**Registry No.** 2, 71382-80-4; 3, 69089-11-8; 4, 71382-81-5; 5, 71382-82-6; 7, 69089-17-4; 8, 71382-83-7; 9, 69120-33-8; 10, 71382-84-8; 12, 71382-85-9; 13, 71382-86-0; 15, 71382-87-1; 17, 71382-88-2; 18, 71382-89-3; dimedone, 126-81-8; ethyl iodide, 75-03-6; LDEA, 816-43-3.

## Modified Retro-Ritter Reaction of 2-Acrylamido-2-methylpropanesulfonic Acid

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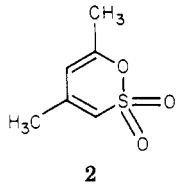
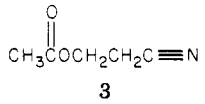
We wish to report an unusual fragmentation reaction observed with 2-acrylamido-2-methylpropanesulfonic acid (1). Warming a suspension of 1 and excess acetic anhydride on a steam bath resulted in gradual dissolution of 1 and formation of a black reaction solution. GLPC analysis indicated the presence of two major and three minor components in addition to acetic acid and acetic anhydride. 4,6-Dimethyl-1,2-oxathiin 2,2-dioxide (2) (>95%) was isolated from the reaction mixture by fractional distillation, while 3-acetoxypropionitrile (3) (41%) and 2,4-dimethylbenzonitrile (4) (4%) were isolated by preparative GLPC.[1]

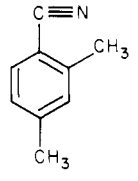
$CH_2{=}CHCONHC(CH_3)_2CH_2SO_3H$
1



2



3



4

Compound 2 was initially identified by examination of its mass and NMR spectra. The mass spectrum indicated that the molecular formula was $C_6H_8O_3S$. The proton spectrum showed two olefinic protons and two methyl groups with no vicinal coupling. A $C(CH_3){=}CHC(CH_3){=}CH$ arrangement was deduced from the undecoupled $^{13}C$ spectrum. The methyl resonance at 19.9 ppm was a quartet of doublets, indicating coupling to only one olefinic proton, while the methyl resonance at 21.2 ppm was a quartet of doublets of doublets which indicated coupling to both olefinic protons. This coupling constant pattern provided definitive assignment of the methyl groups and proved that the assignment suggested by Kausch et al.[2] for 2 was correct.

Corroboration of the structure of compound 2 and unambiguous identification of compound 3 were accomplished by comparison with authentic samples, while compound 4 was identified by comparison of its infrared and $^1H$ NMR with published spectra.[3]

The nature of the major products indicated that compound 1 had been cleaved under the reaction conditions. A possible reaction mechanism accounting for products 2 and 3 involving a modified retro-Ritter reaction as the key step is outlined in Scheme I.

Initial formation of the mixed-anhydride 5 is reasonable under the reaction conditions and has precedent.[4] The subsequent steps involved in the ultimate formation of 3, however, are somewhat less clear. It is tempting to propose nitrilium ion formation via dehydration of 5, followed by a retro-Ritter reaction forming acrylonitrile and cation 11. Conjugate addition of acetic acid to acrylonitrile would then afford 3. This is especially attractive since compound 1 is prepared by a Ritter reaction of acrylonitrile, isobutene, and chlorosulfonic acid.[5]

This sequence of events, however, is apparently not operative since repeated efforts on our part to prepare 3 from acrylonitrile under seemingly equivalent conditions, i.e., acetic anhydride with methanesulfonic acid, have failed. Thus, since acrylonitrile is apparently not a reaction intermediate, cleavage is proposed to occur subsequent to formation of isoimide 6.

The actual cleavage product, then, is isoimide 7 or its N-acetylated derivative 8. Formation of 3 from either 7 or 8 could then take place by a stepwise conjugate addition of acetic acid (path a) followed by elimination of acetic acid or acetic anhydride or, perhaps, via an intramolecular acetyl migration (path b) in which the ketenimine 10 is an intermediate.

Concerning the other major product, compound 2, Scheme I depicts a reasonably straightforward route from cation 11 involving a Prins-type ring-closure step.

The formation of 2,4-dimethylbenzonitrile (4) in the reaction could possibly be explained by a Diels–Alder reaction between 2 and some dienophile such as 7 or 8. Subsequent extrusion of sulfur trioxide, oxidation, and loss of either acetic anhydride or acetic acid could then afford 4. We have, however, been unable to obtain 4 via a Diels–Alder reaction of 2 with acrylonitrile.

