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Infrared Studies of Anion Radicals. IV. Diketones^{1a}

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The reduction of *o*-dibenzoylbenzene (II), *o*-dipentamethylbenzene (III), and benzil (IV) by sodium in THF were studied by ir in NaCl cavity cells. Two reduction stages were observed in each, the first containing an unreduced and apparently unchelated ketone; the second showed ketyl-like absorptions near 1520–1590 cm⁻¹ [as compared with benzophenone (I) ketyl]. The latter are probably chelated species. Fully reduced III showed a characteristic C=C stretch at 1610 cm⁻¹.

Recent progress in the development of methods of studying anion radicals by infrared spectroscopy has provided a probe by which considerable information may be obtained concerning the nature of anion radicals.¹ This report is concerned with the infrared shifts observed in some diketones upon metal reduction. The advantage of ir in this area is the ability to observe some structure regardless of the diamagnetic or paramagnetic species formed. In addition, some correlation can be made with results from epr and other structural analyses in determining the species under observation.

The shifts observed are those of ketone and aryl absorptions in the 1800–1500-cm⁻¹ range. With each compound in this work we find at least two absorptions occurring in this region, and, since these tend to shift about somewhat irregularly, we will not be concerned with their exact assignment, but rather with the general aspects of the spectra.

Reduction to the weakly ion-paired ketyl has been shown to have two effects in this region of the ir. First, weakening of the carbonyl bond to something more like a bond and a half lowers the normal ketone frequency about 100 cm⁻¹ to around 1550 cm⁻¹ (e.g., see benzophenone, Figure 1² and Table I). Second, the aromatic 1600 cm⁻¹ region vibrations are also "loosened" by the presence of the antibonding electron of the anion (or dianion) and are thrown down to approximately the same region, i.e., the 1500's (see paper II of this series).

Experimental Section

Reductions were performed in sealed tubes by sodium metal mirrors in THF or DME solvent, by standard methods previously described.^{2a} Perkin-Elmer 621 and 21 ir instruments were used for measurements, and concentrations required were about $5 \pm 5 \times 10^{-2}$ M. For low-temperature observations, a cold box was constructed of polystyrene foam using double KBr windows for insulation and pure solvent reference cells. Heat removal was effected by use of a coil of copper tubing into which was pulled liquid nitrogen (by means of an air pump) until the internal temperature desired was reached. Temperatures were measured by a thermocouple. Spectra tracings and apparatus diagrams are available in the microfilm edition. See paragraph at end of paper regarding supplementary material.

Results and Discussion

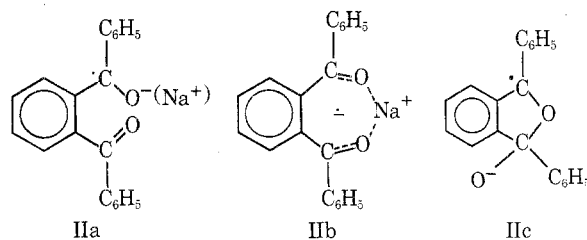
Benzophenone (I). This ketone was used as standard for comparison of the ir shift in the 1500–1900-cm⁻¹ region as a known ketone → ketyl reaction. The ir shifts of the diketones upon reduction are shown in Table I. The reduction stages were followed by prominent changes in

color. These changes are noted and generally conform to previously observed species, though not always structurally known ones. Several of the absorptions recorded did not lend themselves to interpretation, largely because at this stage of our knowledge of the ir of anion radicals we simply do not have enough data on charge-bearing species.

***o*-Dibenzoylbenzene (II).** The first conspicuous color change was to orange in the Na–DME reduction. The organic chemistry of this and other reduction species has been studied in some detail by Herold³ and Novais.⁴ Novais found that, over 3 days, with II in the presence of an excess of sodium, there were several color changes, orange → violet → red → brown, corresponding to several probable reactions. Our system was able to detect only the first two of these steps, because the strongly alkaline solution tends to erode both the salt cell and the epoxy glue fixing it to the Pyrex tube.

The first observable reduction stage of II gives several absorptions in the 1500–1900-cm⁻¹ range which are attributed to at least one unreduced carbonyl group. This group is under considerable electron withdrawal resulting in absorptions (1805 and 1735 cm⁻¹) which are not characteristic of known ketyls like benzophenone. One possible structure for this species could be that of the singly reduced IIa, probably not chelated.

The second stage of reduction exhibits ir absorptions which are almost exactly those of benzophenone ketyl. For this reason the species may possibly be that of the chelate IIb or the intermediate IIc proposed by Novais.⁴ With the present information we are not in a position to distinguish between these two possibilities; however, it is certain that there is no unreduced carbonyl present.



