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# PHOTOCYCLOADDITION OF BIACETYL TO VARIOUS OLEFINS[1]

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Although aliphatic α-diketones undergo inter- and intra-molecular hydrogen abstraction reaction on irradiation[2], their reactions with olefins have not been reported. We now wish to report the photocycloaddition of biacetyl to several olefins, which is the most simple α-diketone and one of the effective triplet quenchers.

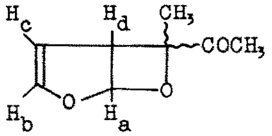
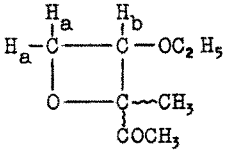
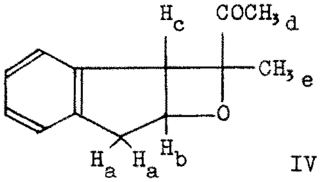
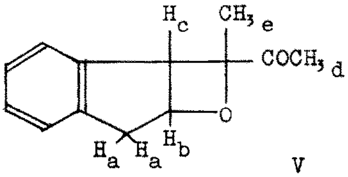
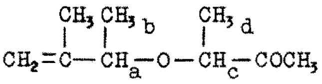
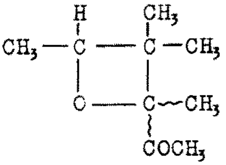
The reactions were carried out in a Pyrex vessel at room temperature using a 350W high pressure mercury lamp filtered through a solution of naphthalene in n-hexane. The photoreactions of biacetyl with furan, ethyl vinyl ether, indene and 2-methyl-2-butene gave 1 : 1 adducts as main products, respectively.

A mixture of biacetyl (8.6g) and furan (34g) was irradiated for 48 hrs. After the removal of unchanged starting materials, a fraction boiling at 94°C/24mmHg (2.5g; 70%, based on biacetyl consumed) was collected. Redistillation gave pure 6-methyl-6-acetyl-2,7-dioxabicyclo[3,2,0]hept-3-ene (I)[3]. The structure of I was determined by IR, NMR, mass spectra and elemental analysis[4]. The NMR and IR data are listed in Table I.

The reaction with ethyl vinyl ether afforded 60% of 4-methyl-4-acetyl-3-ethoxyoxetane (II)[3] (b.p. 50°C/4mmHg) and 10% of III (b.p. 110°C/3mmHg). III seems to be a 2 : 1 adduct of biacetyl and ethyl vinyl ether on the basis of its mass spectrum and elemental analysis, but the structure has not been determined yet.

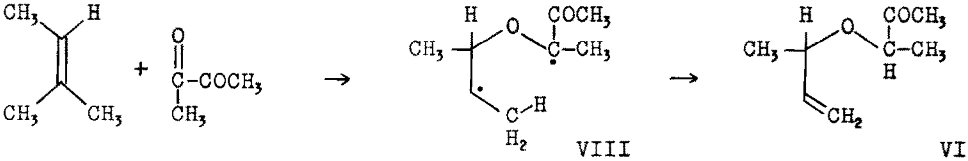
The reaction of biacetyl and indene was carried out in a benzene solution

