The Photochemical Reactivity of Some Benzoylthiophenes. II. Photocycloaddition

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The photochemical reactivity of 2- and 3-benzoylthiophene and their *para*-cyano and *para*-methoxy derivatives, upon irradiation in the presence of isobutylene, has been studied. All six ketones undergo photocycloaddition at the carbonyl group under these conditions. The resulting oxetanes are thermally unstable; they eliminate formaldehyde and yield the 1-aryl-1-thienyl-2-methylpropene. The existing generalizations, potentially useful for predicting this photochemical reactivity, are reviewed.

On a étudié la réactivité photochimique des benzoyl-2 et -3 thiophènes et de leurs dérivés *para*-cyano et *para*-méthoxy lors de leur irradiation en présence d'isobutylène. Dans ces conditions les six cétones subissent une photocycloaddition impliquant le groupement carbonyle. Les oxétanes qui en résultent sont thermiquement instables; ils expulsent de la formaldéhyde et fournissent les aryl-1 thiényl-1 méthyl-2 propènes. On passe en revue les généralisations déjà proposées et qui sont potentionnellement utiles pour prédire cette réactivité photochimique. [Traduit par le journal]

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Introduction

A goal of the organic photochemist is to be able to predict the photochemical reactivity of a molecule based, preferably, upon the structure of the ground state and reasoning by analogy with related compounds. The knowledge of the nature of the accessible electronic excited states, gleaned from spectroscopic studies, may also be useful. Extensive efforts have, in fact, resulted in several generalizations with regard to the photochemical reactivity of carbonyl compounds. In this paper we review these generalizations and compare the predictions with the observed reactivity of 2- and 3-benzoylthiophene and their para-cyano and para-methoxy derivatives upon irradiation in the presence of isobutylene. In addition, the few previous reports concerning the photochemical reactivity of these and similar thiophene ketones will be reviewed in perspective.

Part I of this series reported results of the study of the u.v. absorption and phosphoresence emission spectra of these ketones which made possible the assignment of electronic configuration and energy for several of the electronic excited states (1). The lowest excited singlet in all cases in nonpolar solvents, is an n,π^* state of the carbonyl chromaphore. The lowest triplet of the 2-benzoylthiophene derivatives (1*a*-*c*) has π,π^* character and is assigned to the 2-thienoyl moiety. The 3benzoylthiophene derivatives (2a-c) have an n,π^* triplet, associated with the carbonyl group, of lowest energy. These results are summarized in the partial state diagrams for these molecules which are shown in Fig. 1.



FIG. 1. Partial energy diagrams (a) for the 2-benzoyl-thiophenes, (b) for the 3-benzoylthiophenes.

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Results

Irradiation of the 2- and 3-benzoylthiophenes studied (1a-c and 2a-c) in the presence of isobutylene, results in photocycloaddition at the carbonyl group. The oxetanes (3a-c and 4a-c), formed initially, are thermally unstable; they eliminate formaldehyde and give the olefins (5a-cand 6a-c). We were unable to isolate any of the oxetanes but could detect and characterize, by n.m.r., all but two (3a and b).

The structures assigned to the olefins 5a-c and 6a-c are consistent with the n.m.r. spectra. In the case of 5a, b and 6a, b, the structures have been firmly established by comparison with authentic samples synthesized by dehydration of alcohols made by the Grignard reaction of isopropyl magnesium bromide with the ketones 1a, b and 2a, b.

We found no evidence of photoisomerization of the thiophene ring in the product olefin or in recovered starting ketone. No cyclobutane products which might have arisen from photocycloaddition of the olefin to the thiophene ring were detected. However, the material balance was not always good and the n.m.r. spectrum of the crude reaction mixture indicated that in some cases products, which were not characterized, were formed in small amounts.

Discussion

The possible photochemical reactions of the benzoylthiophenes (1a-c, 2a-c) which must be considered include (1) photocycloaddition to the carbonyl group to give the oxetane; (2) photocycloaddition to the thiophene ring to give the cyclobutane, and; (3) photoisomerization of the

thiophene ring. Obviously the possibility also exists that no photochemical reaction will occur. Of these possibilities photocycloaddition to the carbonyl group is the reaction observed. Armed with the considerable experience obtained from studies of related carbonyl compounds, would this photochemical reactivity have been predictable?

