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The Reaction of Substituted Tropones with Diphenylketene

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Synopsis. The reaction of 2-methoxytropone and diphenylketene afforded (2+8)cycloadduct and 1-methoxy-8,8-diphenylheptafulvene which must be formed by the decarboxylation of the initially-formed (2+2)cycloadduct. 2-Dimethylaminotropone also gave the heptafulvene derivative. However, 2-chloro-, 2-cyano-, and 2,5-dimethoxytropone yielded only (2+8)cycloadducts.

The reaction of 4,5-benzotropone with diphenylketene has long been known to give diphenylbenzoheptafulvene[1] by the decarboxylation of the initially-formed (2+2)cycloadduct. The reactions of tropone with diphenylketene[2] and dichloroketene[3] have also been studied; two (8+2)cycloadducts (I and II respectively) were obtained. However, the reaction of tropone with activated isocyanates has been shown to give troponeimine derivatives; presumably they are formed by the elimination of CO_2 from the (2+2)cycloadducts.[4] Furthermore, we have recently found that 8-oxoheptafulvene, which has a cyclic conjugated ketene moiety, reacts with tropones to give (8+2)cycloadducts and heptafulvalenes and its derivatives, which are formed by the decarboxylation of the (2+2)cycloadducts; we have also found that the (8+2)cycloadducts might be the isomerization products of the (2+2)-cycloadducts.[5]

These results prompted us to investigate the reaction of substituted tropones and diphenylketene; this paper will describe the results of this study.

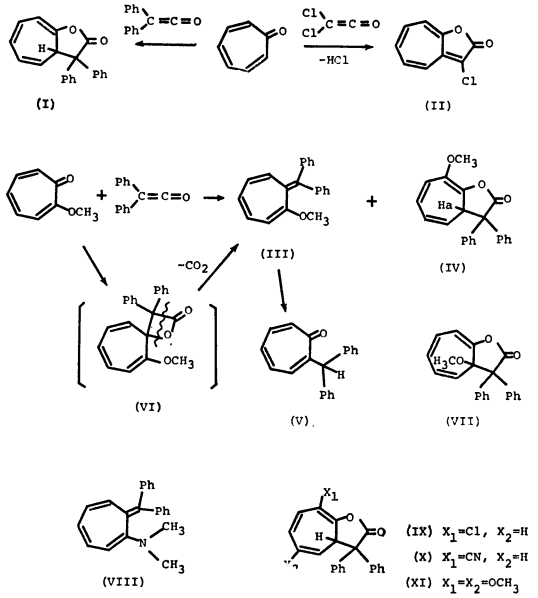
The refluxing of a mixture of 2-methoxytropone and diphenylketene (1: 1.2 molar ratio) in anhydrous benzene and subsequent chromatographic separation afforded two products, yellow plates (III) and colorless plates (IV), in 6.5 and 50% yields respectively.

Compound (III) was proved to be 1-methoxy-8,8-diphenylheptafulvene[6] from elemental analyses and its spectroscopic data, as well as by hydrolysis with hydrochloric acid which gave 2-benzhydryltropone (V). It is clear that Compound (III) is formed by the decarboxylation of the (2+2)cycloadduct intermediate (VI).

Compound (IV) was proved to be the (8+2)cycloadduct by the elemental analyses and by the spectroscopic data. The alternative structure (VII) for Compound (IV) could be excluded on the basis of the existence of a signal ascribable to Ha hydrogen in its NMR spectrum. This result is similar to that in the case of the (8+2)cycloadducts of 8-oxoheptafulvene with substituted tropones.[5]

The reaction of 2-dimethylaminotropone with diphenylketene afforded 1-dimethylamino-8,8-diphenylheptafulvene (VIII) and an unidentified product. However, the reaction of diphenylketene with 2-chloro-, 2-cyano-, and 2,5-dimethoxytropone afforded only (8+2)cycloadducts (IX—XI); no heptafulvene derivatives could be obtained.

It is clear that electron-releasing groups, such as a methoxy or dimethylamino group, stabilize 8,8-diphenylheptafulvene; however, the influence of the substituents of tropone on the mode of the reaction with diphenylketene is not clear.



Experimental

Reaction of 2-Methoxytropone with Diphenylketene. A solution of 2-methoxytropone (500 mg) and diphenylketene (800 mg) in anhydrous benzene (5 ml) was refluxed for 2 hr under a nitrogen atmosphere. The solvent was then removed and chromatographed on a silica-gel column, using $CHCl_3$ as the solvent. From the first effluent, 70 mg of yellow plates (III) (mp 115—116 °C (from ethanol)) were obatined. Compound (III) is stable when standing in the air at room temperature. λ_{max}^{MeOH} nm(log ε); 255^{sh} (3.48) and 333 (3.95). NMR ($CDCl_3$); δ 3.30 (OCH_3), 5.48 (1H, d, J=7.0 Hz), 5.8—6.4 (4H, m) and 6.8—7.4 (10H, m).

