[15] *D. T. Clark*, Int. J. Sulfur Chemistry *C7*, 11 (1972); *M. H. Palmer & R. H. Findlay*, Tetrahedron Letters *1972*, 4165; *M. H. Palmer, R. H. Findlay & A. J. Gaskell*, J. chem. Soc. Perkin II, *1974*, 420.
[16] *L. Pauling*, 'The Nature of the Chemical Bond', Cornell University Press 1960.
[17] *A. D. Baker, D. Betteridge, N. R. Kemp & R. E. Kirby*, Analytical Chemistry *42*, 1064 (1970).
[18] *F. Brogli, P. A. Clark, E. Heilbronner & M. Neuenschwander*, Angew. Chem. *85*, 414 (1973); Angew. Chem., Int. Ed. *5*, 422 (1973).
[19] *M. H. Palmer & R. H. Findlay*, J. chem. Soc. Perkin II *1974*, 1885.
[20] *J. P. Maier, J.-F. Muller, T. Kubota & M. Yamakawa*, Helv. *58*, 1641 (1975).

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177. Low Temperature Photochemistry of the Acetone/2-Propanol System

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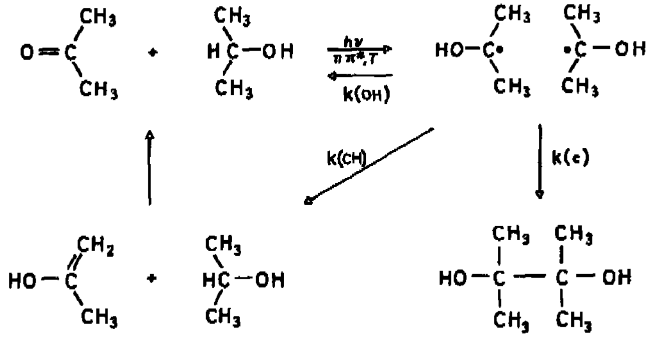
(26. VI. 75)

Summary. During UV.-irradiation of acetone/2-propanol mixtures at −70° products of photoaddition of acetone to intermediate enols are formed. The yields of those products exceed the yield of pinacol, the major room temperature product. At −70° the photoadditions are favoured by the long lifetime of acetone enol (≥ 5000 s).

The photoreactions of acetone and 2-propanol have been studied by many authors [1–6]. At room temperature, the only isolated photoproduct is pinacol (**PIN**) [1]. Additional minor unidentified products have been mentioned by *Gorzny* [2]. Observation of free radicals $(CH_3)_2\dot{C}OH$ by ESR. [3] and UV. [4], and detection of acetone enol by CIDNP. [5] as intermediates lead to the formulation of the reactions of *Scheme 1* as the dominant processes [5] [6]. At room temperature, the enol lifetime is ≈ 14 s [5a]. We recently determined the ratios of rate constants for the reactions of *Scheme 1* (26°, acetonitrile solution) as $k(CH)/k(c) = 3.4 \pm 0.2$ and $k(OH)/k(CH) = 0.3 \pm 0.1$ [6], *i.e.* disproportionation of the radicals to enol and 2-propanol is more important than the other radical terminations.

Scheme 1



The temperature dependence of product yields of the acetone/2-propanol system has been studied by *Gorzny* [2]. He found that the yields of the products which are minor at room temperature increase with decreasing temperature and may even exceed the yield of **PIN**. However, none of the additional products were isolated or identified, and no explanation for their formation was given. Having established the enol as important intermediate in the room temperature photoreaction [5] [6] it appeared to us that secondary photoreactions of the enol might account for *Gorzny*'s unidentified products, in particular since the enol is expected to be more stable at lower temperatures. Therefore, we reinvestigated the photoreaction at $-(70 \pm 2)^\circ$.

340 g of an equimolar mixture of acetone and 2-propanol (both *Fluka* puriss.) were irradiated for 10 h[1]. Gas chromatography[2] (GC.) of the reaction mixture reveals five products of which diacetone alcohol (**DAA**), **PIN** and isopropyloxyacetone (**IPA**) were identified by comparison of their GC. retention times with those of commercially available (**DAA, PIN**) or synthesised (**IPA** [7]) authentic samples. The liquid remaining after removal of acetone and 2-propanol (19 g) was vacuum distilled over a 20 cm *Vigreux* column and collected in four fractions of equal volumes (b.p. 50–100°/18 Torr).