On the basis of structural considerations alone, and in view of the similarity of the ground state reactivity of thiophene and benzene, one might predict photochemical reactivity parallel to that observed for the analogous benzophenone derivatives. Benzophenone and 4,4'-dimethoxybenzophenone are known to form the oxetanes upon irradiation in the presence of isobutylene (2). The photocycloaddition of 4,4'-dicyanobenzophenone had not been previously studied; it also forms the oxetane under these conditions.³ Thus, this first approximation, while correct in this instance, is certainly fortuitous in view of the difference in the nature of the lowest triplets for the 2- and 3benzoylthiophene derivatives assigned on the basis of the spectroscopic study (1).

One generalization of photochemical reactivity of carbonyl compounds that is widely accepted is that carbonyl singlet and triplet n,π^* states are much more reactive toward photocycloaddition

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³The phosphoresence emission from 4,4'-dicyanobenzophenone (MCIP at 77 °K) has the vibrational structure (0-0 - 0-1 separation = 1640 cm⁻¹) and is typical of an n, π^* triplet. The triplet energy ($E_T = 63.4$ kcal mol⁻¹) is low compared with that of benzophenone (68.6 kcal mol⁻¹) and 4-cyanobenzophenone (66.4 kcal mol⁻¹) (3) and reflects the strong electron withdrawing nature of the cyano group.

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with olefins to give the oxetane than are states of other electronic configuration. Since the n,π^* singlet is usually short lived, due to rapid intersystem crossing, the n,π^* triplet is usually the reactive state in these reactions. A corollary therefore is, carbonyl compounds which emit from an n,π^* triplet are generally reactive in this reaction. It should be made clear that "reactivity" in this context refers to the rate controlling steps leading to cycloaddition products and should not be interpreted to mean high quantum yield or even good yield of product, since many complicating factors (eg. reversible formation of an intermediate, lifetime of the excited state, competing reactions with comparable rates, etc.) are not taken into account. Nevertheless, this corollary has been used and the products obtained from a large number of carbonyl compounds can be correlated with triplet emission (2, 4). However, the products obtained upon irradiation of ketones 1a-c belie this generalization since the phosphorescence emission from these ketones is clearly π,π^* in nature.

With some carbonyl compounds, aliphatic ketones for example, the intersystem crossing rate is known to be slow; bimolecular reactions of the n,π^* singlet are then observed (5). The n,π^* singlet could be responsible for the reactivity of 1a-c if intersystem crossing is slow enough. While we have no evidence on this point, the positioning of the excited states summarized in the energy level diagram (Fig. 1*a*), with the π,π^* triplet rather close in energy and below the n,π^* singlet $(E_{n,\pi^{*1}} - E_{\pi,\pi^{*3}} = 4300 \text{ cm}^{-1})$, should lead to a rapid intersystem crossing process so that a bimolecular reaction would be precluded (6). This need not be the case; the energy level diagram for 2-naphthaldehyde is similar to that for 1a-c, (the separation of the π,π^* triplet and n,π^* singlet is, however, significantly larger $(E_{n,\pi^{*1}} - E_{\pi,\pi^{*3}})$ 7000 cm⁻¹)), and photocycloaddition has recently been shown to occur at the carbonyl group and via an n,π^* singlet reaction (7).

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Ketones 1a-c join a growing list of carbonyl compounds, the photochemical reactivity of which is not predictable by attributing characteristic reactivity to the accessible excited states. Furthermore, advances made in understanding the mechanism(s) of the photocycloaddition reaction force a reevaluation of this generalization, particularly when attempting to predict synthetic utility.

