7.32 and 7.92 (2 d, $-C_6H_4-$, 4 H), 8.38 (m, >NH, 1 H).

Anal. Calcd for $C_{18}H_{28}N_2SO_2$: C, 64.26; H, 8.39; N, 8.33; S, 9.53. Found: C, 63.98; H, 8.20; N, 8.18; S, 10.05.

(+)-*trans*-3-*tert*-Butyl-6-methylcyclohexene. A 2.2 M solution of butyllithium in hexane (75 ml) was added dropwise to a stirred suspension of the tosylhydrazone **8** (13.2 g) in anhydrous ethyl ether (140 ml) at 0 °C under a nitrogen atmosphere. The solid **8** first dissolved, then a white precipitate was formed, which turned to yellow and finally to orange. The reaction mixture was stirred at 0 °C for 2 h, left for 12 h at room temperature under nitrogen, and then hydrolyzed. The organic layer was separated, washed with 10% aqueous Na_2CO_3 and water, dried, and evaporated. The residue was dissolved in petroleum ether and filtered through a 40 × 2.5 cm column of silica gel. Evaporation and distillation of the eluate yielded pure (GLC) **9**: bp 72–73 °C (18 mm); $[\alpha]^{25}_{589}$ +117.6°, $[\alpha]^{25}_{546}$ +134.3°, $[\alpha]^{25}_{436}$ +235.5°, $[\alpha]^{25}_{365}$ +378.2° (c 6, $CHCl_3$); NMR δ 0.86 [overlapping s and d, $(CH_3)_3C-$ and CH_3-, 12 H], 5.52 (m, $W_{1/2} \sim 4$ Hz, $-CH=$, 2 H).

Anal. Calcd for $C_{11}H_{20}$: C, 86.60; H, 13.24. Found: C, 86.84; H, 13.25.

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Mechanistic Aspects of the Wolff–Kishner Reaction. 6. Comparison of the Hydrazones of Benzophenone, Fluorenone, Dibenzotropone, and Dibenzosuberone

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A careful determination[1] of the kinetic and activation parameters of the Wolff–Kishner reaction of benzophenone hydrazone in two hydroxylic solvents (butyl carbitol and 1-decanol) as a function of the cation (K, Na, Li, and Mg) in the alkoxide catalyst, the concentration of the latter, and as a function of the presence of dicyclohexyl-18-crown-6 has led to the conclusion that the rate-determining step involves the hydrazone anion and a minimum of two solvent molecules: one hydroxylic solvent molecule that functions as a proton source, and another solvent molecule that acts as a base in the scission of the N–H bond. The rate-limiting step for the Wolff–Kishner reaction of benzophenone hydrazone in a hydroxylic solvent can thus be represented as follows:

(M^+ is solvated)
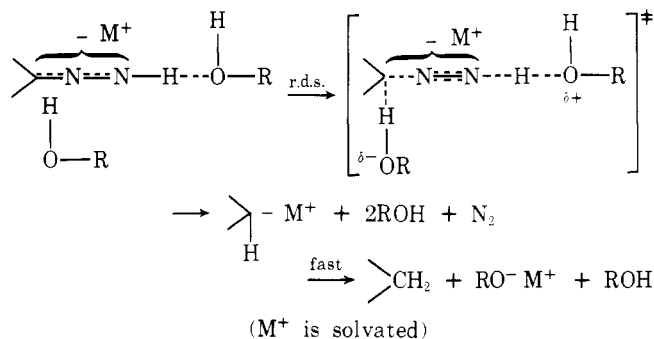
The experimental results also suggest that the reactivity of the hydrazone anion increases with the dissociation of the ionic pair.

In this paper we wish to report the comparison of the behavior of benzophenone hydrazone (I) in the Wolff–Kishner reaction with that of three structurally related compounds (II, III, IV) in which the stabilization of the partial negative charge at the reactive carbon atom should vary as a function of the differences in coplanarity, aromaticity, and antiaromaticity.[2]

Results and Discussion

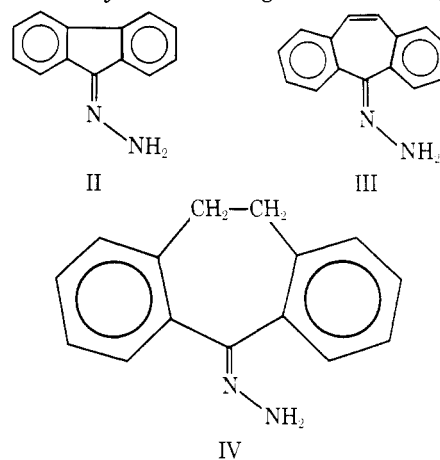The kinetics of the Wolff–Kishner reaction of I–IV were determined in butyl carbitol using the sodium butyl carbito-

Table I. Rate Constants and Activation Parameters for the Wolff-Kishner Reaction of I-IV

Compd	$k^{150.5°} \times 10^3$, $M^{-1} s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol[c]	$\Delta S^{\ddagger}$, eu[c]
I	2.71[a]	28.8 ± 0.5	−3.1 ± 1.1
II	254[a,b]	25.6 ± 0.4	−1.5 ± 0.9
III	1.62[a]	29.1 ± 1.5	−3.3 ± 3.2
IV	0.280[a]	30.2 ± 0.7	−4.4 ± 1.6

[a] Standard deviations of these values are less than 5%. [b] Extrapolated from 91.7–131.0 °C. [c] Errors quoted in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are equal to 1.96 × (standard errors) which gives a 96% "confidence level" (N. C. Barford, "Experimental Measurements: Precision, Error and Truth", Addison-Wesley, Reading, Mass., 1967).