***o*-Dipentamethylbenzoylbenzene (III).** The highly sterically hindered structure of III forces it to undergo a somewhat different route from II in its reduction stages. Epr studies conducted on this diketone⁵ show the color changes to be yellow (no epr spectra made) → brown (paramagnetic) → orange (diamagnetic). The final reduc-

Table I
Ir Absorptions of Ketones and Reduction Products^a

Parent compd	Unreduced compd, cm ⁻¹		First observable reduction stage, cm ⁻¹	Second observable reduction stage, cm ⁻¹
	Ar	C=O		
Benzophenone (standard) (I) (119-61-9) ^b	1605 ± 1 } 1560 ± 1 } ^d	1668 ± 1	(Purple) (3 to -26°) 1590 ± 5 (sh) 1562 ± 0.5 (16592-08-8)	
<i>o</i> -Dibenzoylbenzene (II) (1159-86-0)	1602 ± 1 } 1586 ± 1 } ^d	1668 ± 1	(Orange) (30 to -30°) 1805 ± 2 (s) 1735 ± 2 1668 ± 2 (w) ^c (50987-18-3)	(Purple) (33°) 1595 ± 5 (sh) 1552 ± 3 (s) 1520 ± 2 (w) (50987-20-7)
<i>o</i> -Dipentamethylbenzoyl- benzene (III) (27928-29-6)	1600 ± 1	1653 ± 1	(Greenish-yellow) (30 to -30°) 1682 ± 4 1552 ± 8 (br) (50987-19-4)	(Brown) (30 to -30°) 1564 ± 2 (sh) 1515 ± 2 (s) 1462 ± 1 (?) (50987-21-8)
Benzil (134-81-6)	1600 ± 1 } 1584 ± 1 } ^d	1686 ± 1 1674 ± 2	(Purple) (17 to -25°) 1683 ± 2 (s) 1588 ± 2 (sh) (16827-94-4)	(Orange) (20 to -25°) 1618 ± 5 (sh) 1563 ± 8 (sh) (43049-35-0)

^a Abbreviations used: sh, shoulder; br, broad; s, strong; w, weak; d, doublet generally found with ArC=O. ^b Registry numbers are in parentheses. ^c Probably residual unreduced II.

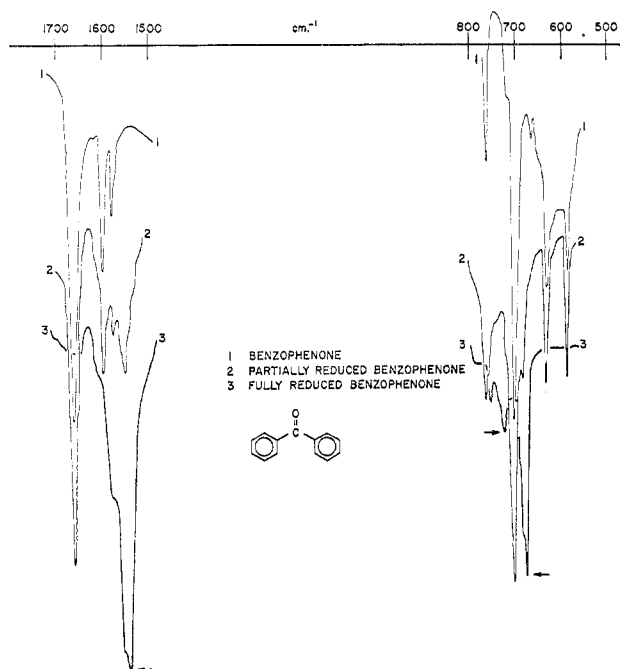
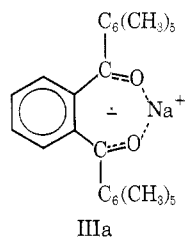


Figure 1.

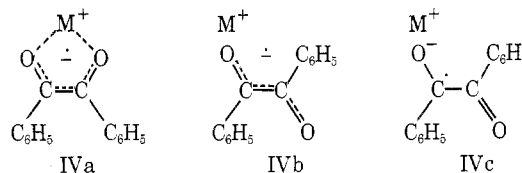
tion stage was not obtainable in our cells for reasons explained above. The yellow-stage ir absorptions show the presence of an unreduced carbonyl and probably also a ketyl, similar in structure to IIa, but with considerably less electron withdrawal.

The second stage is most probably the metal chelate IIIa. The epr spectrum shows that only one Na metal cation is bonded to the chelate,^{3c} and its ir absorptions



are all within the usual ketyl range. The diketone III has been shown not to undergo molecular rearrangement during reduction, as does II.^{3c}

Benzil (IV). Benzil has been shown by Bauld to form easily its anion (purple) and dianion (orange) with potassium in THF.⁶ Both species were found to possess about 75:25 *cis*:*trans* structures (IVa and IVb; monoanion only shown).