It seems a priori reasonable that the most

rigorous, and perhaps least useful (in view of the amount of information required), generalizations of photochemical reactivity will be those based upon extrapolation of characteristic reactivity in different types of reactions. For example, carbonyl compounds that are efficiently reduced, by hydrogen abstraction by the carbonyl oxygen atom, upon irradiation in the presence of hydrogen donors should be expected to undergo photocycloaddition to olefins to form oxetanes. Furthermore, intramolecular hydrogen abstraction, leading to Norrish type II cleavage or photoenolization of β -alkyl- α , β -unsaturated carbonyl compounds should compete with oxetane formation. This generalization assumes an "alkoxy radical-like" state, regardless of electronic configuration, is responsible for these reactions. There is little fundamental basis for this generalization since it is now known that several different types of intermediates can precede any radical intermediate that may be involved. Still, the products obtained from a large number of carbonyl compounds can be predicted on this basis.

There have been very few reports concerning the photochemical reactivity of thiophene carbonyl compounds. For alkyl thiophene ketones, enough is known so that a consistent reactivity pattern seems established. Both 2- and 3-acetylthiophene are known to be stable to irradiation in isopropanol (8). Neckers and co-workers have recently found that *n*-propyl-2-thiophene ketone and *n*-propyl-3-(2,5-dimethylthiophene) ketone⁴ do not undergo the Norrish type II reaction (9). Thus, these ketones are unreactive toward hydrogen abstraction and are not to be expected to give the oxetanes upon irradiation in the presence of olefins.

The photocycloaddition of 2-acetyl thiophene to tetramethylethylene and isobutylene, shown in Scheme 2, has recently been studied (10). The products were reported to be the cyclobutanes which result from cycloaddition of the olefin to the 2,3-position of the thiophene; no oxetanes were detected.⁵

⁴A cautionary note should be made with regard to the expected similarity between the excited states of 3-thiophene ketones and 3-(2,5-dimethylthiophene) ketones. While 3-benzoylthiophene emits from the carbonyl n,π^* triplet, the emission from 3-benzoyl-2,5-dimethylthiophene is very different and is π,π^* in nature.

⁵In a private communication, Dr. Cantrell has expressed doubt concerning the structure assignment of some of the adducts reported in this preliminary communication (10).

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The only alkylthiophene ketone for which an emission spectrum is reported is 2-acetylthiophene. In this case the lowest triplet has been assigned the π,π^* configuration (10). There is good reason to expect the triplet of *n*-propyl-2thiophene to be similar to that of 2-acetylthiophene. It seems likely, in view of the small separation of the n,π^* and π,π^* triplets in 3-benzoylthiophene that the lowest triplet of 3-alkylthiophene ketones will also have the π,π^* configuration. Thus, the lack of hydrogen abstraction by the carbonyl oxygen and the lack of photocycloaddition to the carbonyl group are consistent with predictions based on characteristic reactivity and on the electronic configuration of the excited state.

The reactivity of 2- and 3-benzoylthiophene upon irradiation in hydrogen donating solvents is far from clear. Predictions based on the photocycloadditions reported here would be for hydrogen abstraction by the carbonyl oxygen to occur. Traynard and Blanchi have studied the reactivity of 2- and 3-benzoylthiophene upon irradiation in isopropanol (11). They report quantum yields for the disappearance of the ketone of 0.17 for 2-benzoylthiophene, and 0.25 for 3-benzoylthiophene compared to 1.23 for benzophenone. However, the products of these reactions, which they presumed to be the pinacols, were not isolated and were characterized only by u.v. spectra. Neckers, on the other hand, has been unable to detect photoreduction products from 2-benzoylthiophene under comparable conditions (9). Further work is required to define the reactivity of these ketones toward hydrogen abstraction; it seems clear, however, that the reaction will not be useful for synthesis of the reduction products and, that if hydrogen abstraction does occur, the reaction is much less efficient than with benzophenone.

There was one previous report of a photocycloaddition reaction between 2-benzoylthiophene and an olefin, isobutylene. Cantrell reported photocycloaddition to give the cyclobutane analogous to those obtained with 2-acetylthiophene; however, the product was not isolated and characterized⁵ (10). If the product is in fact the cyclobutane, the difference in conditions which lead to cyclobutane vs. oxetane are not yet clear.

