Tetrahedron Letters No. 22, pp 1951 - 1954.
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0040-4039/79/0522-1951$02.00/0

REGIOSELECTIVE PHOTOCHEMICAL CYCLOADDITIONS OF 2-TRIMETHYLSILYLCYCLOPENTENONE

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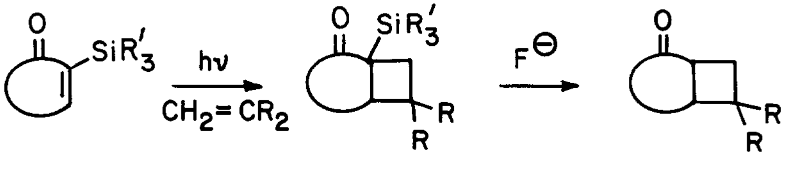
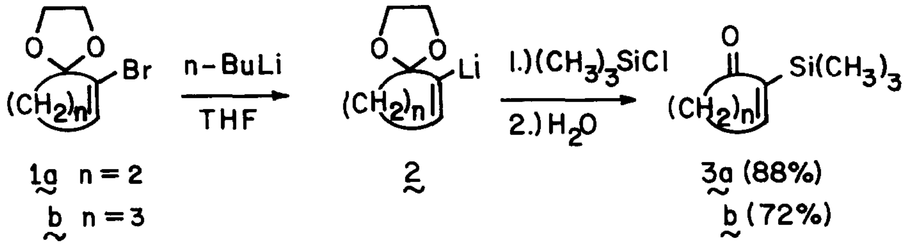
Summary: Photocycloadditions of 2-trimethylsilylcyclopentenone to isobutylene, methylene cyclohexane, and isopropenyl acetate using stannous chloride-filtered light affords regiospecifically the head-to-tail cycloadducts. Desilylation of these compounds affords the respective cycloadducts of cyclopentenone in good yield.

While photochemical cycloadditions of cyclic enones to olefins have been of extensive value in organic synthesis, the low regioselectivity in the reactions with simple olefins has detracted from the synthetic method. Thus, photocycloaddition of cyclopentenone to propene[2] shows virtually no regioselectivity while its reactions with isobutylene[3,4] afford a low yield of cycloadducts in the ratio 2.6:1[5] (head-to-tail:head-to-head). One approach to circumvent this synthetic complication would utilize α-substituted enones which undergo regiospecific addition. This would be followed by cleavage of the substituent under mild conditions to afford cycloadducts of the parent cycloalkenone. A trialkylsilyl-substituted system seemed an interesting case since photocycloaddition followed by treatment with fluoride ion would achieve the overall objective (Scheme). We report here the effect of a trimethylsilyl group in directing regiospecific photocycloaddition of cyclopentenone and the desilylation of these adducts under mild conditions to products of the parent system.

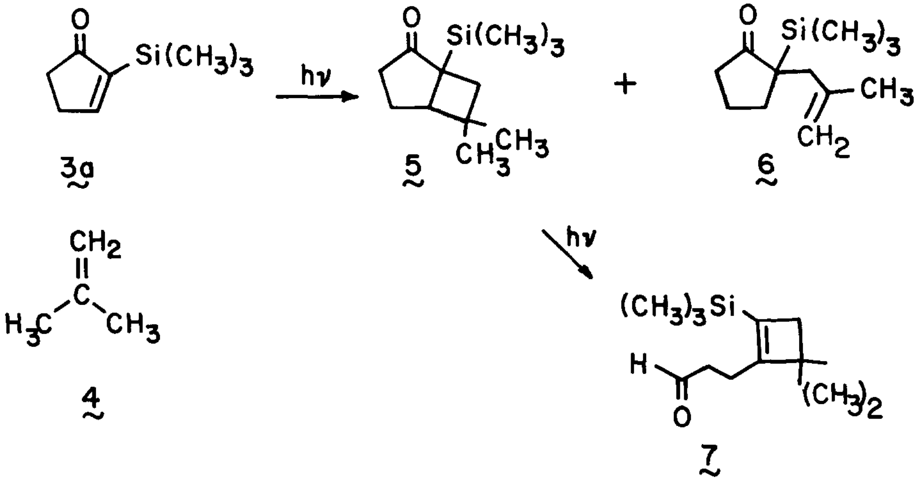


Scheme. Sequence for Regiospecific Photocycloaddition

The title compound was prepared by utilization of the anion 2 in analogy with our recent studies of 2-lithioquinone bisketals.[6,7] Metalation of 1a followed by treatment with trimethylsilyl chloride (2 equiv), addition of water, and workup afforded 3a (bp 60-62° C/5 torr). Similarly, 3b (mp 40-41.5° C) was obtained in 72% yield. Preliminary studies of 3a and isobutylene afforded three products [5 (51%), 6 (18%), and 7 (16%)][8] when irradiated with Pyrex-filtered light from a 450-watt Hanovia medium-pressure source. However, time



dependency studies of the product ratios suggested 7 was a secondary irradiation product; indeed, 7 was the major product on extended irradiation of 3a and isobutylene or of 5.



Utilization of a 0.4 M stannous chloride-filter solution circumvents the problem of secondary irradiation[9] (Figure), and reaction afforded an 82% distilled yield of 5 and 6 (ca. 80:20). While 5 and 6 could be separated by silica gel chromatography, it is more expedient to desilylate the mixture and separate the two products. Gram quantities of the cycloadduct are readily available by this procedure.

