[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Addition of Phenylmagnesium Bromide to Aliphatic Conjugated Benzenesulfonimides

BY ROGER ADAMS AND WALTER REIFSCHNEIDER

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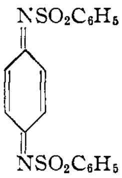
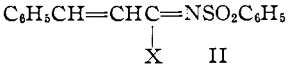
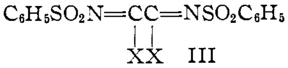
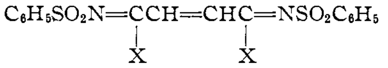
The reactions between phenylmagnesium bromide and the imido ethers prepared through the imide chlorides, from N-benzenesulfonylcinnamide, N,N'-dibenzenesulfonyloxamide and N,N'-dibenzenesulfonylmaleamide have been studied. The first reaction involves a 1,4-addition and rearrangement to 3-benzenesulfonimido-3-methoxy-1,1-diphenylpropane; the second reaction gives products which vary with the amount of Grignard reagent: one mole, 1,2-dibenzenesulfonimido-2-methoxy-1-phenylethane; two moles, N,N'-dibenzenesulfonylbenzildiimide; three moles, N,N'-dibenzenesulfonyl-N,1,2-triphenyl-1,2-diaminoethene; four moles, a complicated mixture consisting of the same product obtained from three moles and N,N'-dibenzenesulfonyl-1,2-diphenyl-1,2-diaminoethene; the third reaction gave a low yield of product, the constitution of which was not elucidated.

The addition of many types of reagents to *p*-quinonedibenzenesulfonimides[1] (I) proceeds with extraordinary ease. The study of additions to somewhat analogous conjugated systems in straight chained aliphatic molecules has now been undertaken. The benzenesulfonimide derivatives which were subjected to the action of phenylmagnesium bromide are shown in IIb, IIIb and IVb. These compounds, in which X = Cl, were made by a two-step process from benzenesulfonamide. By condensation of benzenesulfonamide with cinnamoyl chloride, oxalyl chloride and maleic anhydride, respectively, in presence of phosphorus oxychloride, compounds V, VI and VII resulted.


I


$C_6H_5CH{=}CH\underset{\displaystyle X}{\underset{|}{C}}{=}NSO_2C_6H_5$
II


$C_6H_5SO_2N{=}\underset{\displaystyle X}{\underset{|}{C}}\underset{\displaystyle X}{\underset{|}{C}}{=}NSO_2C_6H_5$
III


$C_6H_5SO_2N{=}\underset{\displaystyle X}{\underset{|}{C}}CH{=}CH\underset{\displaystyle X}{\underset{|}{C}}{=}NSO_2C_6H_5$
IV

a, X = Cl
b, X = OCH_3
c, X = $(C_2H_5)_2N$

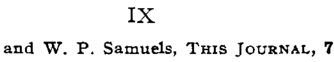
$C_6H_5CH{=}CHCONHSO_2C_6H_5$
V

$C_6H_5SO_2NHCOCONHSO_2C_6H_5$
VI

$C_6H_5SO_2NHCOCH{=}CHCONHSO_2C_6H_5$
VII

When the amides V, VI and VII were treated with phosphorus pentachloride, the conversions to II, III and IV, respectively, where X = Cl, were facile. The chlorine in these molecules is readily replaced. With methanol the corresponding imido ethers (X = OCH_3) are formed and with diethylamine the corresponding amidines [X = $(C_2H_5)_2N$].

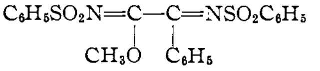
The reaction of phenylmagnesium bromide with each of the imido ethers was studied. Compound IIb was converted into a substance with structure VIII.