Table I NMR and IR Spectra of Products

| Products | Spectra |
|---|---|
|  I | nmr (in CCl$_4$, $\delta$ppm from TMS)<br>1.33(3H,s), 2.28(3H,s), 3.85($H_d$, 1H,m), 5.11 ($H_c$, 1H,t), 6.11($H_a$, 1H,d), 6.62($H_b$, 1H,d)<br>$J_{ad}$=4cps, $J_{bc}$=$J_{cd}$=3cps, $J_{ab}$=$J_{bd}$< 1cps<br>ir 3100, 2960, 1730, 1625, 1355, 970 cm$^{-1}$ |
|  II | nmr 1.23(3H,t), 1.38(3H,s), 2.28(3H,s)<br>3.43(2H,q), 4.10 4.90($H_a$+ $H_b$, 3H,m)<br>ir 2980, 2930, 1450, 1380, 1355, 1120, 960 cm$^{-1}$ |
|  IV | nmr 0.86($H_e$, 3H,s), 2.31($H_d$, 3H,s), 3.13($H_a$, 2H,d), 4.15($H_c$, 1H,d), 5.25($H_b$, 1H,m), 7.20(4H,m). $J_{ab}$=3cps, $J_{bc}$=5.5cps<br>ir 2920, 1720, 1360, 990, 755, 720 cm$^{-1}$ |
|  V | nmr 1.52($H_e$, 3H,s), 1.70($H_d$, 3H,s), 3.18($H_a$, 2H,d), 3.90($H_c$, 1H,d), 5.40($H_b$, 1H,m), 7.17(4H,m). $J_{ab}$=3cps, $J_{bc}$=5.5cps |
|  $CH_2{=}\overset{CH_3}{\overset{\mid}{C}}-\overset{CH_3\ b}{\overset{\mid}{CH_a}}-O-\overset{CH_3\ d}{\overset{\mid}{CH_c}}-COCH_3$ VI | nmr 1.22(3H,d), 1.28(3H,d), 1.72(3H,d, 1.0cps), 2.11(3H,s), 3.70(1H,q), 3.93(1h,q), 4.87 (2H,m). $J_{ab}$=$J_{cd}$=7cps<br>ir 3080, 2960, 1720, 1650, 1360, 1110 cm$^{-1}$ |
|  VII | nmr 0.95(3H,s), 1.10(3H,s), 1.18(3H,d), 1.33 (3H,s), 2.15(3H,s), 4.40(1H,q)<br>ir 2960, 1720, 1350, 990 cm$^{-1}$ |

and a mixture of oxetane isomers IV and V (b.p. 120°C/4mmHg; 60%) was formed in the ratio of 2 : 1, which were separated by preparative VPC (PEG 6000, 3m, 160° C). The chemical shift of the $C_2$-methyl protons of IV and the $C_2$-acetyl protons of V appears at higher fields than the normal chemical shift of them, which suggest that the $C_2$-methyl group for IV and $C_2$-acetyl group for V are in the same side of an oxetane ring as phenyl group, respectively.

The photoreaction of biacetyl with 2-methyl-2-butene resulted in the formation of an acyclic ether VI (50%) and an oxetane VII (25%), which were separated from a yellow fraction boiling at 60—80°C/25mmHg by preparative VPC (Dinonyl Phthalate, 3m, 130°C). The formation of VI is very interesting because this is a novel reaction and it has not occurred in the case of monoketones. It would appear that the reaction proceeds through the intermediate biradical (VIII), which is fairly stable, followed by intramolecular hydrogen transfer via a six-membered transition state. The stability of VIII might be related to the participation of the other carbonyl group of biacetyl.



The photoaddition of biacetyl to furan proceeds in a higher yield than that of acetone to furan[5]. It is probably due to the difference in the triplet energies of both these ketones, that is, a biradical intermediate produced from a carbonyl compound which posesses the higher triplet energy include the more vibrational energy and lead to the decomposition to the reactants rather than the coupling of the biradical to the oxetane[6]. Furthermore, it should be noted that the photoaddition of biacetyl to olefins was more selective than that of monoketones. For example, the addition of acetone to ethyl vinyl ether yielded both 3-ethoxy oxetane (ca. 70%) and 2-ethoxy oxetane (ca. 30%)[7], whereas the reaction of biacetyl produced only 3-ethoxy oxetane. This higher selectivity of the addition of biacetyl might be closely related to the reactivity of triplet biacetyl, that is, the electron density of the n-$\pi^*$ excited oxygen atom. The details of the reaction mechanisms are presently under investigation.

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2) (a) N. J. Turro, "Molecular Photochemistry", Benjamin, 1965.
(b) A. D. Norman, Chem. Comm., **810** (1968).
(c) N. J. Turro, and T-J. Lee, J. Am. Chem. Soc., **91**, 5651 (1969), and references cited there-in.

3) Although two stereoisomeric compounds can be considered in this photocycloaddition, only one of the isomers is obtained. This detailed configuration can not be determined yet.

4) Satisfactory analytical and spectral data have been obtained for all products.

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6) (a) S. Toki and H. Sakurai, ibid., **40**, 2885 (1967).
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