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THE PHOTOLYSIS OF N,N-DIMETHYLACRYLYLMETHACRYLAMIDE[*]

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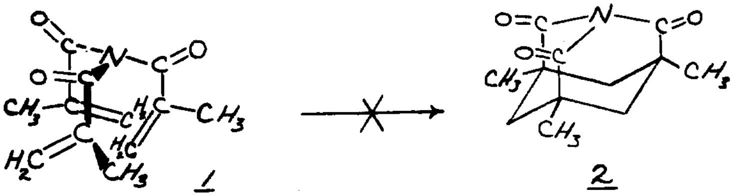
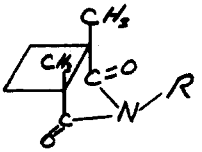
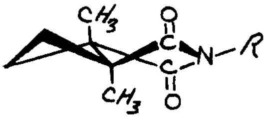
Following a known procedure for the preparation of N,N-diacylamides (1), N,N-dimethacrylylmethacrylamide, 1[**] [m.p. 102-103°, $\lambda_{max}^{CH_3OH}$ 221 mu (ϵ 22,100), ϵ_{300} = 189, $\lambda_{max}^{CHCl_3}$ 5.68, 5.81, 5.89 (shoulder) 6.07 (strong) and 11.39μ], has been obtained in 51% yield by treating methacrylyl chloride (2 moles) in chloroform solution with methacrylamide in the presence of pyridine at -20°. This N,N-diacylamide



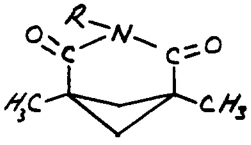
1 2



3a



3b



3c

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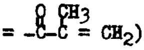
[**] Satisfactory analyses were obtained for all newly prepared compounds.

was irradiated in ether solution (2%) using a Pyrex-jacketed General Electric AH6 lamp in an attempt to prepare the cyclohexane derivative 2. The mixture obtained from the photolysis of 1 consisted of 16% unconverted 1, 18% of a high melting substance (presumably polymeric), 5% of an imide (m.p. 195-196°) and 61% of a photoisomer [m.p. 110-112° (depressed on mixing with 1), mol. wt. obsvd.: 226 (calcd.: 221)]. The infrared spectrum of the photoisomer showed bands 5.67, 5.89 and 6.11 μ (weak) while the n.m.r. spectrum* revealed a vinyl multiplet at 4.11 (2H), a methyl absorption at 8.67 (6H) and a second methyl absorption at 7.97 imposed on the B protons of an A_2B_2 pattern. The total peak area of methyl protons and the A_2B_2 pattern was equivalent to seven protons. Clearly these physical properties demonstrated that the photoisomer was not the desired 2 but rather one of the three possible cyclobutane derivatives, structures 3a - 3c (R =  $-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$). The A_2B_2 pattern for methylene protons is consistent with structure 3c, as well as the cis and trans ring-fused structures 3a and 3b, on the basis of observed(2) long-range coupling over four bonds involving protons bearing a transoid relation to one another.

Hydrogenation of the photoisomer employing a palladium on charcoal catalyst gave the dihydrophotoisomer (m.p. 70-71°, $\lambda_{max}^{CHCl_3}$ 5.58, 5.72, 5.88 μ) whose n.m.r. spectrum demonstrated the presence of an isopropyl group [methyl doublet centered at 8.77 (J = 7 cps.) and a septuplet centered at 6.92 (J = 7 cps., 1H)] and therefore confirmed that one of the three methacrylyl groups of 1 had not entered into the photolytic transformation. Other pertinent features of this spectrum were a methyl resonance at 8.64 (totaling 12 protons with the isopropyl doublet) and an A_2B_2 pattern

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*All n.m.r. spectra except that of the anhydride, 5, were run as 10% solutions in deuterochloroform using a Varian A-60 spectrometer. The anhydride was run as a saturated solution in deuterochloroform. Chemical shifts are given in p.p.m. relative to tetramethylsilane as 10.00.