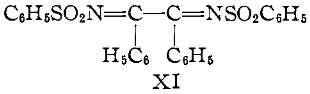

$(C_6H_5)_2CHCH_2\underset{\displaystyle OCH_3}{\underset{|}{C}}{=}NSO_2C_6H_5$
VIII

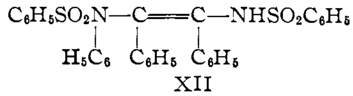
$(C_6H_5)_2CHCH_2CONHSO_2C_6H_5$
IX

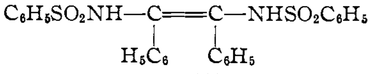
The infrared spectrum of VIII showed the absence of NH bands and the presence of a C=N band at 1610 cm.$^{-1}$. Upon hydrolysis with alkali, two readily-separated compounds were formed. One was β,β-diphenylpropionic acid and the other the benzenesulfonyl derivative of β,β-diphenylpropionamide (IX). The former is a known compound and was identified by comparison with an authentic sample; the latter was synthesized from β,β-diphenylpropionyl chloride and benzenesulfonamide. It appears probable that product VIII is formed by an initial 1,4-addition to the C=C—C=N conjugated system followed by rearrangement of the resulting carbon–carbon double bond to the imide.

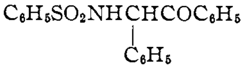
Phenylmagnesium bromide reacted with compound IIIb in quite a different manner, and the character of the product is dependent on the amount of reagent employed. One mole caused replacement of one methoxyl group by a phenyl group (X); two moles, the replacement of two methoxyls (XI); three moles, the replacement of both methoxyls and 1,4-addition (XII); four or more moles led to a mixture from which fractional crystallization resulted in the isolation of XII and XIII.


$C_6H_5SO_2N{=}\underset{\displaystyle CH_3O}{\underset{|}{C}}{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{=}NSO_2C_6H_5$
X


$C_6H_5SO_2N{=}\underset{\displaystyle H_5C_6}{\underset{|}{C}}{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{=}NSO_2C_6H_5$
XI


$C_6H_5SO_2\underset{\displaystyle H_5C_6}{\underset{|}{N}}{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}NHSO_2C_6H_5$
XII


$C_6H_5SO_2NH{-}\underset{\displaystyle H_5C_6}{\underset{|}{C}}{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}NHSO_2C_6H_5$
XIII


$C_6H_5SO_2NH\underset{\displaystyle C_6H_5}{\underset{|}{C}}HCOC_6H_5$
XIV

Structure XI was identified by acid hydrolysis to benzil, and structure XIII by hydrolysis to the benzenesulfonyl derivative of desylamine (XIV) which was synthesized. Compound XIII is probably formed by a 1,4-reduction of XI by phenylmagnesium bromide as the reducing agent.

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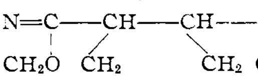
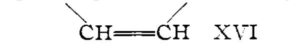
[1] R. Adams and W. P. Samuels, THIS JOURNAL, **77**, 5375, 5383 (1955) and previous papers.

Compound IVb and phenylmagnesium bromide gave a complicated compound, the structure of which was not elucidated. The analyses and infrared spectrum indicated absence of the methoxyl groups. Spectral bands indicated the presence of C═N and CH═C linkages.

The imino ethers of II, III and IV were also examined for their dienophilic character. Upon heating with butadiene or dimethylbutadiene, compound IIb was recovered unchanged. Compound IIIb, however, when heated with these reagents in toluene, rearranged to N,N¹-dibenzenesulfonyl-N,N′-dimethyloxamide (XV), which was identified by synthesis from benzenesulfonylmethylamide and oxalyl chloride. No rearrangement occurred by heating in xylene alone. Moreover, the imido ether IIb did not rearrange by similar treatment.


$\underset{\displaystyle CH_3}{C_6H_5SO_2N}COCO\underset{\displaystyle CH_3}{NSO_2C_6H_5}$ XV


XVI

Compound IVb reacted normally as a dienophile, when subjected to hot butadiene in chloroform, with formation of XVI.

Compounds IIb, IIIb and IVb failed to show diene character when subjected to treatment with maleic anhydride under various conditions.

Acknowledgment.—The authors wish to thank Mr. J. Nemeth, Mrs. Lucy Chang and Mrs. Esther Fett for the microanalyses and Mr. J. Brader for the determination of the infrared spectra.