There are several reported examples of positional isomerization of substituted thiophenes. This reaction has been extensively studied by Wynberg and Kellogg and their co-workers and has recently been reviewed (12). The interchange of the thiophene carbons 2 and 3 of alkyl- and aryl-substituted thiophenes occurs via the intermediate cyclopropenyl thioketone or thioaldehyde and is a fairly general reaction which appears to involve the lowest singlet (π , π *) state. This reaction is apparently inhibited by carbonyl substitution; thiophene aldehyde and acetylthiophene do not photorearrange (13). This correlation is strengthened by the lack of photoisomerization of 1*a*-*c* and 2*a*-*c*.

The qualitative differences in stability of the oxetanes 3a-c, 4a-c, toward loss of formaldehyde, encountered during attempted isolation indicates a decomposition mechanism in which positive charge develops on the benzylic, thienylic carbon. The two oxetanes which we are unable to detect, 3a and b, are those which potentially form the most stable carbonium ion while the relative stability of 4c is a reflection of the electron withdrawing capability of the para-cyano group. This behavior has precedence since 2,2-di(4-methoxyphenyl)-3,3-dimethyloxetane is difficult to isolate; the olefin is obtained in high yield (2). The σ^+ values for 2- and 3-thienyl (-0.85 and -0.49) compared with σ^+ for methoxy -0.78), gleaned from solvolysis studies, indicate an ability of the thiophene ring to stabilize an adjacent carbonium ion (14).

Conclusions

The state diagrams for the 2- and 3-benzoylthiophenes indicate significant differences in the

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relative positions of analogous electronic excited states; in particular 1a-c have a lowest triplet of π,π^* character while 2a-c have an n,π^* triplet of lowest energy. Nevertheless, the qualitative behavior of both series upon irradiation in the presence of isobutylene is the same, photocycloaddition at the carbonyl group. Therefore, for synthetic purposes, the generalization of photochemical reactivity based upon the spectroscopic identification of accessible excited states is not yet useful.

A question is raised concerning the adequacy of predictions based upon reactivity in different types of reactions. Part III of this series reports the extension of this study to 2-benzoyl-3-methylthiophene and 2-(2-methylphenyl)thiophene ketone where photoenolization would be predicted to compete with photocycloaddition. In fact, while photoenolization cannot be observed, photocycloaddition of olefins to these ketones does occur.

Experimental

General

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The synthesis of the ketones 1a-c and 2a-c and the description of the general experimental approach were reported in Part I (1). Irradiations were carried out using a Hanovia 450-W medium-pressure mercury vapor lamp (679A36) in a quartz cooling jacket which was immersed in a constant temperature bath at 10°. The samples, contained in sealed quartz tubes (20 mm diameter) having a volume of 40 ml, were arranged around the lamp at a distance of 25 nm; they were not degassed.

Irradiation of 2-Benzoylthiophene (1a) with Isobutylene

2-Benzoylthiophene (0.16 g) was dissolved in benzene (30 ml) in a quartz irradiation tube and cooled in an ice bath. Isobutylene was bubbled through the solution until a gain in weight of 4 g was observed and the tube was sealed with a rubber cap. The sample was irradiated at 10° for 16 h, an aliquot was withdrawn, and after removal of the benzene and isobutylene the n.m.r. spectrum of the mixture was taken. This spectrum showed complex absorption in the aromatic region (7.94–6.65 p.p.m.) and aliphatic region (2.3–0.7 p.p.m.) with two sharp singlets at 1.98 and 1.68 p.p.m. Irradiation for longer periods caused little further change.

Chromatography of the total reaction mixture after removal of the benzene and isobutylene, gave a fraction eluted with 10% benzene-hexane which had the two singlets at 1.98 and 1.68 p.p.m. in the n.m.r. Bulb-tobulb distillation of this sample gave 40 mg of 1-phenyl-1-(2-thienyl)-2-methylpropene (5a). The i.r. and n.m.r. spectra of this material were identical to those of an authentic sample prepared by the Grignard method: i.r. v_{max}^{neat} , 1600, 1440, 1220, 1020, 830, 760, 700 cm⁻¹; n.m.r., 1.98 (s), 1.68 (s), (allylic protons), 7.40–6.60 p.p.m. (complex), (thienyl and phenyl protons).

