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

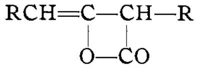
The sulfenyl bromide may be stored indefinitely in a dark bottle without noticeable decomposition; but it decomposes rapidly if exposed to bright sunlight.

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–$CH_2OH$.



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

I

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

| R | 3,5-Dinitrobenzoate[a] Formula | Yield, % | M.p., °C. | Nitrogen, % Calcd. | Nitrogen, % Found | Phenylurethan[a] 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 |
| $n$-$C_4H_9$ | $C_{26}H_{30}O_{12}N_4$ | 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.

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

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[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

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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), $\alpha$- and $\beta$-9,11,13-octadecatrienoic (eleostearic) and 10,12,-14-octadecatrienoic (pseudo-eleostearic).

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[1] Report of a study made under the Research and Marketing Act of 1946.

[2] M. Jacobson, This Journal, **73**, 100 (1951).