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REACTIONS OF SQUARIC ACID AND SOME DERIVATIVES WITH THIONYL CHLORIDE/*N*,*N*-DIMETHYLFORMAMIDE

R. C. De Selms, C. J. Fox and R. C. Riordan
Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650, U.S.A.

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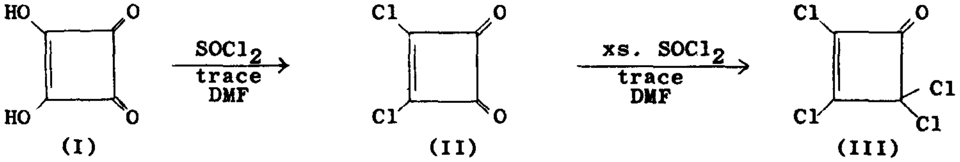
Maahs and Hegenberg in their review of the chemistry of squaric acid (I) state: "Das Säure-dichlorid der Quadratsäure, Dichlor-cyclobutendion, lässt sich aus Quadratsäure nicht herstellen." (1) Since dichlorocyclobutenedione (II) (2) is an important intermediate in the preparation of mono- and diarylated cyclobutenediones, a reinvestigation of this potential route to its synthesis was undertaken. Indeed I does not react with refluxing thionyl chloride alone. However, treatment of I with 2 molar equivalents of thionyl chloride, neat or with benzene as solvent, and catalytic amounts of *N*,*N*-dimethylformamide (DMF), at reflux for 20 min to 2 hr gave II in greater than 75% yields.



Furthermore, excess thionyl chloride and DMF under the same conditions caused an unexpected replacement of one of the carbonyl oxygens with two chlorines yielding perchlorocyclobutenone (III) (3) (76% isolated). One of the carbonyl oxygens in 1,2-diphenylcyclobutenedione was similarly replaced yielding 4,4-dichloro-2,3-diphenylcyclobutenone. (4) The last carbonyl oxygen in both cases was relatively inert to this displacement. Similar treatment of 3-phenylcyclobutenedione was complicated by allylic-type rearrangement of the expected intermediate and gave only mixtures which were not separated.

The type of reaction involved in the conversion of II to III has no analogy in the literature.(5) Since it is dependent upon the presence of DMF, the first step probably involves chloriminium assisted attack of the nucleophilic $Cl^{\ominus}$ of $ClCH{=}\overset{\oplus}{N}Me_2\ Cl^{\ominus}$ on carbonyl yielding an oxyanion which could attack either $ClCH{=}\overset{\oplus}{N}Me_2$ or $SOCl_2$, resulting in the second chlorine substitution *via* the appropriate chloroester.

Further chemical evidence for II, in addition to identity with the literature description,(2) was obtained by conversion of the crude reaction product with 1 molar equivalent of $AlCl_3$ in benzene followed by hydrolysis to 3-chloro-4-phenylcyclobutenedione (6) (64% yield). Under similar conditions perchlorocyclobutenone (III) did not undergo Friedel-Crafts acylation.

References and Footnotes

1. G. Maahs and P. Hegenberg, *Angew. Chem.*, **78**, 927 (1966).
2. G. Maahs, *Ann.*, **686**, 55 (1965).
3. Identical with Aldrich Chemical Co., No. 12,343-9.
4. Obtained in 34% yield purified, mp. 117-8°, λ_{max} (cyclohexane), 245 nm (ϵ 25,000), 313 nm (ϵ 18,000). (Found: C, 66.3; H, 3.9; Cl, 24.9. $C_{16}H_{10}Cl_2O$ requires: C, 66.5; H, 3.5; Cl, 24.5).
5. Conversions of cyclopropenones to *gem*-dichlorocyclopropenes did not require DMF as catalyst using thionyl chloride: S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 4215 (1964); phosgene: B. Föhlisch and P. Bürgle, *Tetrahedron Lett.*, 2661 (1965); or phosphorus pentachloride: Y. Kitahara and M. Funanizu, *Bull. Chem. Soc. Japan*, **37**, 1897 (1964).
6. Identical with that prepared by the method of E. J. Smutny and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 3420 (1955).