### Experimental Section

**Reaction of 2-Acrylamido-2-methylpropanesulfonic Acid with Acetic Anhydride.** 2-Acrylamido-2-methylpropanesulfonic acid[6] (41.1 g, 0.200 mol) was suspended in 300 mL of acetic anhydride and heated on a steam bath. The initially colorless supernatant gradually became black as the white solid dissolved. After 100 min the heating was discontinued. Some unreacted starting material (4.2 g) was recovered from the reaction mixture by filtration.

The filtrate was evaporated in vacuo to remove acetic acid and acetic anhydride. The black oily residue that remained was examined by GLPC with *m*-tolunitrile as an internal standard. GLPC analysis (6 ft × $^1/_8$ in. column, 10% UC W-98 on 80–100 mesh Chromosorb W, 100–250 °C at 10 °C/min; injection port 270 °C; detector 320 °C) showed that five components were present other than residual acetic acid and acetic anhydride.

| component | $t_r$, min | wt % |
|---|---|---|
| 1 | 2.78 | 21 |
| 2 | 5.68 | 2 |
| 3 | 6.79 | 5 |
| 4 | 8.41 | 71 |
| 5 | 11.47 | 1 |

The reaction mixture was fractionally distilled at reduced pressure. A water-white fraction distilling at 79–112 °C (1 torr) was obtained before a white solid collected in the distilling head and condenser. The white solid, component 4 of the mixture, was identified as 4,6-dimethyl-1,2-oxathiin 2,2-dioxide (2) from its spectral properties compared with those of an authentic sample prepared according to literature procedures.[7] Components 1 and 2 were

(1) Yields were determined by an internal standard GLPC technique.
(2) M. Kausch, H. Durr, and S. H. Doss, *Org. Magn. Reson.*, **10**, 208 (1977).
(3) Infrared spectrum No. 33634 and proton NMR spectrum No. 5797, Sadtler Research Laboratories, Inc., Philadelphia, Pa.
(4) M. H. Karger and Y. Mazur, *J. Org. Chem.*, **36**, 528 (1971).
(5) D. Arlt, Netherlands Appl. 6611091 (1967); *Chem. Abstr.*, **67**, 11213 (1967).
(6) (a) H. S. Killam, U.S. Patent 3544597; *Chem. Abstr.*, **74**, 141314 (1971). (b) Available from the Lubrizol Corp., Cleveland, Ohio, under the tradename AMPS.

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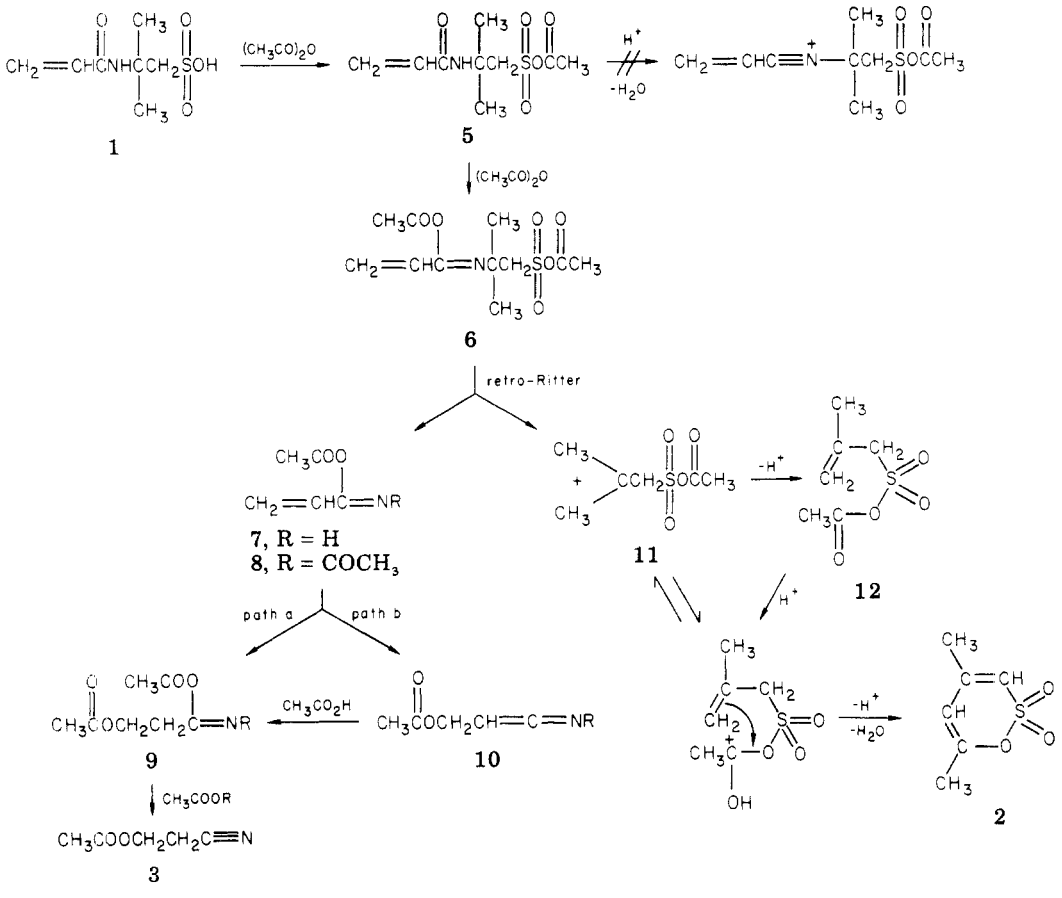
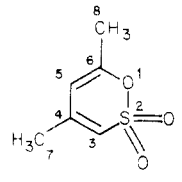
Scheme I



