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 (neamine) 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.

THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH
NEW BRUNSWICK, N. J.

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

BY NORMAN KHARASCH, CHARLES M. BUESS AND SUMNER I. STRASHUN

RECEIVED MARCH 1, 1952

In a previous study,[1] the characterization of a series of olefins *via* 2,4-dinitrobenzenesulfenyl 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.

TABLE I

REACTIONS OF SULFENYL HALIDES WITH OLEFINS

Olefin	Sulfenyl[a] halide	Product	M.p., °C.[b]	Analyses,[d] % Calcd. C	H	Found C	H
Allyl bromide	I	$C_9H_8O_4N_2BrClS$	110–111[c]	30.40	2.27	30.48	2.32
Allyl chloride	I	$C_9H_8O_4N_2Cl_2S$	110–111	34.74	2.59	34.41	3.08
p-Chlorostyrene	I	$C_{14}H_{10}O_4N_2Cl_2S$	150–151	45.05	2.70	45.31	2.48
Cyclohexene	II	$C_{12}H_{13}O_4N_2BrS$	117–118	39.89	3.60	39.96	3.66
1,4-Dihydronaphthalene	I	$C_{16}H_{13}O_4N_2ClS$	156–157	52.68	3.59	52.71	3.71
1,4-Dihydronaphthalene	III	$C_{16}H_{14}O_2NBrS$	94–96	52.75	3.84	52.88	3.81
Indene	I	$C_{15}H_{11}O_4N_2ClS$	126.5–127	51.36	3.16	51.37	3.27
Styrene	II	$C_{14}H_{11}O_4N_2BrS$	142–143	43.86	2.87	44.06	3.13
Vinylacetic acid	I	$C_{10}H_9O_6N_2ClS$	167–169	37.45	2.83	37.49	2.79

[a] I, 2,4-Dinitrobenzenesulfenyl chloride; II, 2,4-dinitrobenzenesulfenyl bromide; III, 2-nitrobenzenesulfenyl 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 sulfenyl chlorides to olefins are already well known, formation of 2-chloroethyl 2′-bromocyclohexyl sulfide from 2-chloroethanesulfenyl bromide and cyclohexene appears to be the only recorded addition of a sulfenyl bromide to an olefin.[2] The adducts of 2,4-dinitrobenzenesulfenyl bromide (II) with cyclohexene and styrene, as well as the adduct of 2-nitrobenzenesulfenyl 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 specified 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 $ArS^{\delta+}X^{\delta-}$, suggests the most probable structures for the 1:1 adducts to the unsymmetrical open-chain olefins of Table I.

2,4-Dinitrobenzenesulfenyl 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 sulfenyl 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-dinitrobenzenesulfenyl chloride[3] and 2-nitrobenzenesulfenyl bromide.[4] The preparation of 2,4-dinitrobenzenesulfenyl bromide is given below. Additions to the olefins were made in glacial acetic acid by the general technique previously described.[1] With the sulfenyl 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 sulfenyl 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-Dinitrobenzenesulfenyl 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 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 $C_6H_3O_4N_2SBr$: C, 25.81; H, 1.08. Found: C, 25.96; H, 1.29.

By another route: 2,4-dinitrothiophenol[5] (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

---

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

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

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

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

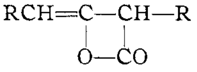
The sulfenyl bromide may be stored indefinitely in a dark bottle without noticeable decomposition; but it decomposes rapidly if exposed to bright sunlight.

Department of Chemistry
University of Southern California
Los Angeles 7, California

The Catalytic Hydrogenation of Alkylketene Dimers

By Carl M. Hill, Lonnie Haynes and Mary E. Hill

In an earlier paper[1] 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 Blanchard[2] and structure I was accepted for the dimers. Hydrogenation yielded glycols, $RCH_2–CHOH–CHR–CH_2OH$.



$$\begin{array}{l} RCH{=}C—CH—R \\ \quad\quad\;\; | \quad\;\; | \\ \quad\quad\;\, O—CO \end{array}$$

I

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 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.

Department of Chemistry
Tennessee A. and I. State University
Nashville 8, Tennessee

Table I

Glycols Formed, $RCH_2—CHOH—CHR—CH_2OH$

R	Formula	B.p. °C.	Mm.	Yield, %	No. OH	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_2H_5	$C_8H_{18}O_2$[b]	82–85	16	80	2.1	65.75	66.06	12.33	12.31
n-C_3H_7	$C_{10}H_{22}O_2$[c]	98–100	12	56	1.9	68.96	68.81	12.64	12.56
n-C_4H_9	$C_{12}H_{26}O_2$[d]	125–127	12	28	1.8	71.30	71.66	12.90	13.04
n-C_5H_{11}[a]	$C_{14}H_{30}O_2$[e]	128–130	23	63	1.8	73.04	73.47	13.04	13.06
n-$C_{10}H_{21}$	$C_{24}H_{50}O_2$	M.p. 175–176		43	2.2	77.84	77.34	13.51	13.59
n-$C_{12}H_{25}$	$C_{28}H_{58}O_2$	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^{20}_4 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^{15}_4 0.9367, $n^{15}D$ 1.4535 by V. Grignard and M. Fluchaire, *Ann. chim.*, **9**, 5 (1928). Observed d^{20}_4 0.9130, $n^{20}D$ 1.4230; *MR*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^{20}_4 0.8919, $n^{20}D$ 1.4265; *MR*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^{20}_4 0.8653, $n^{20}D$ 1.4350; *MR*D (calcd.) 69.90, (found) 69.50.

Table II

Derivatives of the Glycols

	3,5-Dinitrobenzoate[a]					Phenylurethan[a]				
R	Formula	Yield, %	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Formula	Yield, %	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
C_2H_5	$C_{22}H_{22}O_{12}N_4$	49	165–166	10.50	10.80	$C_{22}H_{28}O_4N_2$	53	124–125	7.29	7.00
n-C_3H_7	$C_{24}H_{26}O_{12}N_4$	90	160–161	9.96	9.94	$C_{24}H_{32}O_4N_2$	59	198–200 dec.	6.80	6.90
n-C_4H_9	$C_{26}H_{50}O_{12}N_4$	75	164–165	9.50	9.52	$C_{26}H_{36}O_4N_2$	50	220–222 dec.	6.36	6.02
n-C_5H_{11}	$C_{28}H_{34}O_{12}N_4$	74	163–164	9.06	9.05	$C_{28}H_{40}O_4N_2$	43	223–224	5.98	5.79
n-$C_{10}H_{21}$	$C_{38}H_{54}O_{12}N_4$	88	160–162	7.39	7.32	$C_{38}H_{60}O_4N_2$[b]	26	218–220 dec.	4.61	4.87
n-$C_{12}H_{25}$	$C_{42}H_{62}O_{12}N_4$	63	164–165	6.89	6.71	$C_{42}H_{68}O_4N_2$[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.

---

(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).

Constituents of *Heliopsis* Species. II. Synthesis of Compounds Related to Scabrin[1]

By Martin Jacobson

Received December 1, 1951

The isolation of scabrin, the major insecticidal component of the roots of *Heliopsis scabra* Dunal., was reported in the first paper[2] 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.

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 C_{18} 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).