Found: C, 88.21; H, 6.40%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34%.

From the second effluent, 646 mg of colorless plates (IV) (mp 122—123 °C (from ethanol)) were obtained. NMR ($CDCl_3$); δ 3.48 (Ha, d.d, J=4.5, 1.5 Hz), 3.75 (OCH_3), 4.62 (1H, d.d, J=10.0, 4.5 Hz), 5.8—6.5 (3H, m) and 6.9—7.6 (10H).

Found: C, 79.96; H, 5.59%. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49%.

Reaction of 2-Dimethylaminotropone with Diphenylketene. A solution of 2-dimethylaminotropone (750 mg) and diphenylketene (970 mg) in dry benzene (5 ml) was refluxed for 6 hr. The solution was then chromatographed on a silica-gel column and eluted with benzene; 117 mg (7.8%) of pale yellow needles (VIII) (mp 118—120 °C (from ethanol)), 246 mg of colorless needles (mp 131.5—132 °C,

(Found: C, 87.33; H, 5.97%, λ_{max}^{EtOH} nm; 249)), and 368 mg (49%) of the starting tropone were thus obtained. Compound (VIII) is also stable for standing in the air at room temperature. λ_{max}^{MeOH} nm(log ε); 246 (4.17), 310 (3.91), and 356 (4.03), NMR ($CDCl_3$); δ 2.42 ($N(CH_3)_2$), 6.6—7.5 (15H, m).

Found: C, 88.52; H, 7.22; N, 4.41%. Calcd for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68%.

Reaction of 2-Chlorotropone with Diphenylketene. A solution of 2-chlorotropone (560 mg) and diphenylketene (800 mg) in dry benzene (5 ml) was refluxed for 2 hr. The solvent was then removed, leaving colorless crystals; these crystals were subsequently recrystallized from ethanol to give 1.087 g (82%) of colorless prisms (IX) (mp 149—150 °C). NMR ($CDCl_3$); δ 3.72 (1H, d.d, J=4.5, 2.0 Hz), 4.66 (1H, d.d, J=10.0, 4.5 Hz), 5.90—6.65 (3H, m) and 7.18—7.50 (10H).

Found: C, 75.08; H, 4.50%. Calcd for $C_{21}H_{15}O_2Cl$: C, 75.34; H, 4.52%.

Reaction of 2-Cyanotropone with Diphenylketene. A solution of 2-cyanotropone (262 mg) and diphenylketene (450 mg) in dry benzene (15 ml) was refluxed for 1.5 hr. The solvent was then removed, and the residue was washed with $CHCl_3$ to give 530 mg of colorless crystals. Recrystallization from $CHCl_3$–ethanol gave X as colorless prisms; mp 175—176 °C. NMR ($CDCl_3$); δ 3.70 (1H, d.d, J=4.0, 2.0 Hz), 4.65 (1H, d.d, J=10.0, 4.0 Hz), 6.1 (1H, m), 6.60 (2H) and 7.15—7.5 (10H).

Found: C, 81.02; H, 4.58; N, 4.13%. Calcd for $C_{22}H_{15}O_2N$: C, 81.21; H, 4.65; N, 4.31%.

Reaction of 2,5-Dimethoxytropone with Diphenylketene. A solution of 2,5-dimethoxytropone (336 mg) and diphenylketene (400 mg) in dry benzene (8 ml) was refluxed for 1.5 hr. When the solution was then chromatographed on a silica-gel column, 697 mg of a colorless powder were obtained. Recrystallization from $CHCl_3$–ethanol afforded XI as colorless prisms; mp 125—126 °C. NMR ($CDCl_3$); δ 3.20 (OCH_3), 3.65—3.75 (OCH_3 and 2H), 6.07 (1H, d, J=11.5 Hz), 6.28 (1H, d, J=11.5 Hz) and 7.3 (10H).

Found: C, 76.43; H, 5.54%. Calcd for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59%.

2-Benzhydryltropone (V). A solution of heptafulvene (III, 109 mg) in methanol (16 ml) and 3M HCl (3 ml) was refluxed for 25 min. The solvent was then removed, water was added, and the solution was extracted with $CHCl_3$. The subsequent removal of the solvent gave 90 mg of a pale yellow powder; recrystallization from $CHCl_3$–cyclohexane afforded V as pale yellow plates; mp 123—124 °C. λ_{max}^{MeOH} nm(log ε); 219^{sh} (4.46), 230^{sh} (4.36), and 313 (3.88). NMR ($CDCl_3$); δ 6.04 (1H, s) and 6.5—7.5 (16H, m).

Found: C, 88.27; H, 5.95%. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

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