

Papergrams.—Two systems which have been found to separate neomycin and neamine on the papergram are (1) *n*-butanol 50 parts by volume, water 25 parts, acetic acid 25 parts, and (2) *n*-propanol 50 parts by volume, water 45 parts, acetic acid 5 parts. Resolution of the bases is obtained whether these are applied as the hydrochlorides or as the salts of *p*-(*p*'-hydroxyphenylazo)-benzenesulfonic acid. The location of the bases is determined either by spraying the dried sheet with ninhydrin reagent or by incubating the developed sheet on an agar plate seeded with a microorganism. The crystalline *p*-(*p*'-hydroxyphenylazo)-benzenesulfonates of neomycin A and methanolysis product 1 (neanine) were run side by side on Whatman paper number 1 in descending fashion in the butanol system and the distance from the origin determined after a 30-hour period of time. This distance was identical as shown in Table I. The same compounds were run ascendingly in the propanol system and gave identical R_f values as listed in Table I.

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Derivatives of Sulfenic Acids. VII. Addition of Sulfenyl Halides to Olefins

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In a previous study,¹ the characterization of a series of olefins *via* 2,4-dinitrobenzenesulfonyl chloride (I) was reported, and the reaction involved was discussed. Six new examples of this reaction are now included in Table I. The excellently crystalline products may serve as useful derivatives.

ified with assurance to be the expected β -halo sulfides, *e.g.*, 2-bromocyclohexyl 2'-nitrophenyl sulfide. Application of Markownikoff's rule, considering the polarity of the sulfenyl halides as $\text{ArS}^{\delta+}\text{X}^{\delta-}$, suggests the most probable structures for the 1:1 adducts to the unsymmetrical open-chain olefins of Table I.

2,4-Dinitrobenzenesulfonyl bromide was obtained by reaction of I with potassium bromide (82%); and by action of bromine on 2,4-dinitrothiophenol (75–80%). The preparation of this sulfonyl bromide, in low yield, by brominolysis of 2,4-dinitrophenyl disulfide, was mentioned previously,³ but its analysis and alternate syntheses have not been recorded.

Experimental

Adducts of Table I.—Known procedures were used to prepare 2,4-dinitrobenzenesulfonyl chloride³ and 2-nitrobenzenesulfonyl bromide.⁴ The preparation of 2,4-dinitrobenzenesulfonyl bromide is given below. Additions to the olefins were made in glacial acetic acid by the general technique previously described.¹ With the sulfonyl bromides, the reaction mixtures were heated on the steam-bath for five to ten minutes, then let stand at room temperature for one day, rather than heating until a negative test for the sulfonyl bromide was obtained. The olefins used were either the purified commercial products, or were prepared by standard methods. Yields of the crude adducts were generally 60–80%, and purifications were effected by recrystallization from alcohol or benzene.

2,4-Dinitrobenzenesulfonyl Bromide.—A solution of 7.2 g. of I in 25 ml. of benzene was shaken with 30 g. of dry potassium bromide for 24 hours. The orange solution was

TABLE I
REACTIONS OF SULFENYL HALIDES WITH OLEFINS

| Olefin | Sulfonyl ^a halide | Product | M.p., °C. ^b | Analyses, ^d % | | | |
|-------------------------|------------------------------|---|------------------------|--------------------------|------|---------|------|
| | | | | Calcd. C | H | Found C | H |
| Allyl bromide | I | $\text{C}_9\text{H}_8\text{O}_4\text{N}_2\text{BrClS}$ | 110–111 ^c | 30.40 | 2.27 | 30.48 | 2.32 |
| Allyl chloride | I | $\text{C}_9\text{H}_8\text{O}_4\text{N}_2\text{Cl}_2\text{S}$ | 110–111 | 34.74 | 2.59 | 34.41 | 3.08 |
| <i>p</i> -Chlorostyrene | I | $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_2\text{Cl}_2\text{S}$ | 150–151 | 45.05 | 2.70 | 45.31 | 2.48 |
| Cyclohexene | II | $\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_2\text{BrS}$ | 117–118 | 39.89 | 3.60 | 39.96 | 3.66 |
| 1,4-Dihydronaphthalene | I | $\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_2\text{ClS}$ | 156–157 | 52.68 | 3.59 | 52.71 | 3.71 |
| 1,4-Dihydronaphthalene | III | $\text{C}_{16}\text{H}_{14}\text{O}_4\text{N}_2\text{BrS}$ | 94–96 | 52.75 | 3.84 | 52.88 | 3.81 |
| Indene | I | $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}_2\text{ClS}$ | 126.5–127 | 51.36 | 3.16 | 51.37 | 3.27 |
| Styrene | II | $\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}_2\text{BrS}$ | 142–143 | 43.86 | 2.87 | 44.06 | 3.13 |
| Vinylacetic acid | I | $\text{C}_{10}\text{H}_9\text{O}_6\text{N}_2\text{ClS}$ | 167–169 | 37.45 | 2.83 | 37.49 | 2.79 |

