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# A NEW METHOD FOR SELECTIVE CARBON-CARBON BOND CLEAVAGE

James A. Marshall and Heidi Roebke
Department of Chemistry, Northwestern University
Evanston, Illinois 60201 USA

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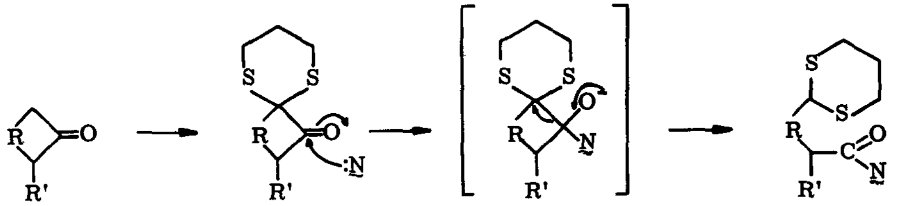
In connection with synthesis-oriented studies on ketone transposition[1] we had occasion to examine the chemistry of α-diketone monothioketals. One of our aims in that area was the development of a new non-oxidative cleavage of carbon-carbon bonds according to the following scheme:



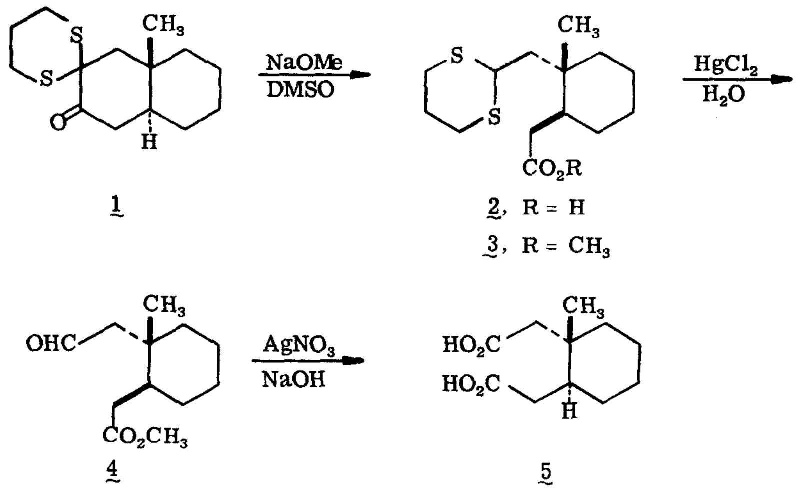
N = nucleophile

The intrinsically interesting nature of the above cleavage reaction together with its potential applicability to synthesis and degradation problems prompts this report of our initial encouraging results.

Treatment of the keto dithiane **1**[1] with excess 0.8 *M* sodium methoxide in dimethyl sulfoxide afforded, after 5 hr at room temperature, the acid **2** [74%, m.p. 110-111.5°, $\delta_{TMS}^{CCl_4}$ 12.0 (acid OH), 4.03 (dithiane α-H, triplet, J = 5.0 Hz.), and 0.88 ppm (angular $CH_3$)]. The structure of acid **2** was confirmed through its conversion, *via* the ester **3** and aldehydo ester **4**[2] [$\delta_{TMS}^{CCl_4}$ 9.56 (aldehyde CH, triplet, J = 3.0 Hz.), 3.63 ($OCH_3$), and 0.98 ppm (angular $CH_3$)] to the diacid **5**[3], m.p. 194-196°, identified by comparison with an authentic sample.

The usual methods for carbon-carbon bond cleavages require oxidizing agents which restrict the nature of R and R' (see the above scheme) in the parent molecule. Furthermore, such reactions generally fail to differentiate the resulting oxidized species. The keto dithiane cleavage scheme not only circumvents both of these potential drawbacks but leads directly to the synthetically versatile dithiane moiety through which further synthetic transformations (*e.g.* reduction, alkylation, acylation, hydrolysis)[4] should be possible.

The isolation of the acid **2** rather than the ester **3** from the methoxide-induced cleavage of keto dithiane **1** makes the nature of the attacking nucleophile problematical. While reasonable care was exercised to exclude water, we cannot rule out the possible fortuitous introduction of atmospheric moisture into the small scale reactions thus far examined. Additional work on this and other facets of the cleavage reaction is underway.



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## References

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2. Cf. E. J. Corey and D. Crouse, ibid., 33, 298 (1968).
3. G. Stork and S. D. Darling, J. Amer. Chem. Soc., 86, 1761 (1964).
4. Cf. E. J. Corey and D. Seebach, Angew. Chem., 77, 1134 (1965); D. Seebach, Synthesis, 1, 17 (1969).