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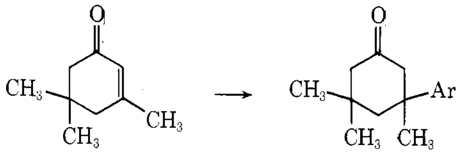
Heteroatom-Directed Photoarylation. A New Method for Introduction of Angular Carbon–Carbon Bonds

Summary: Photocyclization–rearrangement of cyclic 2-thioaryloxyenones to annelated dihydrothiophenes and subsequent desulfurization give 3-arylcycloalkanones in high overall yield.

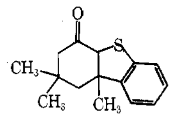
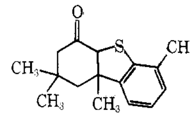
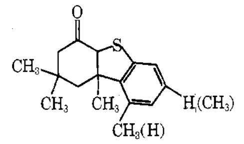
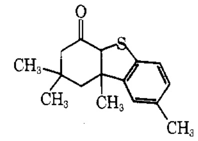
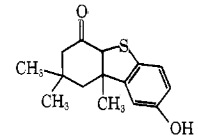
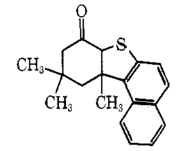
Sir: Introduction of an aryl substituent at a carbon atom β to a carbonyl group by conjugate addition of organocopper reagents to α,β-unsaturated carbonyl substrates has received considerable attention, *e.g.*, **1** → **2**.[1] Unfortunately, copper catalyzed reactions of arylmagnesium halides with α,β-unsaturated ketones usually give mixtures of 1,2- and 1,4-addition products. Conjugate addition may be more effectively performed by use of stoichiometric organocopper reagents prepared from an aryllithium and cuprous iodide; however, the required aryllithium may not always be obtainable. Furthermore, a two- or threefold excess of organocopper reagent is normally required for satisfactory conjugate addition and significant quantities of dimeric by-products may arise from coupling of the organocopper reagent.


1 2

In this paper, we report new methodology for the efficient and experimentally simple introduction of an aromatic nucleus β to a carbonyl group. The key step in the process involves the photocyclization–rearrangement of 2-thioaryloxyenones to dihydrothiophenes, *e.g.*, **3** → **5**.

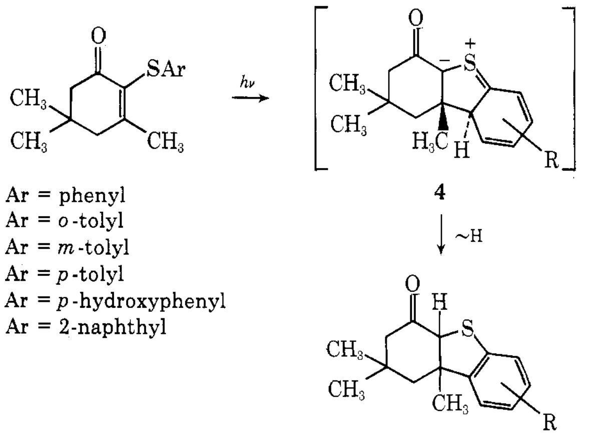
Cyclic 2-thioaryloxyenones **3** were prepared[2] in 92–98% yields by the potassium hydroxide catalyzed reaction of 1 equiv of aryl mercaptan with 2,3-epoxy-3,5,5-trimethylcyclohexanone.[3] Pyrex-filtered irradiation of **3** in benzene–methanol solution (3:1) in a conventional preparative photoreactor gave dihydrothiophenes **5** in excellent yield, Table I. This process presumably occurs by conrotatory photocyclization[4] in the excited state of **3** to give the intermediate thiocarbonyl ylide **4**, which suffers 1,4-hydrogen migration to give dihydrothiophene **5**.[5]

Table I
Photocyclization of 2-Thioaryloxyenones 3 to Dihydrothiophenes 5 and Desulfurization to 3-Arylcyclohexanones 2

2-Thioaryloxyenone	Dihydrothiophene 5 formed	% yield of 5 [a]	% yield of 2 [a]
3a		91	85
3b		88	87
3c		92 [b]	
3d		84	86 [c]
3e		83	83
3f		89 [b]	50

[a] Represents isolated yield of distilled or crystallized product. [b] Ratio of isomers is 70:30. [c] Product identical with that obtained by desulfurization of **5b**.

The conversion **3** → **5** in all cases examined except **3c** is completely regioselective and is applicable to large-scale synthesis. The following procedure for preparation of **5a** is representative. A solution of **3a** (70.4 g) in benzene (1500 ml) and methanol (500 ml) was placed in a photoreactor fitted with a water-cooled immersion well containing a 450-W high-pressure mercury arc lamp. Dry argon was



3a, Ar = phenyl
b, Ar = *o*-tolyl
c, Ar = *m*-tolyl
d, Ar = *p*-tolyl
e, Ar = *p*-hydroxyphenyl
f, Ar = 2-naphthyl

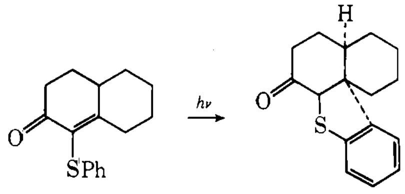
passed into the solution for 30 min prior to and during irradiation, and, after 20 hr, <0.5% **3a** was present in the nearly colorless reaction mixture (vpc analysis). Evaporation of solvent and crystallization from ether–petroleum ether gave **5a** (63.7 g, mp 80–82°).

Conversions of **5** to substituted 3-arylcyclohexanones **2** were best accomplished by desulfurization with freshly prepared Raney nickel in refluxing ethanol solution. While partial to complete hydrogenation of the carbonyl group in **5** accompanied desulfurization, treatment of the crude desulfurization product with Jones reagent gave ketone **2** in good overall yield, Table I.

No reduction of the aromatic ring occurred in **5a–e**; however, desulfurization of **5f** with Raney nickel or nickel boride[6] resulted in extensive reduction of the naphthalene ring. Refluxing the desulfurized ketone with excess dichlorodicyanobenzoquinone in benzene solution gave 3-(α-naphthyl)-3,5,5-trimethylcyclohexanone (**2f**) in moderate yield.

An advantage of photoarylation is demonstrated by the conversion of phenol **3e** to **2e** in 70% overall yield. This result is interesting because conjugate addition of organocopper reagents derived from *m*-bromophenol has not been successful.[7]

The stereochemical control possible with photoarylation is exceptionally high as demonstrated by conversion of 2-thiophenoxyoctalone **6** to dihydrothiophene **7**. Pyrex-filtered irradiation of **6** in benzene–methanol solution gave a single dihydrothiophene **7** (nmr, tlc, and vpc analysis) isolated as an oil in >95% yield. When desulfurized, **7** gave only *cis*-9-phenyldecalone-2 in high yield, which was identified by comparison with the product previously characterized from addition of lithiumdiphenylcuprate to $\Delta^{1(9)}$-octalone-2.[8] Exclusive formation of *cis*-decalone **7** in the photocyclization of **6** may be the result of preferential cyclization from the least hindered face of the enone system in **6**. This hypothesis is being tested in other fused-ring systems.



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