^a I, 2,4-Dinitrobenzenesulfonyl chloride; II, 2,4-dinitrobenzenesulfonyl bromide; III, 2-nitrobenzenesulfonyl bromide. ^b Melting points are not corrected. ^c The melting point of a mixture of the adducts of I to allyl chloride and allyl bromide was not depressed—suggesting formation of mixed crystals. Analogous behaviors appear to be involved in the adducts of I and II with cyclohexene and styrene. The melting points of the adducts of I with these olefins, previously recorded, are essentially the same (117–118° and 143–143.5°)¹ as those of the similar adducts of II (see above); melting points of mixtures of the corresponding pairs were not appreciably depressed. ^d We are indebted to Dr. A. Elek and Mr. J. Pirie for the microanalyses.

While additions of sulfonyl chlorides to olefins are already well known, formation of 2-chloroethyl 2'-bromocyclohexyl sulfide from 2-chloroethanesulfonyl bromide and cyclohexene appears to be the only recorded addition of a sulfonyl bromide to an olefin.² The adducts of 2,4-dinitrobenzenesulfonyl bromide (II) with cyclohexene and styrene, as well as the adduct of 2-nitrobenzenesulfonyl bromide (III) with 1,4-dihydronaphthalene, are now reported.

Independent proofs of structure for the products of Table I were not made. The structures of the 1:1 adducts of I and III with 1,4-dihydronaphthalene, as well as of II with cyclohexene, may be speci-

filtered, the salt cake washed with three 15-ml. portions of benzene, and the filtrate and washings combined.

Evaporation of solvent gave 7 g. (82%) of orange crystals, m.p. 103–105°. The analytical sample (m.p. 104.5–105.5°) was obtained by two recrystallizations from carbon tetrachloride.

Anal. Calcd. for $\text{C}_6\text{H}_7\text{O}_4\text{N}_2\text{SBr}$: C, 25.81; H, 1.08. Found: C, 25.96; H, 1.29.

By another route: 2,4-dinitrothiophenol⁵ (9.6 g., 0.048 mole) was added with stirring during 1.5 hours to 4.8 ml. (0.094 mole) of bromine, in 250 ml. of chloroform, in a 1-liter 3-neck flask—under anhydrous conditions. Evaporation of solvent and excess bromine gave 11.6 g. (85%) of excellent needles, melting at 101–104°. This product was

(3) N. Kharasch, G. I. Gleason and C. M. Buess, *THIS JOURNAL*, **72**, 1796 (1950).

(4) T. Zincke and F. Farr, *Ann.*, **391**, 55 (1912).

(5) C. Willgerödt, *Ber.*, **17**, 352 (1884). *Cf.* also R. W. Bost, P. K. Starnes and E. L. Wood, *THIS JOURNAL*, **73**, 1968 (1951).

(1) N. Kharasch and C. M. Buess, *THIS JOURNAL*, **71**, 2724 (1949).

(2) R. C. Fuson, *et al.*, *J. Org. Chem.*, **11**, 469 (1946).

entirely suitable for synthetic purposes. Recrystallization from carbon tetrachloride gave pure product in 75–80% yields.

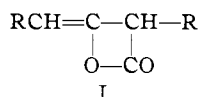
The sulfonyl bromide may be stored indefinitely in a dark bottle without noticeable decomposition; but it decomposes rapidly if exposed to bright sunlight.