Anal. Calcd. for C₁₄H₁₄S: C, 78.48; H, 6.59. Found: C, 78.31; H, 6.65.

Irradiation of 2-(4-Methoxybenzoyl)thiophene (1b) with Isobutylene

2-(4-Methoxybenzoyl)thiophene (1 g) was dissolved in a solution of 25% isobutylene in benzene (40 ml) and irradiated in a quartz tube at 10° for 20 h. An aliquot was withdrawn and after evaporation of the solvent and excess isobutylene the n.m.r. spectrum was taken. This spectrum had complex absorption in the aromatic and aliphatic regions with two sharp singlets at 1.98 and 1.74 p.p.m.

Chromatography of the crude reaction mixture, after evaporation of the solvent and excess isobutylene, on Shawinigans base washed alumina, gave a fraction eluting with 25% benzene-bexane, which retained the singlets at 1.98 and 1.74 p.p.m. Bulb-to-bulb distillation of this sample gave 50 mg of 1-(4-methoxyphenyl)-1-(2-thienyl)-2-methylpropene. The i.r. and n.m.r. spectra were identical with those of an authentic sample prepared by the, Grignard route: i.r. $v_{max}^{CHCI_3}$, 1610, 1510, 1470, 1450 1300, 1290, 1180, 1115, 1035 cm⁻¹; n.m.r., 3.71 (s), (methoxyl); 1.98 (s), 1.74 (s), (allylic protons); 7.20-6.70 p.p.m. (complex), (thienyl and phenyl protons).

Irradiation of 2-(4-Cyanobenzoyl)thiophene (1c) with Isobutylene

2-(4-Cyanobenzoyl)thiophene (2.5 g) was dissolved in 25% isobutylene in benzene (300 ml) and irradiated through quartz in an immersion well reactor (Ace Glass 6515-25-03; 450 Hanovia W medium-pressure mercury vapor lamp) for 20 h. An aliquot was withdrawn and after removal of the benzene and excess isobutylene the n.m.r. spectrum was determined. This spectrum was in accord with formation of the oxetane in about 90% yield. Oxetane formation was consistent with the i.r. spectrum which showed the carbonyl band had essentially disappeared while strong absorption developed a 980 cm⁻¹ typical of oxetanes. i.r. $v_{max}^{ClCl_3}$, 2240, 1715, 1645, 1610, 1500, 1465, 1415, 1370, 980 cm⁻¹; n.m.r., 4.52, 4.15 (quartet, J = 5 Hz), (methylene protons); 1.12 (s), 1.01 p.p.m. (s), (methyles on the oxetane).

An attempt was made to purify the oxetane by crystallization from methanol, chromatography on Shawinigans basic alumina, and sublimation; however, all attempts led to decomposition of the oxetane to 1-(4-cyanophenyl)-1-(2-thienyl)-2-methylpropene. This product was therefore sublimed (180°, 0.01 mm) giving lemon yellow crystals. Recrystallization from methanol yielded 1.92 g (77%) of the olefin as colorless leaflets, m.p. 96–97⁻. i.r. v_{max}^{KBr} , 2240, 1600, 1440, 1220, 870, 818, 710, 700 cm⁻¹; n.m.r., 2.00 (s), 1.78 (s), (allylic protons), 7.75– 6.75 p.p.m. (complex), (thienyl and phenyl protons).

Anal. Calcd. for C₁₅H₁₃NS: C, 75.30; H, 5.48 Found: C, 75.10; H, 5.33.

Irradiation of 3-Benzoylthiophene (2a) with Isobutylene

3-Benzoylthiophene (0.5 g) was dissolved in a 25% solution (by volume) of isobutylene in benzene (40 ml) and irradiated in a quartz tube for 20 h. A sample was withdrawn and after removal of the solvent the n.m.r. spectrum was determined. This spectrum showed a complex aliphatic and aromatic region; however, there was a quartet at 4.40, 4.15 p.p.m. (J = 5 Hz) and a singlet at 1.05 p.p.m. characteristic of the oxetane, and two singlets at 1.90 and 1.74 p.p.m. indicative of the olefin.

