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PHOTOCHEMICAL ADDITION OF ETHYLENE TO 3-CARBOXYCYCLOHEXENONE AND THE DERIVED ESTER AND NITRILE

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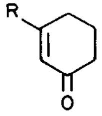
Despite continuing interest in the photochemical cycloaddition of cyclohexenones to olefins,[2-4] there are no examples of this reaction with ketones bearing strongly electron-withdrawing groups in the β position. While our concern has been primarily to establish the synthetic usefulness of such reactions, our observations may be of some general interest. We describe below the addition of ethylene to 3-carboxycyclohexenone (1a), the corresponding ethyl ester (1b),[5] and the related nitrile (1c).[6]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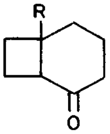
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a, R = COOH

b, R = $COOCH_2CH_3$

c, R = CN

Irradiation of a dilute solution (1.0 mg/ml) of 1a or 1b in benzene saturated with ethylene, using a 450 watt medium-pressure mercury arc (Hanovia type L, no. 679A-36) with Pyrex filter[7] gave in each case the expected cyclobutane (2a or 2b, respectively, yields >90%) within 2.5 hours. Nmr spectra indicated that adducts 2a and 2b were unchanged by treatment with aqueous base or contact with alumina, and we conclude that only *cis*-fused bicyclic systems are formed in these reactions.[2-4] Similar irradiation of 1c was less clean, but 2c could be isolated in >60% yield. Structures 2 were established by ir, nmr, and mass spectral[8] measurements, as well as elementary analysis. All are colorless, distillable oils. Further, these photoproducts were interrelated by basic hydrolysis of both ester 2b and nitrile 2c to give acid 2a, identical in each case with the acid obtained photochemically from 1a.

Carboxylic acid 1a was available from 1b by carbonate catalyzed hydrolysis in aqueous methanol and from the ethylene ketal[6] of 1c by hydrolysis in hot aqueous methanolic base followed by brief treatment with mineral acid. This compound (1a), m.p. 127-129°, was characterized by ir, uv, and nmr spectra and by elementary analysis.

These results indicate that negatively substituted cyclohexenones such as 1 can react satisfactorily with olefins. Indeed the high yields observed make the reaction synthetically quite attractive, and the way is open to preparation of a variety of bridgehead-substituted bicyclo[4.2.0]octanes, compounds of value for both synthetic and physical organic studies.

FOOTNOTES AND REFERENCES

(1) Fellow of the Alfred P. Sloan Foundation.

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(7) Similar conditions using unfiltered light are described in reference 3.

(8) Mass spectra were generously provided by Prof. R. L. Autrey and Mr. W. R. Anderson of Oregon Graduate Center, Portland, Oregon.