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The Catalytic Hydrogenation of Alkylketene Dimers

BY CARL M. HILL, LONNIE HAYNES AND MARY E. HILL

In an earlier paper¹ experiments describing the ozonization and catalytic hydrogenation of five cyclohexyl substituted alkylketene dimers were reported. Ozonization data were in agreement with the work of Hurd and Blanchard² and structure I was accepted for the dimers. Hydrogenation yielded glycols, RCH₂-CHOH-CHR-CH₂OH.



were used. Glycols were formed as before, and derivatives (3,5-dinitrobenzoates and phenylurethans) were prepared as previously reported. The solid glycols were purified by recrystallization from ethanol. Results are described in Tables I and II.

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Constituents of *Heliopsis* Species. II. Synthesis of Compounds Related to Scabrin¹

BY MARTIN JACOBSON

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The isolation of scabrin, the major insecticidal component of the roots of *Heliopsis scabra* Dunal., was reported in the first paper² of this series. It was found to be the N-isobutylamide of an unsaturated 18-carbon straight-chain acid, containing 5 double bonds which are situated in the acid fragment in one of 4 possible combinations—namely, 2,4,8,10,14-, 2,4,8,12,14-, 2,6,8,10,14- and 2,6,10-, 12,14.

TABLE I

GLYCOLS FORMED, RCH₂-CHOH-CHR-CH₂OH

| R | Formula | °C. | B.p. | Mm. | Yield, % | No. OH | Carbon, % | | Hydrogen, % | |
|---|---|--------------|------|-----|----------|--------|-----------|-------|-------------|-------|
| | | | | | | | Calcd. | Found | Calcd. | Found |
| C ₂ H ₅ | C ₈ H ₁₈ O ₂ ^b | 82–85 | | 16 | 80 | 2.1 | 65.75 | 66.06 | 12.33 | 12.31 |
| <i>n</i> -C ₃ H ₇ | C ₁₀ H ₂₂ O ₂ ^c | 98–100 | | 12 | 56 | 1.9 | 68.96 | 68.81 | 12.64 | 12.56 |
| <i>n</i> -C ₄ H ₉ | C ₁₂ H ₂₆ O ₂ ^d | 125–127 | | 12 | 28 | 1.8 | 71.30 | 71.66 | 12.90 | 13.04 |
| <i>n</i> -C ₅ H ₁₁ ^a | C ₁₄ H ₃₀ O ₂ ^e | 128–130 | | 23 | 63 | 1.8 | 73.04 | 73.47 | 13.04 | 13.06 |
| <i>n</i> -C ₁₀ H ₂₁ | C ₂₄ H ₅₀ O ₂ | M.p. 175–176 | | | 43 | 2.2 | 77.84 | 77.34 | 13.51 | 13.59 |
| <i>n</i> -C ₁₂ H ₂₅ | C ₂₈ H ₅₈ O ₂ | M.p. 167–168 | | | 94 | 2.1 | 78.87 | 78.96 | 13.62 | 13.76 |

^a Physical constants for new ketene dimer where R is *n*-pentyl: b.p. 128–130° (8 mm.); *n*²⁰_D 1.4330; *d*²⁰₄ 0.8463. Calcd. C, 75.00; H, 10.71. Found: C, 75.41; H, 10.81. Identity, further established by conversion to 2-*n*-pentyl-1,3-nonanediol.^e ^b Reported b.p. 133–134° (15 mm.) *d*¹⁵₄ 0.9367, *n*¹⁵_D 1.4535 by V. Grignard and M. Fluchaire, *Ann. chim.*, **9**, 5 (1928). Observed *d*²⁰₄ 0.9130, *n*²⁰_D 1.4230; *M*R_D (calcd.) 42.19, (found) 41.00. ^c Reported b.p. 138–139° (1 mm.), *d*²⁸ 0.9203, *n*²⁸ 1.4442 by M. S. Kulpinski and F. F. Nord, *J. Org. Chem.*, **8**, 256 (1943). Observed *d*²⁰₄ 0.8919, *n*²⁰_D 1.4265; *M*R_D (calcd.) 51.43, (found) 50.40. ^d Literature b.p. 128–129° (1 mm.), *d*²⁵ 0.9184, *n*²⁵ 1.4570 reported by M. S. Kulpinski and F. F. Nord, footnote *c*; observed *n*²⁰_D 1.4270. ^e Reported b.p. 125–127° (0.5 mm.), *d*²³ 0.8984, *n*²³ 1.4545 by M. S. Kulpinski and F. F. Nord, footnote *c*; observed *d*²⁰₄ 0.8653, *n*²⁰_D 1.4350; *M*R_D (calcd.) 69.90, (found) 69.50.