Experimental

N-Benzenesulfonylcinnamide (V).—A mixture of 142 g. of benzenesulfonamide, 150 g. of cinnamoyl chloride and 120 ml. of phosphorus oxychloride was heated on a steam-bath for 3 hours. After cooling, ether was added. The solution was filtered from the precipitated solid which was washed with ether and then with ethanol. The solid was purified by recrystallization from ethanol; m.p. 149°. The yield was 210 g. (81.2%).

Anal. Calcd. for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56. Found: C, 62.97; H, 4.55.

3-Benzenesulfonimido-3-chloro-1-phenyl-1-propene (IIa).—A mixture of 48.5 g. of N-benzenesulfonylcinnamide (V) and 38 g. of phosphorus pentachloride in 160 ml. of benzene was refluxed until the solution was completely clear and the hydrogen chloride evolution had stopped. After removal of 150 ml. of the solvent by distillation in vacuum, ether was added. A crystalline product gradually formed and after a few days was removed by filtration, thoroughly washed with ether and recrystallized from benzene; m.p. 90°. The yield was 20.4 g. (39.5%).

Anal. Calcd. for $C_{15}H_{12}ClNO_2S$: C, 58.91; H, 3.96. Found: C, 59.39; H, 4.13.

3-Benzenesulfonimido-3-methoxy-1-phenyl-1-propene (IIb).—A mixture of 8 g. of 3-benzenesulfonimido-3-chloro-1-phenyl-1-propene (IIa) and a solution of 0.65 g. of sodium in 60 ml. of methanol was allowed to stand at room temperature for 5 hours. The solid after removal by filtration was dissolved with hot benzene and separated from sodium chloride by filtration. Upon addition of petroleum ether (b.p. 30–60°) to the benzene solution, white crystals resulted, m.p. 147°; yield 6.1 g. (77.3%).

Anal. Calcd. for $C_{16}H_{15}NO_3S$: C, 63.76; H, 5.02; N, 4.65. Found: C, 63.40; H, 4.79; N, 4.48.

3-Benzenesulfonimido-3-diethylamino-1-phenyl-1-propene (IIc).—A mixture of 3 g. of 3-benzenesulfonimido-3-chloro-1-phenyl-1-propene (IIa) and 2 g. of diethylamine in 30 ml. of benzene was boiled for 5 minutes. The mixture was filtered hot and the volume reduced to 15 ml. by distillation in vacuum. Petroleum ether (b.p. 30–60°) was added till the solution turned slightly turbid. The white substance which crystallized was purified by recrystallization from benzene–petroleum ether (b.p. 30–60°); m.p. 97°. The yield was 3.0 g. (89.3%).

Anal. Calcd. for $C_{19}H_{22}N_2O_2S$: C, 66.64; H, 6.48; N, 8.18. Found: C, 66.78; H, 6.46; N, 8.12.

N,N′-Dibenzenesulfonyloxamide (VI).—To a mixture of 50 g. of benzenesulfonamide in 60 ml. of benzene and 40 ml. of phosphorus oxychloride, 21 g. of oxalyl chloride was added and the mixture heated on the steam-bath for 3 hours. After cooling, the fine crystalline compound was removed by filtration and thoroughly washed with ether. It was purified by recrystallization from ethanol; m.p. 256° dec. (lit. m.p. 256° dec.).[2] The yield was 55 g. (93.9%).

Anal. Calcd. for $C_{14}H_{12}N_2O_6S_2$: C, 45.64; H, 3.28. Found: C, 45.91; H, 3.10.

1,2-Dibenzenesulfonimido-1,2-dichloroethane (IIIa).—A mixture of 32 g. of N,N′-dibenzenesulfonyloxamide (VI), 40 g. of phosphorus pentachloride and 600 ml. of benzene was refluxed till the solution was clear (about 6 hours). The product crystallized upon cooling. It was purified by recrystallization from benzene; m.p. 183°. The yield was 32 g. (90.9%).