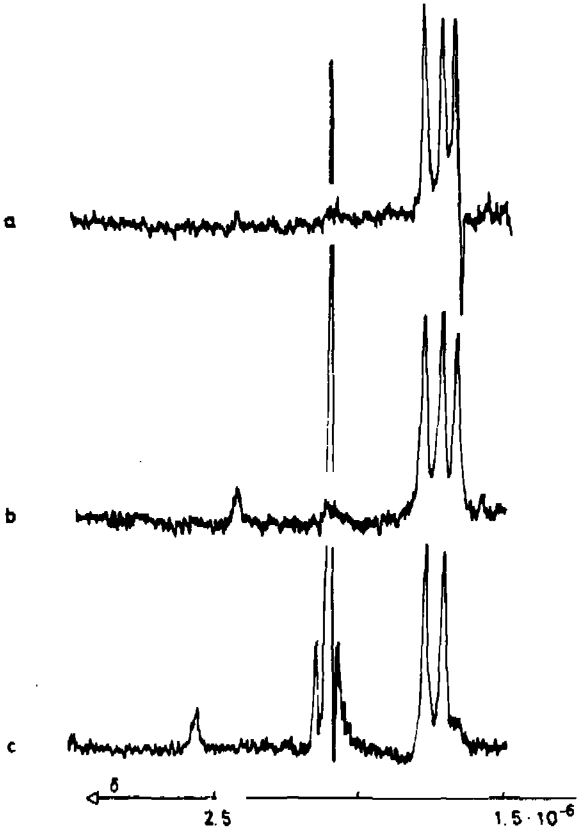


Fig. 1. *Acetone-d₆ (3 M)/2-propanol (6.5 M) – photoreaction, NMR. spectra* (a, b, c: see text).

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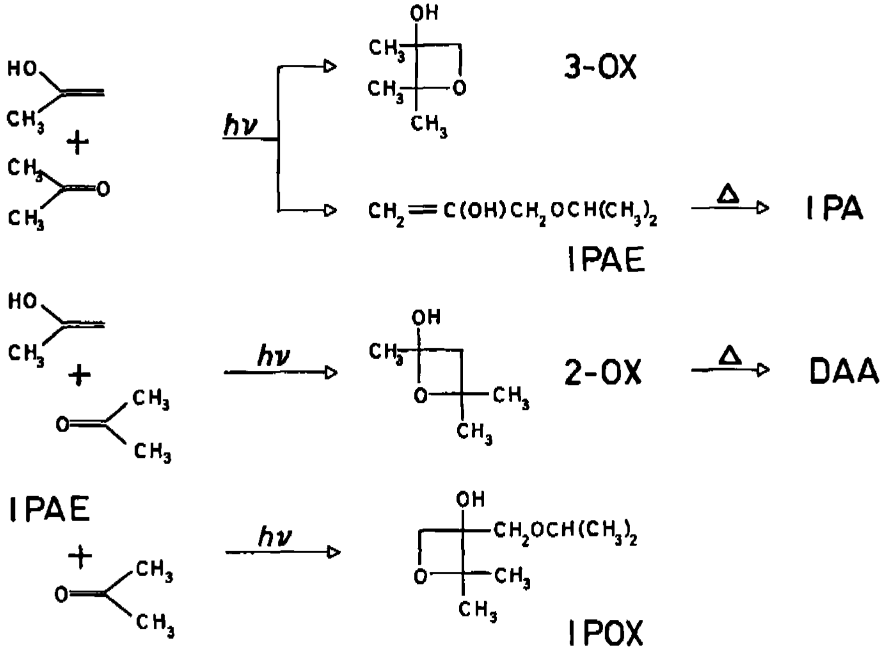
[1] Ar or He atmosphere, low temperature irradiation equipment by *H. Mangels*, Roisdorf, Germany, *Heraeus* lamp TQ 150, unfiltered.

[2] 30 m Ucon LB glass capillary column.

Further separation of the highest boiling fraction by liquid phase chromatography[3]) yields the remaining two products 3-hydroxy-2,2,3-trimethyloxetane[4]) (**3-OX**) and 3-hydroxy-2,2-dimethyl-3-isopropyloxymethyloxetane[5]) (**IPOX**). By quantitative GC.[2]) of the reaction mixture the molar ratio of the products is found to be **3-OX**: **DAA**: **IPA**: **PIN**: **IPOX** = 1:0.5:0.2:0.2:0.1.

The formation of **3-OX** indicates a direct photocycloaddition of acetone to its enol. To establish the reactions leading to **DAA** and **IPA** the photoreaction was carried out at –70° in a modified variable temperature probe of a *Varian* HA-100-NMR. spectrometer, and NMR. spectra were taken during and after reaction. Fig. 1a shows part of a proton spectrum taken during irradiation [8] ($290 < \lambda < 360$ nm) of 3 M acetone-d_6 and 6.5 M 2-propanol in tetramethyl silane. Apart from ^{13}C sidebands of 2-propanol ($\delta = 1.74$) the spectrum exhibits the A/E CIDNP. multiplet effect of the CH_3-group of acetone enol ($\delta = 1.67$ [5a]). After 20 min irradiation, the enol is observed in $4 \cdot 10^{-2}$ M concentration even in the dark (Fig. 1b), and does not decay appreciably within at least 5000 s after irradiation. At $\delta = 2.43$ another product with similar stability is detected. Acetone, acetone-d_5, **DAA**, and **IPA** which have resonances at $\delta \approx 2.10$ are not formed during the low temperature irradiation. Fig. 1c shows a spectrum obtained at –70° with a sample irradiated for 20 min at –70° and

Scheme 2



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[3]) Al_2O_3 neutral II, *Woelm*, elution with hexane/ethyl acetate 1:1.

