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THE REACTION OF JACKSON-MEISENHEIMER COMPLEXES WITH N-BROMOSUCCINIMIDE. THE PREPARATION OF PICRYL KETONES.

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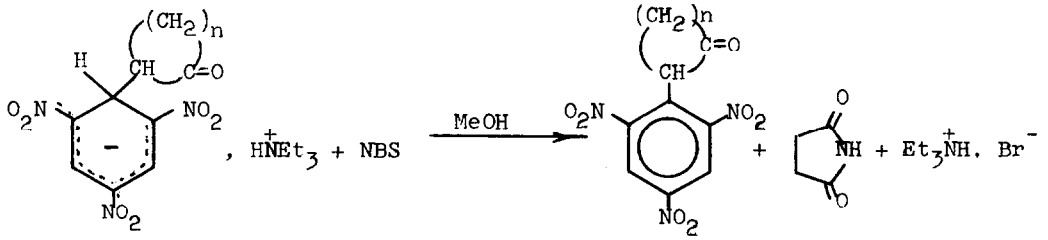
In connection with studies characterizing the chemical reactivity of certain types of Jackson-Meisenheimer complexes[1,2] we have found that N-bromosuccinimide converts I to II in high yield. The complexes I-a and I-b are readily prepared



I-a; n = 3

I-b; n = 4

II-a; n = 3 (mp 117°)

II-b; n = 4 (mp 86°)

by reaction of sym-trinitrobenzene, triethylamine, and the corresponding ketone, and have been described earlier.[3] In methanol solution, the intense colors of I-a and I-b are discharged rapidly after addition of one equivalent of NBS. On standing for 30 hours at 0°C, crystals of succinimide contaminated with $Et_3\overset{+}{N}H,Br^-$ precipitate from solution. After concentrating and cooling the mother liquor,

ketones II-a and II-b crystallize. These have been characterized by pmr, ir, and elemental analysis. The reaction is quite general, and complexes prepared from cyclopropylmethyl ketone and acetophenone are readily converted to their α-picryl derivatives. Unsymmetrical ketones containing more than one acidic methylene yield a mixture of picryl derivatives. Those without α-protons do not form complexes like I. These differences may be of diagnostic value.

Magnetic non-equivalence of the diastereotopic anionic ring protons in I, caused by asymmetry α to the carbonyl[3], is not observed in II. Since the aromatic ring in II is planar, the aromatic protons can interchange by rotation about the carbon-aromatic ring bond.[4]

References

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4. Clarification of this point by a referee is acknowledged.