TABLE II

DERIVATIVES OF THE GLYCOLS

| R | Formula | 3,5-Dinitrobenzoate ^a | | | | Phenylurethan ^d | | | | |
|---|--|----------------------------------|-----------|--------------------|-------------------|--|----------|--------------|--------------------|-------------------|
| | | Yield, % | M.p., °C. | Nitrogen, % Calcd. | Nitrogen, % Found | Formula | Yield, % | M.p., °C. | Nitrogen, % Calcd. | Nitrogen, % Found |
| C ₂ H ₅ | C ₂₂ H ₂₂ O ₁₂ N ₄ | 49 | 165–166 | 10.50 | 10.80 | C ₂₂ H ₂₈ O ₄ N ₂ | 53 | 124–125 | 7.29 | 7.00 |
| <i>n</i> -C ₃ H ₇ | C ₂₄ H ₂₆ O ₁₂ N ₄ | 90 | 160–161 | 9.96 | 9.94 | C ₂₄ H ₃₂ O ₄ N ₂ | 59 | 198–200 dec. | 6.80 | 6.90 |
| <i>n</i> -C ₄ H ₉ | C ₂₆ H ₃₀ O ₁₂ N ₄ | 75 | 164–165 | 9.50 | 9.52 | C ₂₆ H ₃₆ O ₄ N ₂ | 50 | 220–222 dec. | 6.36 | 6.02 |
| <i>n</i> -C ₅ H ₁₁ | C ₂₈ H ₃₄ O ₁₂ N ₄ | 74 | 163–164 | 9.06 | 9.05 | C ₂₈ H ₄₀ O ₄ N ₂ | 43 | 223–224 | 5.98 | 5.79 |
| <i>n</i> -C ₁₀ H ₂₁ | C ₃₈ H ₅₄ O ₁₂ N ₄ | 88 | 160–162 | 7.39 | 7.32 | C ₃₈ H ₆₀ O ₄ N ₂ ^b | 26 | 218–220 dec. | 4.61 | 4.87 |
| <i>n</i> -C ₁₂ H ₂₅ | C ₄₂ H ₆₂ O ₁₂ N ₄ | 63 | 164–165 | 6.89 | 6.71 | C ₄₂ H ₆₈ O ₄ N ₂ ^c | 33 | 229–230 | 4.22 | 4.21 |

^a % Nitrogen determined by micro Dumas method. ^b *Anal.* Calcd.: C, 71.62; H, 9.87. Found: C, 72.00; H, 9.75. ^c *Anal.* Calcd.: C, 75.90; H, 10.24. Found: C, 75.62; H, 10.10.

In the present work, the hydrogenation experiments were extended to six more alkylketene dimers, all prepared by the general method of Sauer.³ Experimental details were the same as in reference 1 except that ethanol was used as solvent in place of ethanol-hexane, and hydrogen pressures and temperatures were different.

Samples of 3–4 g. of dimer and 25 ml. of ethanol

(1) C. M. Hill, M. E. Hill, H. I. Schofield and L. Haynes, *THIS JOURNAL*, **73**, 166 (1952).

(2) C. D. Hurd and C. A. Blanchard, *ibid.*, **72**, 1461 (1950).

(3) J. C. Sauer, *ibid.*, **69**, 2444 (1947).

In view of the high toxicity of scabrin to house flies,² it was decided to prepare the N-isobutylamides of several of the more readily available C₁₈ acids for insecticidal testing. The acids chosen as starting materials were *cis*-9-octadecenoic (oleic), *trans*-9-octadecenoic (elaidic), 9,12-octadecadienoic (linoleic), 9,12,15-octadecatrienoic (linolenic), α - and β -9,11,13-octadecatrienoic (eleostearic) and 10,12-, 14-octadecatrienoic (pseudo-eleostearic).

(1) Report of a study made under the Research and Marketing Act of 1946.

(2) M. Jacobson, *THIS JOURNAL*, **73**, 100 (1951).