Anal. Calcd. for $C_{14}H_{10}Cl_2N_2O_4S_2$: C, 41.49; H, 2.49. Found: C, 41.28; H, 2.45.

1,2-Dibenzenesulfonimido-1,2-dimethoxyethane (IIIb).—A mixture of 10 g. of 1,2-dibenzenesulfonimido-1,2-dichloroethane (IIIa) and 1.1 g. of sodium in 100 ml. of methanol was refluxed for 1 hour. After cooling, the solid was removed by filtration and dissolved in benzene. After filtering from the sodium chloride, petroleum ether (b.p. 30–60°) was added to the filtrate until the solution became slightly turbid. White crystals were obtained which were purified by recrystallization from benzene–petroleum ether (b.p. 30–60°); m.p. 185°. The yield was 8.5 g. (86.9%).

Anal. Calcd. for $C_{16}H_{16}N_2O_6S_2$: C, 48.47; H, 4.07. Found: C, 48.41; H, 3.90.

1,2-Dibenzenesulfonimido-1,2-diethylaminoethane (IIIc).—To a solution of 13.5 g. of 1,2-dibenzenesulfonimido-1,2-dichloroethane (IIIa) in 100 ml. of benzene, 10 ml. of diethylamine was added. A vigorous reaction occurred and after it had subsided the solution was refluxed for 20 minutes. While the reaction mixture was still hot, the diethylamine hydrochloride was removed by filtration and ether was added to the warm filtrate. The product crystallized and was purified by recrystallization from benzene–ether; m.p. 201°. The yield was 13.7 g. (85.9%).

Anal. Calcd. for $C_{22}H_{30}N_4O_4S_2$: C, 55.20; H, 6.32; N, 11.71. Found: C, 55.11; H, 6.20; N, 11.69.

1,4-Dibenzenesulfonimido-1,4-dichloro-2-butene (IVa).—A mixture of 68 g. of N,N′-dibenzenesulfonylmaleamide[3] (VII), 82 g. of phosphorus pentachloride, 120 ml. of tetrachloroethane and 120 ml. of benzene was refluxed for about 5 hours till a clear solution was obtained. After cooling the red solution, an equal volume of absolute ether was added and the solution allowed to stand overnight. The imidechloride (IVa) was recrystallized from benzene–ether; m.p. 150–151°. The yield was 57 g. (76.6%).

Anal. Calcd. for $C_{16}H_{12}Cl_2N_2O_4S_2$. C, 44.55; H, 2.81. Found: C, 44.94; H, 2.74.

1,4-Dibenzenesulfonimido-1,4-dimethoxy-2-butene (IVb).—A mixture of 7.3 g. of 1,4-dibenzenesulfonimido-1,4-dichloro-2-butene (IVa) and 80 ml. of absolute methanol was allowed to stand for 20 hours with ice cooling. The product was removed by filtration and recrystallized from benzene–petroleum ether (b.p. 30–60°); m.p. 195–196°. The yield was 5.4 g. (75.5%).

Anal. Calcd. for $C_{18}H_{18}N_2O_6S_2$: C, 51.17; H, 4.29; N, 6.63. Found: C, 51.41; H, 4.40; N, 6.63.

1,4-Dibenzenesulfonimido-1,4-bis-diethylamino-2-butene (IVc).—A mixture of 5.5 g. of 1,4-dibenzenesulfonimido-1,4-dichloro-2-butene (IVa), 55 ml. of benzene and 9 ml. of

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(2) M. V. Charante, *Rec. trav. chim.*, **32**, 94 (1913).

(3) T. W. Evans and W. M. Dehn, THIS JOURNAL, **52**, 2531 (1930).

diethylamine was refluxed for one hour and the solution filtered while hot. The substance which crystallized after cooling was removed by filtration and recrystallized from benzene; m.p. 175°. The yield was 4.8 g. (74.6%).

Anal. Calcd. for $C_{24}H_{32}N_4O_4S_2$: C, 57.12; H, 6.39; N, 11.10. Found: C, 56.80; H, 6.55; N, 11.13.

