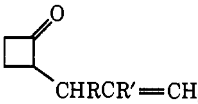
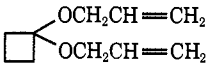
A Synthesis of α-Substituted Cyclobutanones and Its Application to the Confirmation of the Rearrangement of a Bicyclo[2.2.1]heptane to a Bicyclo[3.1.1]heptane Derivative

Sir:

Recently there has been considerable interest in methods for the synthesis of α-substituted cyclobutanones.[1] None of these methods involves substitution of cyclobutanone itself.[2] We have found that 2-allylcyclobutanone (**1**) can be conveniently prepared from cyclobutanone diallyl ketal (**2**).[3] The ketal **2**, bp 81–82° (15.5 mm), $n^{26}\text{D}$ 1.4445,[6] was prepared in 93% yield from cyclobutanone and allyl alcohol in the presence of 2,2-dimethoxypropane and *p*-toluenesulfonic acid (TSA). Heating of **2** at 185° in the presence of TSA gave **1**, bp 89–90° (72 mm), $n^{26}\text{D}$ 1.4476, in quantitative yield. The hitherto unknown, functionally substituted cyclobutanone **1** provides a potential source of a variety of α-substituted cyclobutanones, as illustrated below. The potential generality of the reaction of **2** to give **1** has been demonstrated by the successful preparation of the cyclobutanones **3** and **4** from the corresponding analogs of **2**.

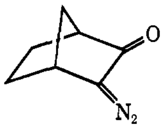


1, R = R′ = H
3, R = H; R′ = Me
4, R = Me; R′ = H



2

It has previously been reported from these laboratories[7] that one of the products formed on acid-catalyzed decomposition of 3-diazo-2-norbornanone (**5**) is the ketol **6**; this represented the first demonstration of the rearrangement of a bicyclo[2.2.1]heptane derivative to a bicyclo[3.1.1]heptane derivative.[8] However, Friedman[9] has cast doubt on the structural assignment **6**, stating erroneously that it was based solely on nmr data. We have now confirmed the assignment by the independent synthesis from **1** of 2-oxocyclobutanepropionaldehyde (**7**), the retroaldol cleavage product previously obtained from **6**.[7]



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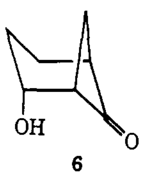

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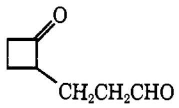

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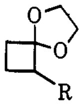

8, R = $CH_2CH{=}CH_2$
9, R = $CH_2CH_2CH_2OH$
10, R = CH_2CH_2CHO

Treatment of **1** with ethylene glycol in the presence of TSA gave the ketal **8**, bp 67–68° (7.5 mm), in 93% yield. This was subjected to hydroboration with disiamylborane followed by treatment with aqueous sodium hydroxide and hydrogen peroxide to give the alcohol **9**, which was oxidized with chromium trioxide in pyridine to the aldehyde **10**, which in turn was converted by acidic hydrolysis to **7**, bp 77–78° (1.3 mm); the overall yield of **7** from **8** was 49%. The remote possibility that **7** had undergone acid-catalyzed rearrangement to 3-oxocyclobutanepropionaldehyde is excluded by the ^{13}C nmr spectrum of the product, which shows seven distinct signals. Its ir and pmr spectra are identical with those of the product obtained from **6**.

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[1] M. Hanack, J. Häffner, and I. Herterich, *Tetrahedron Lett.*, 875 (1965); M. Hanack and I. Herterich, *ibid.*, 3847 (1966); M. Hanack, I. Herterich, and V. Vött, *ibid.*, 3871 (1967); B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **93**, 3773 (1971); H. H. Wasserman, H. W. Adickes, and O. Espejo de Ochoa, *ibid.*, **93**, 5586 (1971); J. R. Salaün and J.-M. Conia, *Tetrahedron Lett.*, 2849 (1972).

[2] *Cf.* J.-M. Conia and J.-P. Sandré, *Bull. Soc. Chim. Fr.*, 752 (1963).

[3] This method has previously been applied to cyclopentanones and cyclohexanones,[4] but not to cyclobutanones. The only related method in the cyclobutanone series is restricted to the formation of polyhalogenated compounds.[5]

[4] N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **26**, 3112 (1961).

[5] C. G. Krespan, *Tetrahedron*, **23**, 4243 (1967).

[6] Satisfactory elemental analyses have been obtained for all compounds whose boiling points are given; the ir, pmr, and mass spectra of all compounds were in accord with expectation.

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[8] Other examples of such rearrangements have been reported subsequently: C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *ibid.*, **89**, 3940 (1967); Y. Lin and A. Nickon, *ibid.*, **92**, 3496 (1970); W. Kirmse, G. Arend, and R. Siegfried, *Angew. Chem., Int. Ed. Engl.*, **9**, 165 (1970).

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Radical Intermediates in Photosubstitution Reactions of Anthraquinones

Sir:

We wish to propose a mechanism for photosubstitution reactions of aromatic compounds possessing low-lying n,π* states and to present preliminary findings which suggest occurrence of the process with substituted anthraquinones.[1]

Letsinger and coworkers[2] and Havinga and coworkers[3] have studied photosubstitution reactions of nitrophenyl ethers and acetophenones[4] with nucleophiles. These reactions appear to occur by direct nucleophilic attack on the rings of π,π* excited molecules.[3,5] Aromatic carbonyl or nitro compounds with lowest energy n,π* states are typically inert toward direct nucleophilic photosubstitution but readily undergo photoreduction initiated by hydrogen abstraction or electron transfer.[6,7] We were struck by the possibility

[1] This work was presented at the 8th Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., Nov 9, 1972.

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[7] (a) H. A. Morrison in "The Chemistry of the Nitro and Nitroso Groups," Part I, H. Feuer, Ed., Interscience, New York, N. Y., 1969, Chapter 4. (b) G. G. Wubbels, J. W. Jordan, and N. S. Mills, *J. Amer. Chem. Soc.*, **95**, 1281 (1973).