Table II. Kinetic Results for the Wolff–Kishner Reaction of Fluorenone Hydrazone (II), Dibenzotropone Hydrazone (III), and Dibenzosuberone Hydrazone (IV)

Expt no.	Hydra-zone	$[HyH]_0$, M	$[RO^-Na^+]$, M Init	$[RO^-Na^+]$, M Final	Temp, °C	$t_f/t_{1/2}$	$k_1 \times 10^5$, s^{-1}	$k_2 \times 10^2$, M^{-1} s^{-1}
121	II	0.060	0.0274	0.0254	131.0	8.7	148	6.22
117	II	0.040	0.0945	0.0920	111.3	8.3	99.9	1.17
119	II	0.049	0.0587	0.0575	111.3	7.1	63.2	1.19
120	II	0.041	0.0248	0.0224	111.3	1.2	24.7	1.14
123	II	0.047	0.1031	0.1005	91.2	6.6	16.9	0.178
122	II	0.058	0.0592	0.0584	91.2	1.9	9.37	0.171
142	III	0.043	0.0108	0.0106	195.2	8.4	40.3	4.50
141	III	0.032	0.0770	0.0755	195.2	12.3	339	5.32
145	III	0.033	0.123	0.122	171.8	7.8	90.8	0.860
146	III	0.033	0.114	0.114	150.5	5.8	17.2	0.171
147	III	0.035	0.136	0.136	150.4	7.1	18.4	0.153
110	IV	0.043	0.0865	0.0815	195.6	8.1	66.1	0.94
109	IV	0.039	0.1310	0.1265	195.6	10.9	106	0.981
111	IV	0.033	0.154	0.152	171.6	5.6	19.4	0.147
137	IV	0.035	0.126	0.124	171.5	5.1	16.5	0.153
113	IV	0.028	0.697	0.697	171.6	13	124	0.206
138	IV	0.027	0.158	0.158	150.6	1.6	3.94	0.0281
139	IV	0.028	0.492	0.486	150.6	6.4	12.0	0.0279

late catalyst as described elsewhere.[1] Compounds I, III, and IV were studied in the temperature range 150.4–195.6 °C, while II, because of its higher reactivity, was studied in the temperature range 91.2–131.0 °C. A comparison of the rate constants (at 150.5 °C) and of the activation parameters is given in Table I.

While the relative rates of the Wolff–Kishner reaction of I–IV show significant differences, it is apparent from the comparison of the activation parameters that, except for the case of II, the rates are governed primarily by the differences in the enthalpies of activation. The entropies of activation of I, III, and IV fall into a narrow range of -3.75 ± 0.65 eu and it can be assumed that the transition states of the rate-determining steps of all three compounds have similar structures. The relatively small increase in the enthalpies of activation as we proceed from I to III and IV appears to reflect the increasingly more costly proton transfer from a hydroxylic solvent molecule to the sp^2 carbon atom of the hydrazone moiety. It is apparent, however, that the antiaromaticity of the potential dibenzotropyl carbanion has a small effect on the reactivity of III.

The behavior of fluorenone hydrazone (II), on the other hand, stands out in accord with the expected highly stabilized carbanion character of the hydrazone anion:
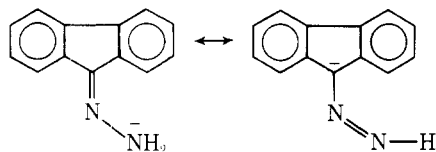
The results listed in Table I clearly demonstrate that the proposed high electron density at the carbon terminal of the hydrazone anion of II causes a significant decrease in the enthalpy of activation, most likely because of the relatively easier transfer of a proton from oxygen to carbon. The more positive entropy of activation in the case of II suggests that, again because of the relatively greater stability of the fluorenyl carbanion, the transition state lies closer to the product of the rate-limiting step, i.e., the nitrogen molecule is more highly separated in the case of II than in the analogous systems I, III, and IV.

Experimental Section

Materials. The preparation of benzophenone hydrazone and the purification of butyl carbitol have been described elsewhere.[1]

Fluorenone hydrazone was purchased from Aldrich Chemical Co. and crystallized from ethanol before use.

Dibenzotropone hydrazone and **dibenzosuberone hydrazone** could not be prepared in the usual manner[3] since this procedure yielded the corresponding alcohols in 40–60% yield. The hydrazones were obtained by allowing the ketones to react for 2 h with an excess of 95% hydrazine in refluxing ethylene glycol under nitrogen. The reaction mixture was cooled and diluted with water, and the hydrazones were extracted with benzene and recrystallized from petroleum ether. Dibenzotropone hydrazone (III), mp 78 °C.

Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 82.42; H. 5.31; N, 12.44.

Dibenzosuberone hydrazone (IV), mp 82 °C.

Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.90; H, 6.19; N, 12.50.

Kinetic Experiments. The apparatus, procedure, treatment, and accuracy of the data and the results for benzophenone hydrazone were reported elsewhere.[1] The kinetic results obtained with the hydrazones of fluorenone (II), dibenzotropone (III), and dibenzosuberone (IV) are summarized in Table II.

Registry No.—I, 5350-57-2; II, 13629-22-6; III, 61047-37-8; IV, 61047-38-9; dibenzotropone, 2222-33-5; dibenzosuberone, 1210-35-1; hydrazine, 302-01-2.

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Structure Assignments and Reactivities of Bromochlorocarbene–Olefin Adducts

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Bromochlorocarbene appears to have been the first dihalocarbene with dissimilar halogens to have been added to olefins from which geometrically isomeric adducts are possible