The Reaction of Phenylmagnesium Bromide with 3-Benzenesulfonimido-3-methoxy-1-phenyl-1-propene (**IIb**); **3-Benzenesulfonimido-3-methoxy-1,1-diphenylpropane** (**VIII**).—To a cooled solution of 3.5 g. of 3-benzenesulfonimido-3-methoxy-1-phenyl-1-propene (IIb) in 80 ml. of benzene, was added dropwise 40 ml. of 1 *M* ethereal solution of phenylmagnesium bromide. When the addition was completed the mixture was boiled for 15 minutes, then cooled and the addition product decomposed by means of saturated aqueous ammonium chloride. The layers were separated and the aqueous layer was extracted twice with benzene. The combined solutions of benzene were extracted once with water, then dried and finally the volume was reduced by distillation to about 15 ml. After addition of petroleum ether (b.p. 30–60°), 2.4 g. of a white product crystallized. It was purified by recrystallization several times from benzene–petroleum ether (b.p. 30–60°), m.p. 121°. After standing for some time an additional 0.4 g. of the substance crystallized. The total yield was 2.8 g. (44.1%).

Anal. Calcd. for $C_{22}H_{21}NO_3S$: C, 69.63; H, 5.58; N, 3.69. Found: C, 69.82; H, 5.56; N, 3.43.

The infrared spectrum showed absorption for C=N at 1610 cm.$^{-1}$ and no absorption for N–H.

Hydrolysis of 3-Benzenesulfonimido-3-methoxy-1,1-diphenylpropane (**VIII**); **β,β-Diphenylpropionic Acid and N-Benzenesulfonyl-β,β-diphenylpropionamide** (**IX**).—A solution of 0.7 g. of compound VIII in 30 ml. of acetone and a solution of 1 g. of potassium hydroxide in 40 ml. of water were refluxed together for 15 minutes. After removing the acetone by evaporating to half of the volume, concentrated hydrochloric acid was added to the clear solution. A white substance precipitated. The mixture was heated to boiling and the solid removed by filtration while hot. Long needles crystallized from the filtrate and were purified by crystallization from ethanol–water; m.p. 152.5° (lit.[4] m.p. 151°). The yield was 0.2 g.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.65; H, 6.29.

A melting point of a mixture of this product with an authentic sample of β,β-diphenylpropionic acid showed no depression. The insoluble substance, precipitated by acidification of the alkaline hydrolysis mixture, was recrystallized from benzene–petroleum ether; m.p. 182.5–183°. The yield was 0.15 g.

Anal. Calcd. for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24. Found: C, 68.92; H, 5.57.

It was identical with N-benzenesulfonyl-β,β-diphenylpropionamide (IX) synthesized below by an unequivocal method.

N-Benzenesulfonyl-β,β-diphenylpropionamide (**IX**).—A solution of 2 g. of β,β-diphenylpropionic acid in 20 ml. of benzene was refluxed for one hour with a small excess of thionyl chloride. After removing the excess thionyl chloride by reducing the volume to about 10 ml. by distillation, 20 ml. of phosphorus oxychloride and the theoretical amount of benzenesulfonamide were added and the mixture heated for 3 hours on the steam-bath until hydrogen chloride evolution stopped. After standing overnight the product crystallized. It was recrystallized from benzene–petroleum ether (b.p. 30–60°); m.p. 182.5–183°. The yield was 2.4 g. (74.3%).

Anal. Calcd. for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24. Found: C, 69.12; H, 5.47.

The Reaction of Phenylmagnesium Bromide with 1,2-Dibenzenesulfonimido-1,2-dimethoxyethane (**IIIb**): **General Procedure.**—A suspension of 3.96 g. (0.01 mole) of finely powdered 1,2-dibenzenesulfonimido-1,2-dimethoxyethane (IIIb) in 100 ml. of benzene was cooled and a 1 *M* solution of phenylmagnesium bromide in ether was added dropwise. After boiling the mixture for 15 minutes, it was cooled and saturated aqueous ammonium chloride added slowly to decompose the addition compound. The layers were separated and the aqueous portion was extracted three times with benzene. The combined benzene solutions were extracted once with water. After drying over anhydrous magnesium sulfate the volume of the benzene solution was reduced to about 15–20 ml. by distillation and about 50 ml. of ether was added. The reaction product crystallized.