[4]) NMR. (CCl_4): 1.25 (*s*, 3 H); 1.33–1.35 (6 H); 3.75 (*s*, OH); 4.09 (*d*, $J = 6$, 1 H); 4.26 ($d \times q$, $J = 6$ and 0.5, 1 H).

[5]) NMR. (C_6H_6): 0.94 (*d*, $J = 6$,6 H); 1.30 (*s*, 3 H); 1.56 (*s*, 3 H); 4.10 (*d*, $J = 6.5$, 1 H); 4.10 (*s*, OH); 4.26 (*m*, $J = 6$, 1 H); 4.30 (*d*, $J = 9$,1 H); 4.45 ($d \times d$, $J = 6.5$ and 0.5, 1 H); 5.60 ($d \times d$, $J = 9$ and 0.5, 1 H).

stored for 5 min at +50°. Obviously, the enol and the product at $\delta = 2.43$ disappear on warming. Instead, acetone ($\delta = 2.10$), acetone-d_5 ($\delta = 2.07$) and **DAA** (CH_2, $\delta = 2.57$; $COCH_3$, $\delta = 2.15$) are formed. Spectra taken with higher resolution reveal that **IPA** also forms on warming. The concentration of acetone is equal to that of the intermediate enol, whereas the diacetone alcohol CH_2-intensity corresponds to that of the product at $\delta = 2.43$. These findings show that acetone, **DAA**, and **IPA** only result from rearrangements of thermally unstable primary photoproducts.

Scheme 2 gives the reactions to which we attribute the formation of **3-OX**, **DAA**, **IPA**, and **IPOX**. The main steps are photocycloadditions of triplet acetone to enols resulting from radical disproportionations. They are analogous to known reactions of excited carbonyl compounds with enol ethers [9] [10] and alkenes [11] and to the interpretation of the formation of **3-OX** and **DAA** during UV.-irradiation of pure acetone [12]. We believe, that the resonance at $\delta = 2.43$ (Fig. 1b) belongs to the CH_2-protons of **2-OX**.

Further strong evidence for enols as precursors of **3-OX**, **DAA**, **IPA**, and **IPOX** is the finding that addition of HCl (0.1M) to the solutions quenches their formation completely while increasing the yield of **PIN**.

Our identification of *Gorzny*'s low temperature products [2] and their explanation by photocycloadditions of enols with acetone support the previous view [5] [6] that enols are important intermediates in ketone photochemistry.

A complete kinetic analysis of the reactions of *Schemes 1* and *2* is in progress.

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REFERENCES

[1] a) *G. Ciamician & P. Silber*, Ber. deutsch. chem. Ges. *44*, 1280 (1911); b) *C. Weizmann, E. Bergmann & Y. Hirshberg*, J. Amer. chem. Soc. *60*, 1530 (1938); c) *G. Leuschner & K. Pfordte*, Liebigs Ann. Chem. *619*, 1 (1958).

[2] *K. Gorzny*, Ph. D. thesis, University of Bonn 1968.

[3] *R. Livingston & H. Zeldes*, J. chem. Physics *44*, 1245 (1966).

[4] *G. Porter, S. K. Dogra, R. O. Loutfy, S. E. Sugamori & R. W. Yip*, J. chem. Soc. Faraday, Trans. I, *69*, 1462 (1973).

[5] a) *G. P. Laroff & H. Fischer*, Helv. *56*, 2011 (1973); b) *J. Bargon & K. G. Seifert*, Ber. Bunsenges. physik. Chem. *78*, 187 (1974) and private communications.

[6] *B. Blank, A. Henne, G. P. Laroff & H. Fischer*, V. IUPAC-Symposium on Photochemistry, Enschede 1974; Pure appl. Chemistry, in press.

[7] *R. A. Barnes & W. M. Budde*, J. Amer. chem. Soc. *68*, 2339 (1946).

[8] *B. Blank, A. Henne & H. Fischer*, Helv. *57*, 920 (1974).

[9] *S. H. Schroeter & C. M. Orlando*, J. org. Chemistry *34*, 1181 (1969).

[10] *N. J. Turro & P. A. Wriede*, J. Amer. chem. Soc. *92*, 320 (1970).

[11] *H. A. J. Carless*, J. Chem. Soc. Perkin II, *1974*, 834.

[12] *J. T. Przybytek, S. P. Singh & J. Kagan*, Chem. Commun. *1969*, 1224.