Although we are accustomed in these cases to writing the carbonyl function as >C=O, the ir observations for the monoanion indicate that it may be more correct to show *one* of the carbonyls as essentially remaining in the keto form. This is surprising, in that it is to be expected that, with the sodium cation, even more *cis* chelate would be found than with potassium, and, in the chelate, both C=O functions should at least be nearly equivalent and considerably lower in frequency than a "pure" keto form.⁷

The dianion, however, seems quite regular, with the C=C stretching frequency being found at 1616 cm⁻¹ and the typical ketyl-type frequency appearing at 1563 cm⁻¹.

Temperature Dependence. Since several authors⁸ have noted some temperature variations in the ion pairs of ketyls, we found it of interest to investigate the possibility of a shift in the ketyl frequency with temperature owing to the proximity of the metal cation. Consequently, a cold chamber (see Experimental Section) was devised to provide a 60° lowering of temperature. The temperature ranges used are included in Table I. However, no shifts in any frequencies were to be found over a considerable range of temperature. Some slight variations were observed in intensity, but these must be deemed relatively unimportant.

The conclusion to be drawn from these observations must be that either the metal-oxygen bonds are so tight that in these compounds the temperature variations were not effective enough to shift the C=O absorption, or that

Table II
Ir Absorptions of Butanol Salts^a

	K salt (neat), cm ⁻¹	K salt (in DME), cm ⁻¹
2-Butanol (50986-98-6) ^b	385 ± 5	450 ± 5 (w)
	410 ± 5	515 ± 5 (w, br)
	Other very weak peaks	
	2500-900, nearly 100% abs, no structure	2500-700, nearly 100% abs, no structure
	350 ± 10 (br)	<400 cutoff
	430 ± 5 (s)	435 ± 5 (w)
2-Methyl-2-propanol (865-47-4)	485 ± 5 (br)	480 ± 5 (s)
		510 ± 5 (br)
		540 ± 5
		570 ± 5
	2500-600, <100% abs, no sharp structures	2500-1500, <100% abs, no structure
	v br abs 1900-1600 and 1500-1000	
	3090 ± 5 (br, s)	3090 ± 5 (br, s)

^a Some broad C-H stretching bands at ca. 2950, 2890, and 2800 cm⁻¹ were present in all spectra. ^b Registry numbers are in parentheses.

they were so "loose" that our method (ir) is insufficiently sensitive to detect such a shift.

Some problems with water absorption (1635 cm⁻¹) on the cells were experienced, but these were overcome by exercising great care with humidity control.

Low-Frequency Absorptions. Several broad absorptions appeared in the lower frequency regions of the first reduction stages of the anions, but they were not analyzed: II, 1020-1060, 850-720 cm⁻¹; III, 1150, 1010 cm⁻¹; and IV, 695-760 cm⁻¹.

Absorptions of Metal Salts of Alcohols. In order to verify that no extraneous absorptions were to be found in the observing range of 1850-1500 cm⁻¹, 2-butanol and 2-methyl-2-propanol were reduced in exactly the same manner as the ketyls. The reductions by potassium were carried out both in DME and neat until no further OH absorptions (3300 cm⁻¹) were found. The results found are shown in Table II. No interfering absorptions at all were to be found in the 1850-1500-cm⁻¹ regions, although several interesting but unassigned structures were to be found in the 600-400-cm⁻¹ region. This region is being investigated further for possible oxygen-metal vibrations.

In this latter region, it was necessary to open the slits completely or use a 2X program, owing to the slight solu-

bility of the salts in DME. However, the salts formed a gel which was present at all times in the sample beam.

The hydrogen pressure in the cell-tube system was calculated at slightly greater than 1 atm and presented no problem.

In conclusion, it has been shown that not only is it feasible to observe by ir the charged reduction species of diketones, but that considerable structural information may be derived from such studies. In all three diketones studied we have noted that the first reduction stage appears to have an unchelated, unreduced ketone function, while further reduction results in typical ketyl-like absorptions in the 1520-1590-cm⁻¹ region.

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Supplementary Material Available. Infrared absorption spectra tracings of compounds II, III, and IV, their reduction products, and the two alcoholate salts will appear following these pages in the microfilm edition of this volume of the journal. Also available in microfilm are detailed drawings of the cold box used for low-temperature studies and of the sample reduction tube. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-1295.

References and Notes

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- (2) Figure 1 is reproduced by permission of the Chemical Society (London) from D. H. Eargle, Jr., and E. Cox, *Chem. Soc., Spec. Publ.*, **No. 22**, 116 (1966).
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