A. **One Mole of Grignard**; **1,2-Dibenzenesulfonimido-2-methoxy-1-phenylethane** (**X**).—The reaction product was recrystallized from benzene–petroleum ether (b.p. 30–60°), m.p. 134.5°. The yield was 2.1 g. (46.4%).

Anal. Calcd. for $C_{21}H_{18}N_2O_5S_2$: C, 57.00; H, 4.10; N, 6.33. Found: C, 57.40; H, 4.17; N, 6.20.

The infrared spectrum showed absorption for C=N at 1630 and 1575 and for $-OCH_3$ at 1096 cm.$^{-1}$.

B. **Two Moles of Grignard**: **N,N′-Dibenzenesulfonylbenzildiimide** (**XI**).—The product was recrystallized from benzene–petroleum ether (b.p. 30–60°); m.p. 187°. The yield was 1.9 g. (38.9%).

Anal. Calcd. for $C_{26}H_{20}N_2O_4S_2$: C, 63.92; H, 4.13; N, 5.73. Found: C, 63.85; H, 4.08; N, 5.85.

The infrared spectrum showed absorption for C=N at 1570 cm.$^{-1}$; the simplicity of the spectrum indicates symmetry of the molecule.

This product was hydrolyzed in the following way. A mixture of 0.2 g. of N,N′-dibenzenesulfonylbenzildiimide (XI) and 20 ml. of concentrated hydrochloric acid and ethanol (1:1) was refluxed for 20 hours. After evaporation of most of the ethanol and cooling, the precipitated substance was removed by filtration. It was purified by recrystallization several times from ethanol–water; m.p. 95°. The product was benzil.

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.80. Found: C, 80.10; H, 4.95.

C. **Three Moles of Grignard**: **N,N′-Dibenzenesulfonyl-N,1,2-triphenyl-1,2-diaminoethene** (**XII**).—The product was recrystallized from benzene–ether, m.p. 242°. The yield was 1.7 g. (30.0%).

Anal. Calcd. for $C_{32}H_{26}N_2O_4S_2$: C, 67.82; H, 4.62; N, 4.95. Found: C, 67.92; H, 4.80; N, 4.67.

The infrared spectrum showed absorption for NH at 3270 cm.$^{-1}$ and for three types of monosubstituted benzene; the spectrum shows an excellent structure correlation for the compound postulated.

D. **Four or More Moles of Grignard**: **Compound XII and N,N′-Dibenzenesulfonyl-1,2-diphenyl-1,2-diaminoethene** (**XIII**).—The solid product was fractionally crystallized from benzene–ether. The less soluble fraction proved to be XII. The more soluble compound in benzene–ether proved to be XIII, m.p. 178°.

Anal. Calcd. for $C_{26}H_{22}N_2O_4S_2$: C, 63.65; H, 4.52; N, 5.71. Found: C, 63.89; H, 4.40; N, 5.66.

The infrared spectrum showed absorption for NH at 3340 and 3220 cm.$^{-1}$ and no absorption for C=N.

Hydrolysis of N,N′-Dibenzenesulfonyl-1,2-diphenyl-1,2-diaminoethene (**XIII**); **N-Benzenesulfonyldesylamine** (**XIV**).—A mixture of 0.4 g. of compound XIII and 10 ml. of concentrated hydrochloric acid in 30 ml. of ethanol was refluxed for 5 hours. After evaporation of most of the ethanol and cooling, the product precipitated and was removed by filtration. It was purified by recrystallization from ethanol; m.p. 136°.

Anal. Calcd. for $C_{20}H_{17}NO_3S$: C, 68.35; H, 4.88; N, 3.99. Found: C, 68.05; H, 5.21; N, 3.90.