isolated from the fractional distillation forecut which was enriched in the two components by preparative GLPC, using the same conditions as previously described and a $^1/_4$-in.-diameter column containing the same packing. Component 1 was identified as 3-acetoxypropionitrile (**3**) by comparison with an authentic sample. Component 2 was identified as 2,4-dimethylbenzonitrile (**4**) by comparison with published spectra.[3]

The undecoupled $^{13}C$ spectrum of **2** has not been previously reported and the assignments are as follows: $\delta$ 19.9 (qd, $^1J$ = 130.1, $^3J$ = 2.7 Hz, C-8), 21.4 (qdd, $^1J$ = 129.1, $^3J$ = 5.3, $^3J$ = 3.7 Hz, C-7), 105.7 (dd heptet, $^1J$ = 167.7, $^3J$ = 6.8, $^3J$ = 4.6 Hz, C-5), 113.1 (d quintet, $^1J$ = 184.8, $^3J$ = 7 Hz, C-3), 146.1 (q, $^2J$ = 6 Hz, C-4), 156.6 (dq, $^2J$ = 7, $^2J$ = 6 Hz, C-6).



**Preparation of 3-Acetoxypropionitrile.** Acetic anhydride (51 g, 0.50 mol) and hydracrylonitrile (Aldrich) (35.5 g, 0.50 mol) were heated on a steam bath for 6.5 h. When cool, the reaction mixture was treated with solid $Na_2CO_3$ to remove acetic acid. The mixture was filtered, and the filtrate was fractionally distilled. The water-white fraction distilling at 99–102 °C (20 torr) [lit.[8] bp 110–111 °C (25 torr)] weighed 44 g (68% yield). Data for **3**: IR (neat) 2290, 1740 cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ ($Me_4Si$) 2.10 (s, 3 H), 2.65 (t, $J$ = 6 Hz, 2 H), 3.35 (t, $J$ = 6 Hz, 2 H).

(7) R. H. Eastman and D. Gallup, *J. Am. Chem. Soc.*, **70**, 864 (1948).
(8) G. C. Tesoro and S. B. Sello, U.S. Patent 3 338 883 (1967).

**Acknowledgment.** The authors thank their colleague Dr. Frederick J. Palensky for valuable discussions during the course of this work.

**Registry No.** 1, 15214-89-8; 2, 4941-84-8; 3, 927-56-0; 4, 21789-36-6; acetic anhydride, 108-24-7.

## Reaction of 3-Bromo-4*H*-1-benzopyran-4-one with β-Diketones and β-Keto Esters To Give Functionalized Furans

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*Received June 7, 1979*

4*H*-1-Benzopyran-4-ones (chromones) bearing a reactive functional group at carbon three have been receiving increased attention of late owing to the variety of heterocyclic compounds available from such substrates.[1] We

(1) U. Peterson and H. Heitzer, *Justus Liebigs Ann. Chem.*, 1663 (1976); S. Klutchko, J. Shavel, Jr., M. von Strandtmann, *J. Org. Chem.*, **39**, 2436 (1974); S. Klutchko, M. von Strandtmann, *Synthesis*, 61 (1977); C. K. Ghosh *Synth. Commun.* **8**(7), 487 (1978); C. K. Ghosh and K. K. Mukhopadhyay, *Synthesis*, 779 (1978).

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