The problem of secondary irradiation being solved by use of the stannous chloride filter, a number of photocycloadditions of 3a to representative olefins were examined as well as the desilylations of the cycloadducts. In all

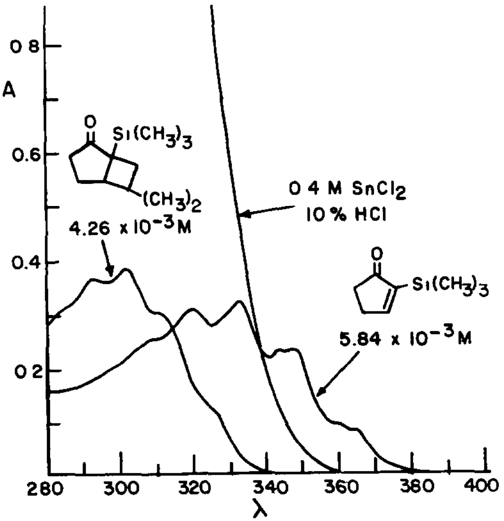
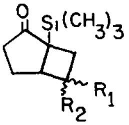
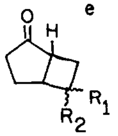


Figure. UV Spectra of 3a, 5, and $SnCl_2$ Solution cases the reactions were characterized by good yields (not optimized) of easily purified cycloadducts which were readily desilylated under mild conditions. Unfortunately, the directing effect of the trimethylsilyl group is not sufficient to afford regiospecific reactions with monosubstituted olefins (i. e., propene), and the cyclohexenone analog, 3b does not undergo photocycloaddition to isobutylene under our reaction conditions.

Table. Photocycloaddition and Desilylation Results[a]

3a (M)	Olefin (M)	 [b]	 [e]
0.02	$CH_2=C(CH_3)_2$ (1.25)	5 (51%), 6 (18%), 7 (16%)[c]	74%
0.04	$CH_2=C(CH_3)_2$ (2.49)	5 (66%), 6 (16%)	--
0.02	$CH_2=$⬡ (0.22)	$R_1 = R_2 = -(CH_2)_5-$ (76%)	66%
0.05	$CH_2=CH_2$ (--)	$R_1 = R_2 = H$ (58%)	--
0.02	$CH_2=C(CH_3)(OAc)$ (1.45)	$R_1 = CH_3$, $R_2 = OAc$ (70%)[d]	80%
0.38	$CH=CH(CH_3)$ (3.88)	mixture of regioisomers (87%)	76%

[a] Yields have not been optimized for the photocycloadditions or the desilylations. Compound purity and structure were established by VPC, IR, PMR, exact mass measurement, and ^{13}C NMR.

[b] Irradiations were conducted using light from a 450-watt Hanovia medium pressure source with the immersion well filled with 0.4 M $SnCl_2$ in 10% HCl (path length ~5 cm). Irradiations were conducted by placing the material to be irradiated in pentane alongside the light source in a 0 °C bath.

[c] Pyrex filter.

[d] Only one stereoisomer has been detected, mp 45-48 °C.

[e] Desilylations were performed by stirring a solution of cycloadducts in DMSO with 1.5 equiv of $KF \cdot 2H_2O$ for 3 h. Dilution with water followed by extraction with ether afforded the desilylated products.

The ready availability of large quantities of 3a[10] together with its higher yields and better regioselectivity in cycloaddition reactions than cyclopentenone indicates that it is much preferred to the latter compound for many photocycloadditions. Presumably, this would also be true for congeners of 3a. Furthermore, facile procedures for elimination of β-silyl derivatives suggest utility of these adducts in the regioselective synthesis of bicyclic olefins.[11]

Acknowledgment. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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8. Compounds 5 and 6 were identified by desilylation with potassium fluoride followed by comparison of the compounds with authentic samples. Compound 7 was assigned its structure on the basis of spectroscopic data: 2720 ($\mathrm{C}\overset{O}{\underset{H}{}}$), 1725 ($\rangle$C=O), and 1610 ($\rangle$C=C$\langle$) cm^{-1}; 0.00 δ (9H, s), 1.10 (6H, s), 2.10 (2H, str, br, s), 2.4 (4H, str, br, s), and 9.68 (1H, s).

9. This problem has apparently occurred in at least several cyclopentenone photocycloadditions: P.E. Eaton, J. Amer. Chem. Soc. 84, 2454 (1962); T.J Cantrell and J.S. Soloman, ibid. 92, 4656 (1970); G.L. Lange, H.M. Campbell, and E. Neidert, J. Org. Chem. 38, 2117 (1973); see also R. Srinivasan, Advan. Photochem. 1, 83 (1964).

10. A 250-ml three-necked round-bottomed flask was equipped with an addition funnel, overhead stirrer, and N_2 inlet. To the dry flask was then added 20.4 g (0.10 mol) of 1a and 80 ml of freshly distilled anhydrous ether. After cooling to -70°C, 65 ml of 1.63 M n-BuLi/hexane solution was added over a period of 30 min. The reaction was warmed to 0°C at which time the solution turned cloudy white. After recooling to -70°C, 21 g (0.20 mol) of trimethylsilyl chloride was added and the reaction warmed to RT. A white precipitate formed which dissolved when the reaction was quenched with 20 ml of H_2O. Workup followed by distillation (15-cm Vigreux column) afforded 13.2 g (88%) of 3a, bp 60-62°C (5 mm): NMR (CCl_4) δ 0.00 (9H, s), 1.93-2.20 (2H, m), 2.35-2.65 (2H, m), and 7.50 (1H, t, J = 3 Hz).

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(Received in USA 3 January 1979)