centered at 7.67 (4H). Hydrolysis of the dihydrophotoisomer with 10% sodium hydroxide in methanol-water afforded a dicarboxylic acid [neut. equiv. obsvd.: 87.3 (calcd.: 86.1), $\lambda_{max}^{CHCl_3}$ 3.10-3.50 and 5.85 μ] whose melting point of 158-159.5° is different from the reported (3) melting points of either of the two isomeric dicarboxylic acids considered to be *cis*- (m.p. 134-135°) and *trans*-1,2-dimethylcyclobutane-1,2-dicarboxylic acid (m.p. 237-238°).* The n.m.r. spectrum of our dicarboxylic acid showed the carboxylic acid resonance at -1.2, the methyl resonance at 8.51, and most significantly, an AX quartet centered at 7.45 with J_{AX} = 13.5 cps. and Δ_{AX} = 76 cps. The observation that the dicarboxylic acid gives a simple AX pattern for the methylene protons is uniquely consistent with the structure of *cis*-1,3-dimethylcyclobutane-*cis*-1,3-dicarboxylic acid, 4 (R=H). Both *cis*- and *trans*-1,2-dimethylcyclobutane-1,2-dicarboxylic acids would be expected to give A_2B_2 patterns for the methylene protons as is in fact the case for *cis*- and *trans*-1,2-dichloro-1,2-dicyanocyclobutane and methyl *cis*- and *trans*-1,2-dibromocyclobutane-1,2-dicarboxylate (4). Conversion of our dicarboxylic acid to an anhydride (m.p. 200-200.5°, $\lambda_{max}^{CHCl_3}$ 5.52 and 5.66 μ) also demonstrated the cis arrangement of the carboxylic acid groups. The n.m.r. spectrum of this anhydride exhibited the characteristic A_2B_2 pattern for the methylene protons (centered at 7.76) in addition to the methyl resonance at 8.64.

Since the dicarboxylic acid obtained from the photoisomer has the structure 4 (R=H), it follows that the photoisomer must be 3c (R =  $-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$).

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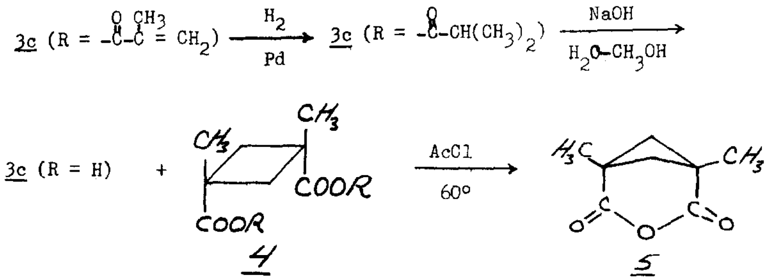
*These two acids were obtained by the hydrolysis of the dimethyldicyanocyclobutanes obtained from the thermal dimerization of methacrylonitrile (3). The dimers were considered to be the *cis*- and *trans*-1,2-dimethyl-1,2-dicyanocyclobutanes, rather than the 1,3-isomers on the basis of analogy to the thermal dimerization of acrylonitrile which produces 1,2-dicyanocyclobutanes. It is now certain that the structure assignments for the cyclobutane dimers of methacrylonitrile are correct since both dimers show a characteristic A_2B_2 pattern. The A_2B_2 pattern would not be expected should the dimers be the *cis*- and *trans*-1,3 isomers.

The transformations in terms of this structure are summarized below.



When the dihydrophotoisomer, 3c (R = $-\overset{O}{\overset{\|}{C}}-CH(CH_3)_2$) is hydrolyzed with less concentrated base, the imide 3c (R = H) (m.p. 195-196°, $\lambda_{max}^{CHCl_3}$ 2.92, 5.68, 5.76) is produced in addition to the acid 4 (R = H). This imide could be hydrolyzed to the dicarboxylic acid 4 (R = H) and was found to be identical with the imide produced from the photolysis of 1. The n.m.r. spectrum of the imide shows the characteristic A_2B_2 pattern for the methylene protons.

The particularly striking feature of the photolysis of 1 is the specificity of the photoisomerization process in affording only the cyclobutane derivatives 3c (R = $-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$, H). The path of the photoisomerization undoubtedly is controlled by stereoelectronic factors. Of the possible photoisomerization routes, only in those where the methacrylyl groups are arranged in a head-to-tail fashion would both the steric interference of approaching groups and the degree of twisting of the π-orbital of the conjugated methacrylyl groups be minimized in the transition state(5) A Dreiding model of 1 shows these conditions are met best in the arrangement of methacrylyl groups leading to 3c.

A second noteworthy aspect of the work reported herein is the difference in the type of methylene n.m.r. resonance exhibited by the bridged cyclobutanes (amides, imide, and anhydride) and non-bridged cyclobutanes [dicarboxylic acid and dimethyl ester, 4 (R = CH_3) ($\lambda_{max}^{CCl_4}$ 5.77 μ)]. While the bridged cyclobutanes give A_2B_2 patterns, the non-bridged cyclobutanes give simple AX quartets. This result provides an interesting example of the dependence of long-range coupling on geometry, specifically on the puckering of the cyclobutane ring with the resulting development of a transoid relation of protons. An attempt was made to observe the dimethyl ester 4 (R = CH_3) in its two puckered conformations. However, the n.m.r. spectrum determined at 30° and -50°* in deuterochloroform were essentially identical; both spectra exhibited an AX quartet centered at 7.53 (J_{AX} = = 13.5 cps., Δ_{AX} = 66 cps.). The spectrum determined at -50° showed no signs of the widening of lines nor the development of a complex pattern between the inner two lines of the AX quartet.

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*Attempts to examine the dimethyl ester in carbon disulfide solution at -100° failed because the solutions unexpectedly formed a glass at this lower temperature.

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