N-Benzenesulfonyldesylamine (**XIV**).—To a solution of 2.5 g. of desylamine hydrochloride in 50 ml. of water, a solution of 5 g. of potassium hydroxide in 15 ml. of water was added and then 1.8 g. of benzenesulfonyl chloride in portions with vigorous shaking. The clear solution was acidified and the precipitated product was separated by filtration. It was washed with water, then with a small quantity of ethanol and finally with ether. The product was recrystallized from ethanol. Colorless needles were obtained, m.p. 136°, yield 3.2 g. (90.2%).

Anal. Calcd. for $C_{20}H_{17}NO_3S$: C, 68.35; H, 4.88. Found: C, 68.11; H, 4.79.

The Reaction of Phenylmagnesium Bromide with 1,4-Dibenzenesulfonimido-1,4-dimethoxy-2-butene (**IVb**).—To a cooled suspension of 4 g. of finely powdered 1,4-dibenzenesulfonimido-1,4-dimethoxy-2-butene in 120 ml. of benzene was added dropwise 100 ml. of 0.75 *M* ethereal solution of

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(4) G. G. Henderson, *J. Chem. Soc.*, **59**, 734 (1891).

phenylmagnesium bromide. After boiling for 15 minutes, the mixture was cooled and a saturated solution of ammonium chloride was added to decompose the addition compound. After extraction of the aqueous solution with benzene, the benzene solutions were extracted once with water, dried, and concentrated in vacuum to 20 ml. After standing several days, a white product separated. The yield was 0.95 g. It was purified by crystallization from benzene–petroleum ether (b.p. 30–60°), m.p. 268–269°.

Anal. Calcd. for $C_{36}H_{30}N_2O_4S_2$: C, 69.88; H, 4.89; N, 4.53. Found: average of 5 anal.: C, 69.64; H, 4.98; N, 4.42.

The Reaction of Butadiene with IIb, IIIb and IVb.—A. 3-Benzenesulfonimido-3-methoxy-1-phenyl-1-propene (IIb) when heated with butadiene in chloroform at 90° or in xylene at 170° or with 2,3-dimethylbutadiene in chloroform at 90° was recovered unchanged.

B. A mixture of 4 g. of 1,2-dibenzenesulfonimido-1,2-dimethoxyethane (IIIb), 8 ml. of xylene and 1 g. of butadiene was heated for 21 hours at 170–175° in a sealed tube. Upon addition of ether to the cooled reaction mixture, a white substance crystallized and was recrystallized several times from benzene–ether; m.p. 145.5°. The yield was 3.2 g. (80%). The same product resulted when 2,3-dimethylbutadiene was used in place of butadiene.

Anal. Calcd. for $C_{16}H_{16}N_2O_6S_2$: C, 48.47; H, 4.07; N, 7.07. Found: C, 48.57; H, 4.04; N, 7.04; OCH_3, 0.

The product proved to be identical with N,N′-dibenzenesulfonyl-N,N′-dimethyloxamide (XV), obtained by the action of methyl iodide on the silver salt of N,N′-dibenzenesulfonyloxamide (III) and by the reaction between benzenesulfonylmethylamide and oxalyl chloride.

No reaction took place when chloroform was used as solvent or when xylene was used without the butadiene.

C. A mixture of 4.22 g. of 1,4-dibenzenesulfonimido-1,4-dimethoxy-2-butene (IVb), 8 ml. of chloroform, 1 g. of butadiene and 2 mg. of hydroquinone was heated in a sealed tube for 18 hours at 90–95°. After cooling, the substance which crystallized was removed by filtration, washed with ether and recrystallized from benzene, m.p. 238°. The yield was 3.9 g. (81.8%).

Anal. Calcd. for $C_{22}H_{24}N_2O_6S_2$: C, 55.44; H, 5.08; N, 5.88. Found: C, 55.63; H, 4.80; N, 5.64.

The infrared spectrum showed absorption for C=N at 1599 cm.$^{-1}$, *-OCH$_3$* at *1098* cm.$^{-1}$ and *HC=CH (cis)* at 735 cm.$^{-1}$.