Chromatography of the reaction mixture on Shawini-

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gans base washed alumina gave a fraction eluting with 20% benzene-hexane which showed the two singlets at 1.90 and 1.74 p.p.m. No oxetane was obtained from the column. Bulb-to-bulb distillation of this fraction yielded 60 mg of 1-phenyl-1-(3-thienyl)-2-methylpropene. The i.r. and n.m.r. spectra of this material were identical to those of an authentic sample prepared by the Grignard route: i.r. v_{max}^{CDC13} , 1605, 1490, 1450, 1285, and 1035 cm⁻¹; n.m.r., 1.90 (s), 1.74 (s), (allylic protons): 7.45–6.64 p.p.m. (complex), (phenyl and thienyl protons).

Irradiation of 3-(4-Methoxybenzoyl) thiophene (2b) with Isobutylene

3-(4-Methoxybenzoyl)thiophene (1 g) was dissolved in a 25% solution (by volume) of isobutylene in benzene (40 ml) and irradiated in a quartz tube at 10° for 20 h. A sample was withdrawn and after evaporation of the solvent the n.m.r. spectrum was determined. A quartet at 4.20, 3.93 p.p.m. (J = 7 Hz) characteristic of oxetane formation, and two singlets in the aliphatic region at 1.88 and 1.76 p.p.m. for the olefin were observed.

Chromatography on Shawinigans basic alumina gave a fraction eluted with 25% benzene-hexane which retained the two singlets at 1.88 and 1.76 p.p.m. in the n.m.r. Bulb-to-bulb distillation of this fraction gave 46 mg of 1-(4-methoxyphenyl)-1-(3-thienyl)-2-methylpropene. The i.r. and n.m.r. spectra of this sample were identical to those of a sample prepared by the Grignard route: i.r. $v_{max}^{\text{CDC1}_3}$, 1610, 1515, 1250, 1180, and 1040 cm⁻¹; n.m.r., 1.88 (s), 1.76 (s), (allylic protons); 3.76 (s), (methoxyl); 7.16-6.71 p.p.m. (complex), (thienyl and phenyl protons).

Irradiation of 3-(4-Cyanobenzoyl) thiophene (2c) with Isobutylene

3-(4-Cyanobenzoyl)thiophene (0.1 g) was dissolved in a 25% solution of isobutylene in benzene (20 ml) and irradiated in a quartz tube at 10° for 20 h. Removal of the solvent gave a dark oil, the n.m.r. spectra of which indicated the formation of the oxetane in about 90% yield with no concomitant olefin formation: n.m.r., 4.39, 4.15 (quartet, J = 5 Hz), (methylene protons), 1.07 and 1.00 p.p.m (s), (methyl groups on oxetane).

Attempted bulb-to-bulb distillation of the oxetane gave 1-(4-cyanophenyl)-1-(3-thienyl)-2-methylpropene.i.r. $v_{max}^{CDC1_3}$, 2250, 1715, 1660, 1610, 1515, 1295, 1275, 1175 cm⁻¹; n.m.r., 1.90 (s), 1.73 (s), (allylic protons); 8.20–6.70 p.p.m. (complex), (phenyl and thienyl protons). Anal. Calcd. for C₁₅H₁₃NS: C, 75.30; H, 5.48. Found:

C, 75.13; H, 5.49.

Preparation of 1-Phenyl-1-thienyl-1,2-methylpropenes

The procedure developed by Garbisch was used (15). Magnesium (0.24 g), 2-bromopropane (1.24 g), and dry ether (15 ml) were placed in a dry flask fitted with a reflux condenser and drying tube. A crystal of iodine was added and the reaction started, the ether boiled gently until nearly all the magnesium had dissolved and then the reaction was heated under reflux for 10 min. The reaction mixture was cooled and the benzoylthiophene (0.15 g) in dry ether (5 ml) was added with stirring. After 10 min the reaction mixture was poured into 10% aqueous ammonium chloride (50 ml), the ether layer was separated and the aqueous layer extracted with two portions of

ether (50 ml). The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. Removal of the ether left the alcohol as a yellow oil.

