 2-Cyano-2-propyl Radicals with Diphenylfulvene.—To study the reaction of 2-cyano-2-propyl radicals with diphenylfulvene, azobisisobutyronitrile (initial concentration 2.6×10^{-2} M) was decomposed in a degassed benzene solution of diphenylfulvene (5.1×10^{-2} M) at 78° for 10–12 hours.[4] Two crystalline substances, A, m.p. 258-260°, and B, m.p. 235-236°, were isolated along with intractable gummy non-crystalline residues. Elementary analyses and molecular weight measurements showed compounds A and B to be isomeric substances of the empirical formula, R–F–F–R,

(4) A preliminary experiment in which diphenylfulvene was heated alone in benzene at 80° for 10 hours showed that less than 1% of the fulvene had decomposed, thereby ruling out the possibility of the reaction products being contaminated to any extent by fulvene decomposition products.