

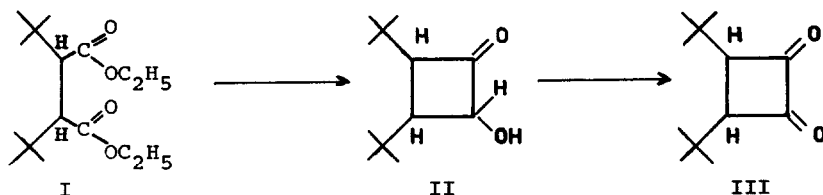
SYNTHESIS AND PROPERTIES OF 3,4-DI-t-BUTYLBUTANEDIONE

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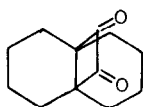
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3,4-Di-t-butylbutanedione (III) was prepared by the following route:

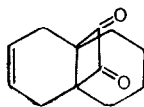


The 2,3-di-t-butylsuccinic acid ester I was prepared as described by Ebersson¹ and the mixture of dl and meso diester was used as starting material in the acyloin condensation. When toluene was used as solvent in this reaction a very good yield (90%) of hydroxy ketone II was obtained², while in xylene as solvent the yield was only 30%. From glc it appeared that only one of the diastereomers of diester I (the dl form) had reacted. The hydroxy ketone II³ is a stable white solid, mp 110-113°; it gives a 2,4-dinitrobenzoate³, mp 146.5-148°. Oxidation of II with dimethyl sulfoxide and acetic anhydride⁴ gave the diketone III³ in 55% yield as a beautiful pink solid, mp 89.5-91.5°. From the infrared spectrum (no OH absorption), the NMR spectrum [τ 7.27 (2 protons), τ 8.98 (18 protons)] and a negative FeCl₃ test, we concluded that no enol form was present in this diketone. Enolization of III might enhance the steric interference between the two large t-butyl groups.

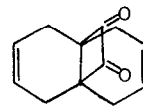
While our work was in progress, several representatives of these 1,2-cyclobutanediones (IV - VI) were described by Bloomfield^{5,6}. From earlier work, a number of perhalogen substituted 1,2-cyclobutanediones⁷ and the fully enolized phenylcyclobutane-1,2-dione⁸ were known.



IV



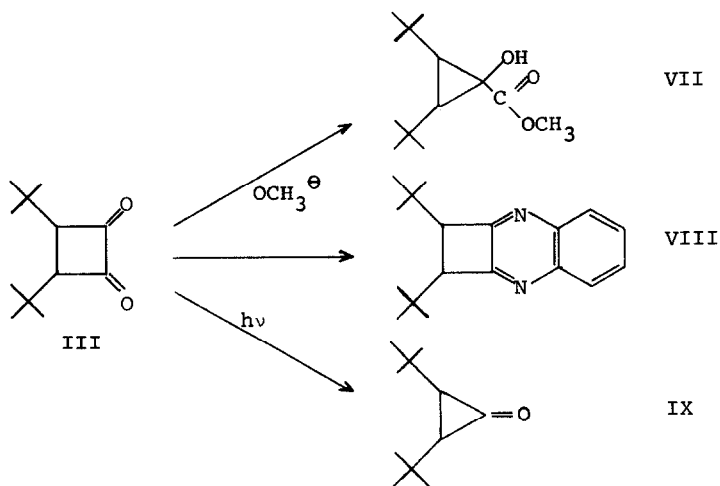
V



VI

The infrared and ultraviolet spectra of our saturated diketone III corresponded very closely to the data given by Bloomfield⁶ for his unsaturated diketone VI and not as one would expect to those for the saturated diketone IV. The ultraviolet spectrum of diketone III had its maximum at λ 536 m μ (ϵ 64) [diketone VI, λ_{\max} 537.5 m μ (ϵ 71.7); diketone IV, λ_{\max} 461 m μ (ϵ 73)]. The infrared spectrum of diketone III shows two carbonyl absorptions with equal intensities at 1758 and 1785 cm^{-1} [diketone VI, 1759 and 1794 cm^{-1} ; diketone IV, 1812 (strong), 1772 (very strong), 1785 cm^{-1} (shoulder)]⁹.

Diketone III gave a benzilic acid type rearrangement to the



hydroxy cyclopropane carboxylic acid ester VII³. A quinoxaline derivative VIII³ was formed in 60% yield when diketone III was treated with *o*-phenylenediamine in boiling acetic acid.

An imidazole derivative of III could not be obtained. Irradiation of diketone III gave the di-t-butylcyclopropanone IX¹⁰ and a polymeric product.

REFERENCES

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2. This very high yield in the cyclization to a four-membered ring of this diester, without the addition of chlorotrimethylsilane⁵, is remarkable.
3. Satisfactory elemental analytical data have been obtained for all new compounds. The diketone III is stable at 0° in the dark.
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9. Personal communication with Dr. Bloomfield led us to the conclusion that the similarity of the UV and IR spectra of III and VI is probably fortuitous.
10. J.B. Pazos and F.D. Greene, J. Am. Chem. Soc., 89, 1030 (1967).