The alcohol was not purified but was immediately dehydrated to the olefin by shaking with 25% sulfuric acid in acetic acid (5 ml) for 30 s. This mixture was poured into a mixture of ether (50 ml) and water (150 ml). The ether layer was separated and the aqueous layer extracted twice with ether (50 ml). The combined ether extracts were washed twice with 10% sodium bicarbonate (150 ml), followed by water (100 ml), and then dried over anhydrous calcium chloride. Removal of the ether gave a red oil which was chromatographed on Shawinigans base washed alumina and in all cases gave the olefin upon elution with 25% benzene-hexane. After removal of the solvent the samples were bulb-to-bulb distilled giving clear oils.

I-Phenyl-1-(2-thienyl)-2-methylpropene

The yield by the above procedure was 45 mg (26%). The i.r. and n.m.r. spectra of this sample were essentially the same as those observed for the olefin obtained from the irradiation of 1a with isobutylene.

1-(4-Methoxyphenyl)-1-(2-thienyl)-2-methylpropene

The yield of olefin by the above procedure was 62 mg (37%). The i.r. and n.m.r. spectra of this olefin were essentially the same as those observed for the olefin obtained from the irradiation of 1b with isobutylene.

Anal. Calcd. for $C_{15}H_{16}OS$: C, 73.75; H, 6.60. Found : C, 73.61; H, 6.72.

1-Phenyl-1-(3-thienyl)-2-methylpropene

The yield of olefin by the above procedure was 53 mg (31%). The i.r. and n.m.r. spectra of this olefin were essentially the same as those observed for the olefin obtained from the irradiation of 2a with isobutylene.

Anal. Calcd. for $C_{14}H_{14}S$: C, 78.48; H, 6.59. Found: C, 78.55; H, 6.59.

1-(4-Methoxyphenyl)-1-(3-thienyl)-2-methylpropene

The yield of olefin by the above procedure was 65 mg (39%). The i.r. and n.m.r. spectra of this olefin were essentially the same as those observed for the olefin obtained from the irradiation of 2b with isobutylene.

Anal. Calcd. for C₁₅H₁₆OS: C, 73.75; H, 6.60. Found: C, 73.57; H, 6.84.

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- D. R. ARNOLD and R. J. BIRTWELL. J. Am. Chem. Soc. 95, 4599 (1973).
- (a) D. R. ARNOLD, R. L. HINMAN, and A. H. GLICK. Tetrahedron Lett. 1425 (1964); (b) D. R. ARNOLD, Adv. Photochem. 6, 301 (1968).
- 3. W. G. HERKSTROETER, A. A. LAMOLA, and G. S. HAMMOND, J. Am. Chem. Soc. 86, 4537 (1964).
- (a) J. P. WAGNER and G. S. HAMMOND. Adv. Photochem. 5, 21 (1968); (b) J. P. WAGNER. Acc. Chem. Res. 4, 168 (1971).
- 5. J. C. DALTON and N. J. TURRO. Annu. Rev. Phy. Chem. 21, 499 (1970).

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- 6. A. A. LAMOLA. J. Chem. Phys. 47, 4810(1967); R. M. HOCKSTROSSER. Acc. Chem. Res. 1, 266 (1968); M. A. EL-SAYED. Acc. Chem. Res. 1, 8 (1968).
- 7. N. C. YANG, M. KIMURA, and W. EISENHARDT. J. Am. Chem. Soc. 95, 5058 (1973).
- 8. N. D. HEINDEL, J. Heterocycl. Chem. 3, 379 (1966). D. C. NECKERS. Private communication.
 T. S. CANTRELL. Chem. Commun. 155 (1972).
- 11. P. TRAYNARD and J. P. BLANCHI. J. Chim. Phys. 69, 284 (1972).
- 12. H. WYNBERG. Acc. Chem. Res. 4, 65 (1971).
- A. COUTURE and A. L. COMBIER. Tetrahedron, 27, 1059 (1971); Chem. Commun. 891 (1971).
- E. A. HILL, M. L. GROSS, M. STASIEWICZ, and M. MANION. J. Am. Chem. Soc. 91, 7381 (1969). 14.
- 15. E. W. GARBISCH. J. Org. Chem. 26, 4165 (1961).