N,N′-Dibenzenesulfonyl-N,N′-dimethyloxamide (XV).—To a solution of 33 g. of benzenesulfonylmethylamide in a mixture of 50 ml. of thionyl chloride and 50 ml. of benzene, 12.3 g. of oxalyl chloride was added and the mixture heated for 4 hours. The solvents were removed by distillation under vacuum and the residue extracted with petroleum ether to remove traces of thionyl chloride. The residue was then taken up in ether and petroleum ether was added. A colorless substance crystallized and was recrystallized from benzene–petroleum ether (b.p. 30–60°); m.p. 145.5°. The yield was 26 g. (86%).

Anal. Calcd. for $C_{16}H_{16}N_2O_6S_2$: C, 48.47; H, 4.07. Found: C, 48.82; H, 4.27.

This method is much superior to that employing the silver salt of N,N′-dibenzenesulfonyloxamide (III) and methyl iodide.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH CENTER OF THE NATIONAL ANILINE DIVISION OF THE ALLIED CHEMICAL & DYE CORPORATION AND THE INSTITUTE OF RESEARCH OF LEHIGH UNIVERSITY]

Rearrangement of the Double Bond in *cis*-4-Cyclohexene-1,2-dicarboxylic Anhydride

BY M. E. BAILEY[1] AND E. D. AMSTUTZ

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cis-4-Cyclohexene-1,2-dicarboxylic anhydride (IV) was found to undergo isomerization at elevated temperatures under the influence of acid catalysts to form progressively: *cis*-3-cyclohexene-1,2-dicarboxylic anhydride (III), 2-cyclohexene-1,2-dicarboxylic anhydride (II) and 1-cyclohexene-1,2-dicarboxylic anhydride (I). Distillation of the final product yielded pure I. Fractional crystallization of an intermediate mixture containing high concentrations of III followed by recrystallization from toluene, yielded pure III. No *trans*-4-cyclohexene-1,2-dicarboxylic anhydride (V) was detectable at any stage. Identity of the products was established and rates of the isomerization were determined at two temperatures by use of infrared absorption spectra.

cis-4-Cyclohexene-1,2-dicarboxylic anhydride (IV) is easily obtainable from maleic anhydride and butadiene. In contrast with many other diene addition products it is not thermally reversible to the dieneophile and diene from which it is derived. For these reasons and because of the unique properties of many of its derivatives, IV has come to possess considerable academic as well as commercial importance. The other cyclohexene-1,2-dicarboxylic anhydrides are known but have not been of any particular interest because their reported methods of synthesis are cumbersome and inefficient. The present paper reports a hitherto unknown chemical property of IV which provides an easy route to some of the other isomers.

When IV is heated with acid catalysts, anhydride functionability is retained and average molecular weight is unchanged, but other properties are altered substantially. Possible explanations are *cis–trans* isomerization and double bond rearrangement which would lead to other *cis* isomers of cyclohexene-1,2-dicarboxylic anhydride.

In the first case, rupture of carbon–carbon bonds would be required, in the second, migration of a proton would need to occur. In order to determine which, if either, of these mechanisms applies, samples of the products which might be formed, *i.e.*, *trans*-4-cyclohexene-1,2-dicarboxylic anhydride (V), *cis*-3-cyclohexene-1,2-dicarboxylic anhydride (III), 2-cyclohexene-1,2-dicarboxylic anhydride (II) and 1-cyclohexene-1,2-dicarboxylic anhydride (I), were prepared for purposes of comparison, by the use of methods of synthesis already established.

The infrared absorption spectra for all five of these isomers were determined. All show strong absorptions between 5.4 and 5.9 μ which are characteristic of 1,2-dicarboxylic anhydrides. Between 6.0 and 12.0 μ there were important differences in the spectra. It was possible to distinguish the various isomeric anhydrides from each other by selection of strong absorption bands characteristic of each isomer. Their relative concentrations were deter-

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[1] National Aniline Division, Allied Chemical and Dye Corporation, Buffalo, New York.