tions and that at 2525 Å. for alkaline solutions.[7] Neutral and nearly neutral solutions were acidified with sulfuric acid and the absorption determined at 2505 Å. Concentration of residual 8-quinolinol in the chloroform phase was determined by difference in each case. The distribution coefficient was then evaluated as the ratio of the molar concentration of 8-quinolinol in the chloroform phase to the total molar concentration of all 8-quinolinol species in the aqueous phase. Substitution of concentrations for activities was permissible because of the low concentration levels employed.

Discussion

Table I

Distribution of 8-Quinolinol between Chloroform and Water at 25°

pH	Σc_{H_2O}[a] mole/liter, × 10^5	c_{CHCl_3}[b] mole/liter, × 10^3	c_{CHCl_3}/c_{H_2O}	Molecular HOn in aqueous layer, %
2.06	9.90	0.0575	0.58	0.12
2.65	4.28	0.0792	1.85	0.44
3.75	4.40	1.17	26.4	5.32
4.43	1.51	1.36	89.9	21.2
6.05	0.489	1.72	352	92
7.00	.351	1.21	350	99
7.05	.475	1.71	360	99
8.21	.489	1.72	352	98
9.24	.055	0.121	221	80.5
10.50	2.06	1.36	65.8	18.4
12.00	4.82	0.105	2.18	0.71

[a] Sum of concentrations of molecular, cationic and anionic species. [b] Concentration of molecular species.

Variation in distribution coefficients with pH, as indicated in Table I, are easily understood in terms of the amphoteric character of 8-quinolinol. The basic and acidic properties of the compound are described by the equilibria

$$\mathrm{HOn} + \mathrm{H}^+ \rightleftarrows \mathrm{HOn{\cdot}H}^+ \qquad (2)$$

$$\mathrm{HOn} \rightleftarrows \mathrm{H}^+ + \mathrm{On}^- \qquad (3)$$

where HOn represents molecular 8-quinolinol. The basic and acidic dissociation constants have been determined[2,8-10] and permit evaluation of the concentrations of all three species at any pH. Since the only species existent in chloroform is the molecular one, it follows that essentially complete concentration of 8-quinolinol in the chloroform phase can be expected only over that pH range in which the quantity of the molecular species is maximum in the aqueous phase. As shown in Table I, *ca.* 99% of the 8-quinolinol in the latter phase is in the molecular form in the pH range 7.0–8.2, with more than 90% being molecular at as low a pH as 6.0. In this pH range, the average experimental distribution coefficient of 353 closely approximates that calculated for molecular 8-quinolinol.

On the other hand, in either more acidic or more alkaline aqueous solutions, only a small fraction of the 8-quinolinol present is in the molecular form. The experimentally determined distribution coefficients, as based upon the total 8-quinolinol concentration in the aqueous phase, decrease correspondingly. Thus, although the distribution coefficients given in Table I are really theoretical values for only the 6.0–8.2 pH range, they are of practical importance in determining optimum pH conditions for 8-quinolinol extractions.

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(8) K. Stone and L. Friedman, This Journal, **69**, 209 (1947).

(9) J. P. Phillips and L. L. Merritt, *ibid.*, **70**, 410 (1948).

(10) H. Irving, J. A. D. Ewart and J. T. Wilson, *J. Chem. Soc.*, 2672 (1949).

Isolation of Methylchrysene from Petroleum

By R. J. Moore, R. E. Thorpe and C. L. Mahoney

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In the course of examining a Mid-continent medium petroleum distillate by silica gel chromatography, a white crystalline material has been isolated which is identified as 1-methylchrysene. After recrystallization from ethanol, the melting point was 253° (compared with 251° found by Brode and Pattersen[1]). The ultraviolet absorption spectrum was identical to that reported for synthetic 1-methylchrysene and the parent mass found with a high temperature mass spectrometer was 242, corresponding to $C_{19}H_{14}$. Excepting the n-paraffins, we believe that this is the highest molecular weight pure hydrocarbon thus far isolated from native petroleum.

(1) W. R. Brode and J. W. Pattersen, This Journal, **63**, 3252 (1941).

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Carbazic Acid Esters as Carbonyl Reagents

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The common derivatives of aldehydes and ketones such as phenylhydrazones, substituted phenylhydrazones, oximes and semicarbazones, as well as a rather large number of lesser known condensation products, are described extensively in the literature and textbooks for qualitative organic analysis. However, it appears that little use[2] has been made of the esters of carbazic acid as carbonyl reagents. These materials are stable, crystalline solids which can be synthesized readily from hydrazine and an organic carbonate.

The present work describes the preparation of a number of carbonyl derivatives of methyl and ethyl carbazates which have not been reported previously. The data obtained for a series of carbomethoxyhydrazones are given in Table I. The properties of the carboethoxyhydrazones are listed in Table II.

Formaldehyde, benzalacetophenone and benzil gave mixtures of products with both methyl and

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(1) From a thesis submitted by Henry D. Barnstorff to the Graduate School of the University of Missouri, 1949, in partial fulfillment of the requirements for the degree of Master of Arts.

(2) A relatively few derivatives are recorded in the following leading references: K. v. Auwers and Th. Breyhan, *J. prakt. Chem.*, **143**, 259 (1935); H. J. Backer and W. Meyer, *Rec. trav. chim.*, **45**, 82 (1926); H. DeGraff, Diss. Leiden (1930), *C. A.*, **24**, 5723 (1930); O. Diels and P. Fritzsche, *Ber.*, **44**, 3018 (1911); D. N. Majumdar and P. C. Guha, *J. Indian Chem. Soc.*, **10**, 685 (1933); and R. B. Woodward, T. P. Kohman and G. C. Harris, This Journal, **63**, 120 (1941).